SOLID STATE

	CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
1	Definite geometry	* No definite geometry
2	Long range Order	* Short range order
3	Sharp melting point	* Do not have sharp m.p.
4	Definite heat of fusion	* Do not have definite heat of fusion
5	When cut generates plain and smooth surfaces	* Forms rough and irregular surfaces
6	Anisotropic ie. they have diferent optical and electrical properties in different directions	* Isotropic i.e have same properties in all directions
7	True solids	* Pseudo -solids or supercooled liquid
8	eq. Sugar, NaCl, Quartz	* eq. Rubber, plastic.

Types of Solids

Solids	*Types of Particles*	*Bonding/Attractive forces*	*Examples*
Molecular Solids			
(a) Non polar	Non-polar Molecules	Dispersion Forces	H_2, N_2, He, Ar I_2, P_4
(b) Polar	Polar molecules	Dipole-Dipole	HCl, HBr, SO_2
(C) H-bonded	Polar molecules	H-Bonding	H_2O (ice)
	Contaning O, N, F & H		
* Ionic Solids	Ions	Electrostatic or coulombic	LiBr, NaCl, $CuSO_4$
* Covalent Solids	atoms	Co-valent	SiO_2, Diamond
Or Network solids			graphite, SiC. P_4O_{10}
* Metallic Solids	Kernels and mobile e	Metallic bond	Fe, Cu, Rb, Brass

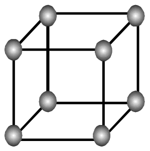
Crystal lattice : A well order arrangement of atoms, molecules or ions in 3D space.

* 2D lattices – 5 (hexagonal, square, rectangular, rhombic, parallelogram)

* 3D lattices (Bravais lattice) – 14

Unit Cell : The smallest 3D portion repeated in a crystal lattice.

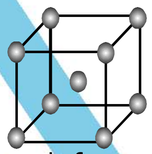
Types of cubic unit cells:



1. **Primitive unit cell or simple cubic :** Particles at all corners of a unit cell.

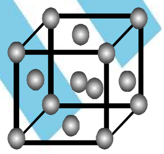
No of particles $= Z = \frac{1}{8} \times 8 = 1$, Rank = 1

2. **Body Centrad Cubic (bcc): Particles** at all corners as well as 1 particle at the centre of a unit cell.



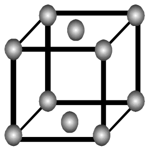
$Z = \frac{1}{8} \times 8 + 1 = 2$

3. **Face centered cubic(fcc):** Particles at all corners as well as at the centre of each face



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

4. **End Centered :** Particles at all corners as well as at the centre of any 2 opposite faces.

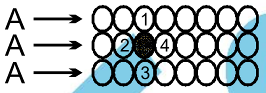


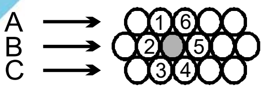
$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 2 = 2$ Rank = 2

(Rank = No of atoms per unit cell)

Close Packing in One dimension :  CN =2

Close Packing in 2 dimension :



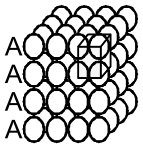


(i) Square close packing
CN = 4

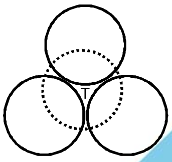
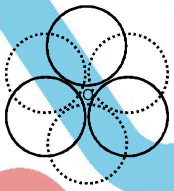
(ii) Hexagonel close packing
CN = 6

Close packing in 3 Dimensions:

(a) Simple Cubic (AAA....Pattern)



Layers are placed one over the other such that each row of spheres are vertically as well as horizontally aligned. (CN = 6).

	Tetrachedral Void	Octahedral Void
1	Open space between 4 spheres of 2 layers of atoms	Open space between six touching spheres of 2 layers of atoms
2	4 Spheres lie at the corners of a regular tetrahedron	6 Spheres lie at the vertices of a regular octahedron
3	Smaller	Larger
4	There are 2 voids per atom of crystal	There is one void per atom in a crystal.
5	Radius ratio is 0.225	Radius ratio is 0.414.
6		

*** (Trigonal void Cubic voids have radius ratio 0.155 & 0.732

3D close packing in hexagonal close packing

Placing third layer over second

(i) Covering tetrahedral voids –forms ABAB ....Pattern or hcp.

(ii) Covering octahedral Voids – In this 4th layer spheres are vertically aligned with 1st layer

* Form ABC ABC pattern.

* Called ccp or fcc

$$\text{(P.E) Packing efficiency} = \frac{\text{Volume occupied by spheres in unit cell} \times 100}{\text{Total Volume of unit cell}}$$

$$= \frac{\text{NO of spheres} \times \text{volume of 1 sphere} \times 100}{\text{Volume of unit cell}}$$

(a = edge length of unit cell)

	Unit cell	**Particles**	**Radius of atom(r)**	**P. Efficiency**
1.	Simple cubic	1	$r = \frac{a}{2}$	52.4%
2.	bcc	2	$r = \frac{\sqrt{3}a}{4}$	68%
3.	hcp, ccp, fcc	4	$r = \frac{a}{2\sqrt{2}}$	74%

Density of unit cell:

$\rho = \dfrac{M \times z}{N_A \times a^3}$ Z = Rank , M = Molar Mass, $N_A = 6.022 \times 10^{23}$ a^3 = Volume of unit cell

a = edge length of unit cell

Crystal defects : Imperfection in solids –2 types

(i) Line defect	(ii) Point defect
Irregularity in a row	ions/atoms are missing from their lