

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	No free motion	Random motion to	Totally random.
particles	only vibration allow.	a limited extent is	
		allowed.	
(ii) Inter molecular	Very strong	Intermediate strength	Very weak (<u>~</u> zero)
forces			
(iii) Average	Average separation is fixed	Average separation is	No fixed volume.
separation	so volume is fixed	almost constant so almost	
(volume)		fixed volume.	
(iv) Shape	Definite shape as the	Average separation is	No fixed shape.
	location of particles are	fixed but location of	
	fixed.	particle is not fixed so no	
		definite shape.	
(v) Effect of change	Are incompressible.	Liquid are also almost	Highly compressible.
in pressure &		incompressible.	
temperature.		-	
(vi) Heat capacities	Heat capacity is	Same as solid.	Heat capacity is
	almost independent		dependent on process.
	of 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 → dispersion force. (ii) Polar → dipole-dipole. (iii) Polar & H-bonding. 	$\begin{array}{cccc} I_2, & Xe(s), & C_6H_6, \\ CCI_4, & H_2, & HCI, \\ SO_2, & SF_4, & H_2O(s), \\ H_3BO_3(s) \end{array}$	Very soft Soft Hard	Very low Low Low
(ii) Ionic solid. solid \rightarrow insulator Molten & aqueous \rightarrow conducting.	lons	Coulombic non directional long range.	NaCl, ZnS, CaF₄, 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 → Hard depending on metallic bond.	Low → High
(iv) Covalent or network. Insulator except C (graphite).	Atoms	Covalent bond.	C(diamond), SiC, SiO ₂ , AIN, graphite.	Very hard Graphite → Soft only conducting.	Very high
			1		

– Solved Examples -

- *Ex-1* Identify molecular solid, covalent solid, ionic solid: P₄(s), S₈ (s), SiC (s), Al₂O₃(s), He (s), Al₂Cl₆(s).
- $\label{eq:solution} \mbox{Sol.} \quad \mbox{Molecular solid} \ \rightarrow \mbox{P}_4(s), \mbox{ } S_8 \ (s), \mbox{ } He \ (s), \mbox{ } Al_2 Cl_6(s)$
 - Covalent solid \rightarrow SiC
 - Ionic solid $\rightarrow AI_2O_3(s)$.

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,	1	No particular pattern is followed particle are
	ion) follow a definite repeating arrangement.		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 :	4	These have a range of temperature in which they melts as. There melting point and enthalpy of fusion is not fixed. Liquid Liquid + solid Temp T_1 T_2 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_1 T_2 T_2 T_2 T_1 T_2 $T_$
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 partical. Ex. : Glass, Plastic, Amorphous silica, Rubber, Starch.

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 a1D, 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 \rightarrow distance between two lattice point.

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

Parallelogram





1.

2.

Non primitive: (a) Body centered (B.C.): (b) Face centered (F.C.): (c) End centered (E.C.): (c) End centered (E.C.):

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.

\rightarrow 3-egde length (a, b, c) and 3-angle between these. (α , β , γ), [a-b $\rightarrow\gamma$], b-c $\rightarrow\alpha$], [c-a- β].

100-4	Seven Crystar System					
S.No.	Crystal System	Edge length	Angles	Unit cell found	Examples	
1	Cu bic	a = b = c	$\alpha=\beta=\gamma=90^{\text{o}}$	SC, BCC, FCC (3)	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, Na2O, CaF2, KCl, Pb, Alum.	
2	Te tragonal	a = b ≠ c	$\alpha=\beta=\gamma=90^{\text{o}}$	SC, BC (2)	Sn (white tin), SnO2, TiO2, ZnO2, NiSO4, urea.	
3	Or thorhombic	a≠b≠c	$\alpha=\beta=\gamma=90^{\text{o}}$	SC, BC, FC, EC (4)	Rhombic sulphur, BaSO4, KNO3, PbCO3, , CaCO3 (aragonite)	
4	Mo noclinic	a≠b≠c	$\begin{aligned} \alpha &= \gamma = 90^{\circ} \\ \beta &\neq 120^{\circ}, \\ \neq 90^{\circ}, &\neq 60^{\circ} \end{aligned}$	SC, EC (2)	Monoclinic sulphur, PbCrO4, Na2SO4, 10H2O, Na2B4O7.10H2O	
5	He xagonal	a=b≠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	$\alpha=\beta=\gamma\neq90^{\text{o}}$	SC (1)	CaCO₃ (Calcite), HgS(Cinnabar), NaNO₃, ICl.	
7	Triclinic	a≠b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^{o}$	SC (1)	K ₂ Cr ₂ O ₇ , CuSO ₄ .5H ₂ O, H ₃ BO ₃	

Tab-4 Seven Crystal System

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.



- 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) A₇B₃
 (B) AB₃
 (C) A₇B₂₄
 (D) A₂B₃
 - (A) A₇B₃ (B) AB₃ (C) A₇B₂₄ (C)
- **Sol.** $A = 7 \times \frac{1}{8} = \frac{1}{8}$; $B = 6 \times \frac{1}{2} = 3$

Ans.

Formula = $A_{7/8}$ B₃ or A₇B₂₄

 $X = \frac{1}{2} \times 6 = \frac{3}{4}$

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.

Sol.

(i)

$$Y = \frac{1}{8} \times 2 + \frac{1}{2} \times 3 = \frac{7}{4}$$
$$Z = \frac{1}{2} \times 3 + 1 + 1 = \frac{5}{2} = \frac{10}{4}$$

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

(ii) 1 amu = 1.67×10^{-24} gram

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

Density of the unit cell = Mass of total atoms present in a unit cell

Volume of that unit Cell

$$d = \frac{Z(M/N_A)}{a^3 \times 10^{-30}} \, g cm^{-3} \Rightarrow \left[d = \frac{ZM}{N_A \, (a^3 \times 10^{-30})} g cm^{-3} \right]$$

Where Z = no. of atoms in a unit cell

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

M = molar mass

 N_A = Avogadro number (6.023 × 10²³)

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.

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



- 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



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 Pattern repeated.
 - \rightarrow 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).

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

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

(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	12
(i) Nearest	a (distance b/w 1 & 2)	$\left\{\frac{3\times 8}{4}=6\right\} \Longrightarrow 6$	
(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. \rightarrow 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 $\frac{\sqrt{3}}{2}a = 2R$.

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

	<u> Solved</u> E	Examples —					
Ex-6	How many 'nearest'	and 'next nearest' r	eighbou	rs respectivel	y does pota	ssium have i	n b.c.c. lattice?
Ans.	(B)	(b) 0, 0		(0) 0, 0		(D) 0, 2	
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 ow layer. 					nd none in its own	
	(B) each atom touc	hes four atoms in t	he layer	above it, fou	r in the laye	er below it a	ind one in its own
	(C) two atoms touch own layer.	n four atoms in the la	ayer abo	ve them, four	in the layer	below them	, and none in their
	(D) each atom touc	hes eight atoms in t	he layer	above it, eigh	nt in the laye	er below it a	nd none in its own
Ans.	(A)						
Ex-8	Potassium crystalliz	es in body centered	cubic lat	ttice with a un	nit cell length	n a = 5.2 Å	
	(B) What is the dista	ance between neare	st neight iearest n	ours? eighbours?			
	(C) How many near	est neighbours does	each K	atom have?			
	(E) What is calculat	ed density of crystal	line K.	CITIN Has:			
Ans.	(A) 4.5 Å, (B)	5.2, (C) 8,	(D) 6	(E) 0.92 g/m	L		
Sol.	(A) $2r = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3}}{2}$	$\frac{\times 5.2}{2} = 4.5 \text{ Å}$		(B) distance	= a = 5.2 Å		
	(C) 8			(D) 6			
	(E) d = $\frac{2}{(5.2 \times 10^{-8})^3}$	$\frac{39}{\times 6.02 \times 10^{23}} = 0.92$	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).

T = tetrahedral void O = octahedral void



* Now there will be two method to place III layer on the II layer.

(1) Hexagonal close packing (HCP) AB-AB-AB----Type.

* 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 why this generate ABAB- - - - AB pattern. One type of void always remain on occupied.



Exploded view

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

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



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

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

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

(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) = $\frac{\text{mass}}{1 \text{ mass}} = \begin{bmatrix} Z \times M \\ Z \times M \end{bmatrix}$ (7 - 6)
- (v) Density (d) = $\frac{\text{mass}}{\text{volume}} = \left[\frac{Z \times M}{N_A \times \text{volume}}\right]$ (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.



- * Illrd 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).



a ≠ 2R

 \Rightarrow

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

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

(iii) Packing fraction: P.F. =
$$\frac{4 \times \frac{7}{3} \pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74(74\%)$$

(iv) Coordination number, (CN) = 12

(v) Density (d) =
$$\frac{Z \times M}{N_A \cdot a^3}$$
 g/cm³ (a = Edge length of FCC unit cell)

Tab-8

Type of neighbour	Distance	No. of neighbours	
(i) Nearest	<u>a</u> √2 a (1 & 2)	12	
(ii) (next) ¹	a (1 & 3)	6	Reference Figure

Note: HCP and CCP are the only two type of close packed lattice (because of their effective efficiency 74%).

Solved Examples

Ex-9 A metal crystallizes in two cubic phases i.e., FCC and BCC whose unit cell lengths are 3.5Å and 3.0 Å respectively. The ratio of their densities is:
 (A) 3.12
 (B) 2.04
 (C) 1.26
 (D) 0.72

Sol.
$$d = \frac{ZM}{a^3N_1} \frac{d_1}{d_2} = \frac{4}{(3.5)^3} \times \frac{(3)^3}{2} = 1.26.$$

Ex-10 In a ccp structure, the: (A) first and third layers are repeated (C) second and fourth layers are repeated

(B) first and fourth layers are repeated

(D) first, third and sixth layers are repeated.

Ans. (B)

Ans.

Ans.

(C)

Ex-11 Lithium borohydride crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are a = 6.8 Å, b = 4.4 Å and c = 7.2 Å. If the molar mass is 21.76, then the density of crystals is: (A) 0.6708 g cm⁻² (B) 1.6708 g cm⁻³ (C) 2.6708 g cm⁻³ (D) None of these

(Å) 0.6708 g cm⁻² (B) 1.6708 g cm⁻³ (C) 2.6708 g cm⁻³ (D) None of these. (A)

Sol.
$$d = \frac{ZM}{a^3 N_A} = \frac{4 \times 21.76}{6.8 \times 10^{-8} \times 4.4 \times 10^{-8} \times 7.2 \times 10^{-8} \times 6.023 \times 10^{23}} = 0.6708 \text{ g cm}^{2-}.$$

- Ex-12 An fcc lattice has lattice parameter a = 400 pm. Calculate the molar volume of the lattice including all the empty space:

 (A) 10.8 mL
 (B) 96 mL
 (C) 8.6 mL
 (D) 9.6 mL
- (A) 10.8 mL (B) 96 mL (C) 8.6 mL (D) Ans. (D)

Sol. Volume of 4 atoms = $a^3 = (4 \times 10^{-8})^3$ cm³ volume of N_A atoms = $\frac{(4 \times 10^{-8})}{4} \times 6.023 \times 10^{23} = 9.6$ ml.

Section (D): Voids

Th-14 Types of voids found in close packings:

- * Although the close packed structure have maximum packings efficiency, but there are some empty space left in arrangement.
- **D-10** Voids (Interstitial Voids): Although the close packed structures have the maximum packing efficiency, there are indeed empty spaces left in the arrangements. These empty spcesa are known as voids or. Interstitial Voids.

* Maximum size of sphere which can be place in void space is depends on size of void.

- R = Radius of sphere (**Bigger atom or ion**)
- r = Radius of sphere placed in void. (Smaller atom or ion)

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.



D-12 3-Dimensions void:

Tetrahedral void [3D-4 coordinate void]

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



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

D-13

<u>3-Octahedral void</u>: [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.





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





(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 [Edge center] × $\frac{1}{4}$ + 1[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

cedge center and contribution of each sphere present on edge center is $\frac{1}{2}$ so.

Tetrahedral void (TV) = 8 [Inside the body] + 12 [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 × 2	Octahedral void = Z × 1
CCP (FCC)	4	8	4
HCP	6	12	6

Solid	State				_
	-Solved	Examples —			
Ex-13(a) In a face centre tetrahedral and oc	d cubic arrangement ahedral voids?	of metallic atoms, what	is the relative rati	o of the sizes of
Ans.	(A) 0.543 (A)	(B) 0.732	(C) 0.414	(D) 0.637	
Sol.	$\frac{r_{\text{tetrahedral}}}{r_{\text{octahedral}}} = \frac{0.225 \text{ R}}{0.414 \text{ R}}$	= 0.543.			
(b)	The numbers of te (A) 200 and 100(B	trahedral and octahedra) 100 and 200(C) 200 a	al holes in a ccp array of and 200 (D) 100 a	100 atoms are resp nd 100	ectively
Ans.	(A)				
Ex-14 Ans.	Copper has a face What is the size of copper lattice witho (Hint.: Calculate th 0.53Å	-centred cubic structure of the largest atom whit out distorting it? The radius of the smalles	e with a unit-cell edge len ch could fit into the inte t circle in the figure)	gth of 3.61Å. rstices of the	
Sol.	$r_{octahedral} = 0.414 R$			Z_	
	For FCC 4R = $\sqrt{2}$	а			
	$\mathbf{R} = \frac{\sqrt{2} a}{4}$				
	$r = \frac{0.414\sqrt{2} a}{4} = \frac{1}{4}$	$\frac{0.414\sqrt{2} \times 3.61}{4} = 0.53$	Å		

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					
$0.155 \leq r_{\text{+}}/r_{\text{-}} < 0.225$	triangular void	3	Boron oxide				
$0.225 \leq r_{\text{+}}/r_{\text{-}} < 0.414$	tetrahedral void	4	Zinc sulphide				
$0.414 \le r_{\text{+}}/r_{\text{-}} < 0.732$	octahedral void	6	Sodium chloride				
0.732 ≤ r ₊ /r _− < 1	cubical void	8	Caesium chloride				
NOTE In invite one							

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

 \Rightarrow 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.

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

$$r_{+} + r_{-} = \frac{1}{2} \times \frac{a_{fcc}}{2} \sqrt{3}$$
$$a_{fcc} = \frac{4}{\sqrt{3}} (r_{+} + r_{-})$$

Th-18 Structure of some ionic compound: (1) NaCl type of structure (Rock salt structure):

"coordination number of cation"

"coordination number of anion"

* Experimental
$$\frac{r_{Na^{+}}}{r_{C\Gamma}} = 0.51$$
 (0.414 < $\frac{r_{Na^{+}}}{r_{C\Gamma}}$ < 0.732)

(i) CI- 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 CI^- ion per unit cell = 4

Effective number of Na⁺ ion per unit cell = 4 (iii) Formula of unit cell No. Cl

(iv) Formula of unit cell Na₄Cl₄ 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 $\sqrt{2}a \neq 4R_{cr}$ → as anion–anion are not in contact.

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

(vi) Coordination number:

Coordination number of CI^- = Number of Na⁺ ion touching it = 6. Coordination number of Na⁺ = 6 [placed in octahedral void of CI^- ions].



Tab-11

For	CI⁻:	

Type of neighbour	Distance	No. of neighbours
(i) Nearest	Na⁺ ,	6
(ii) (next) ¹	C⊢ ,	12

Example: Note:

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

Lattice of NaCl is FCC of CF in which all octahedral void are occupied by Na⁺. or \rightarrow FCC of Na⁺ in which octahedral void are occupied by CF.







(i) Ca²⁺ ion form the FCC lattice.

F⁻ ion occupies all tetrahedral voids.
 (ii) Coordination number of F⁻ ion = 4

- * Coordination number of Ca^{2+} 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 = CaF₂.
 (v) Effective number of formula unit cell (Z) = 4.

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

Q It occupies tetrahedral void.

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

Other examples: CaF₂, SrF₂, BaF₂, BaCl₂.

Tab-13 For Ca2+

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

Tab-14 <u>For F-</u>

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

(4) Na₂O [Sodium oxide] [A₂B type]

* Anti-fluorite structure [4: 8 coordination compound] \Rightarrow (O²⁻ ion at FCC lattice). Na⁺ = All the tetrahedral void.

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

(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 CI^- ion = 1. (iii) Formula of ionic compound = CsCl. So Z = 1.

(iv) Density (d) = $\left| \frac{Z \times M}{N_{A} \times a^{3}} \right|$

* anion-anion contact is not there so,

$$[\mathbf{r}_{\mathsf{C}} + \mathbf{r}_{\mathsf{C}_{\mathsf{S}}+}] = \frac{\sqrt{3} \, \mathsf{a}_{\mathsf{S}_{\mathsf{C}}}}{2}$$

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

(vi) Coordination number of CI^+ ion = 8.

Other example: CsCl, CsBr, Csl.

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

4: 4
$$\xrightarrow{P\uparrow}$$
 6: 6 ; 8: 8 $\xrightarrow{T\uparrow}$ 6: 6

STRUCTURES OF SOME CRYSTALS						
S.No.	Crystal	C.N		Z	Structural arrangement	E.g.
		Cation	Anion	Total formula unit		
1	NaCl	6	6	Na⁺ = 4 Cl⁻ = 4	Na ⁺ = at all octahedral voids Cl ⁻ \rightarrow FCC	LiCl
2.	ZnS (wurtizite)	4	4	Zn ²⁺ = 6 S ^{2–} = 6	Zn ²⁺ = At 1/2 TV S ²⁻ = HCP	Agl
3.	ZnS (Blende)	4	4	Zn ²⁺ = 4 S ^{2–} = 4	Zn ²⁺ = At 1/2 of TV S ^{2–} = FCC	CuCl CuBr Cul, Cds
4.	CaF ₂ (Fluorite)	8	4	Ca ²⁺ = 4 F ⁻ = 8	Ca²+ = FCC F⁻ = All TV	BaF ₂ SrF ₂
5.	Na ₂ O	4	8	Na+ = 8 O ^{2–} = 4	Na ⁺ = All TV O ²⁻ = FCC	
6.	CsCl	8	8	Cs⁺ = 1 Cl⁻ = 1	Cr⁺ = Body centered void (Cubic void) Cl⁻ = At corners	CsCN Csl CaS

# Rutile	(TiO ₂)	CN
Cation		6
Anion		3
# Perovskite	(CaTiO₃)	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 S²⁻ location and all Zn²⁺ 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 = x³.



e.g. **Constant** Solution 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 AB₂ 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 (CaF₂) structure.
- Ex-16 CsBr has b.c.c. structure with edge length 4.3 A. The shortest inter ionic distance in between Cs⁺ and Br⁻ is:
 (A) 3.72
 (B) 1.86
 (C) 7.44
 (D) 4.3
- (A) 3.72 (B) 1.86 Ans. (A)

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

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:

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.

(i) Stoichiometric defects:



D-17 Schottkey: When atoms/point are totally missing from the lattice. Net density of crystal will get decreased

 $\rho_{exp} < \rho_{theoritical}$

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





- **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 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 increases by adding apporpirate 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 increases by doping with some group-13 element such as B, AI or Ga.

2. Goup-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. Gorup-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 contains 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, AIP 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 Onners 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.



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.
- 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 as called as Ferromagnetic substances e.g. Fe Ni Co and CrO₂.

This type of magnetism arise 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 ferro magnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called Anti-ferromatic 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. Fe₃O₄, ferrites of the formula M²⁺, Fe₂O₄ where M = Mg, Cu, 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 paramagentic 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 Fe₃O₄ 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.

Th-28 Effect of Temperature on Metal (Conductor) Semiconductor or Insulator:

- 1. The conductivity of semiconductors and insulators increases with increase in temperature
- 2. The conductivity of metal (conductors) decreases with increase in temperature.

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:
 - (i) Ferromagnetism (ii) Paramagnetism (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 as called as Ferromagnetic substances e.g. Fe Ni Co and CrO₂.

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, AIP 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.

Solid State**IISCELLANEOUS SOLVED PROBLEMS (MSPs)**1.Calculate the number of formula units in each of the following types of unit cells:(a) MqO in a rock saft type unit cell(b) ZnS in zinc blende structure(c) platimum 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 Aby: 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 = 4tetrahedral 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 PL, which crystallises with four equivalent atoms in a cubic unit cell does titainum crystallise? (Ti = 48)Sol.Density d =
$$\frac{zM}{a^N}$$
d = 4.54 g/cm², M = 48g mol⁻¹, Z = ? Nn = 6.023 x 10²³ mol⁻¹II value of z is known, structure can be decidedz = $\frac{dN_a^2}{M} = \frac{4.54 \cdot 6.023 \times 10^{-2} \cdot (41.26 \times 10^{-13})^2}{4} = 4$ Thus, litanium 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 TiC).Sol.C.N. of Cs⁺¹ is also = 6 and that of O²⁻ or O²⁻ = 6 in MgOWe know in CSClC.N. of Cs⁺¹

- **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

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

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

10. CsCI crystallises in a cubic that has a CI⁻ at each corner and Cs⁺ at the centre of the unit cell. If $r_{Cs^+} = 1.69$ Å and $r_{Cr^-} = 1.81$ Å, 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^{\oplus} and Cl^{Θ}. = 1.69 + 1.81 = 3.50 Å

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

$$\therefore \qquad \frac{a\sqrt{3}}{2} = 3.50 \text{ Å} \qquad \therefore \qquad a = 4.04 \text{ Å}$$

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), $a = 2\sqrt{2}$ $r = 3.9$ Å
Density $= \frac{ZM}{a^3 N_0} = \frac{4 \times 195}{(3.9 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 21.83$ g/cm³.

- 12. Calculate the edge length of the unit cell of sodium chloride given density of NaCl is 2.17×10^3 kg m⁻³ and molecular weight 58.5×10^{-3} 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 =
$$\frac{zM}{a^3N_c}$$

where a = length of the unit cell

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 × 10⁻¹⁰ m = 5.64 Å = **564 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.

Thus, d (density) =
$$\frac{2M}{a^3 N_0}$$
 a = 2√2 r = 2√2 × 1.42 × 10⁻⁸ cm
∴ d = $\frac{4 \times 56}{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3}$ = 5.743 g/cm³

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

Hence, Number of trivalent cations $(A^{3+}) = 1 \times \frac{1}{2} = \frac{1}{2}$ Number of tetrahedral voids per ion in lattice = 2 Hence, Number of divalent cations $(B^{2+}) = 2 \times \frac{1}{8} = \frac{1}{4}$ 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/cm^3 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 g/cm³ a = 300 pm = 3 × 10⁻⁸ cm

	<i>.</i>	$a^3 = 27 \times 10^{-24} \text{ cm}^3$				
		$N_0 = 0.02 \times 10^{23}$. 1 .		
		$M = \frac{dN_0 a^3}{dN_0 a^3} = \frac{5.20 g/cm^3 \times 6.02 \times 6.02}{dN_0 a^3}$	10 ²³ r	$\text{mol}^{-1} \times 2$	$27 \times 10^{-24} \text{ cm}^3$ = 21.13 g mol ⁻¹	
		Z	4		- 3	
	Thus,	6.02×10^{23} atoms have = 21.13 g				
	<i>.</i>	3.01×10^{24} atoms have = $\frac{21.13}{6.02 \times 10^{24}}$	$\frac{3}{0^{23}}$ ×	3.01 ×′	10 ²⁴ g = 105.65 g	
16.	Calciun contain	n crystallises in a face-centred cu ed 0.1% vaccancy defects.	ıbic u	init cell	with a = 0.556 nm. Calculate the density	if it
Sol.	Thus, c	ensity can be determined using d	$=\frac{zN}{a^{3}N}$	M N _o		
	d(with v	vaccance defect) = $\frac{3.996 \times 10^{-7}}{(0.556 \times 10^{-7})^3 \times 10^{-7}}$	40 6.02	×10 ²³ :	= 1.5448 g/cm ³	
		CH	IEC	K LIS	Т	
		Theories (Th)		D-17:	Schottky Defects	
Th-1:	General Cha	aracteristics of Solids		D-18:	Frenkel Defects	
Th-2:	Types of SC	LIDS on the basis of arrangement of particle	es□	D-19:	Interstitial Defects	
Th-3:	Internal arra	ngement of particle in crystalline solid		D-20:	Metal excess defects due to interstitial cations	Ц
1h-4:	Characterist	ics of a Unit Cell		D-21:	Metal deficiency due to cation vacancies	
Th-5:	Unit cell	9 U		D-22:	Conductors	
10-6: Th 7	Types of un	I CEII		D-23.	Somicondutors	
Th 0.	The type of	f a suba		D-24.	Intrinsic Semiconductors	
Th 0:	Contribution	of different Lattice point in one cubical unit		D-20.	Doping	
111-3.	Contribution	of unreferit Lattice point in one cubical unit		D-27	13-15 Compouds	
Th-10	Structure of	Solids		D-28	12-16 Compounds	
Th-11	3-D Lattice		п	D-29	Super Conductivity	
Th-12	Arrangemer	t of hexagonal closed packed sheets	П	D-30:	Transition Temperature	Π
Th-13:	ABC-ABC	arrangement (Cubic close packing (CCP)) or	D-31:	Paramagnetism	
	Face centre	d cube (FCC))		D-32:	Diamagnetic materials	
Th-14:	Types of vo	ds found in close packings		D-33:	Ferromagnetism	
Th-15:	Location of	void		D-34:	Anti Ferro Magnetism	
Th-16:	Hexagonal	close packing (HCP) unit cell		D-35:	Ferrimagnetism	
Th-17:	Structure of	ionic compounds		D-36:	Curie temperature	
Th-18:	Structure of	some ionic compound		D-37:	Domain	
Th-19:	Other impor	tant structure			Table (Tab)	

	Location of Volu	_		
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 Semicondcutor			
Th-25:	p-Type Semiconductor			
Th-26:	Application of n-type and p-type semicondcutiors			
Th-27:	Magnetic Properties			
Th-28: Effect of Temperature of Metal (Conductor) Semiconducto				
	or Insulator			
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)	
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:	Semicondutors	
D-25:	Intrinsic Semiconductors	
D-26:	Doping	
D-27:	13-15 Compouds	
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	
	<u>Table (Tab)</u>	
Tab-1	: Properties of solid, liquid and gas.	
Tab-2	: Types of solid	
Tab-3	: Crystalline and amorphoux 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	2: Nearest neighbour in S ²⁻	
Tab-13	3: Nearest neighbour in Ca ²⁻	
Tab-14	I: Nearest neighbour in F ⁻	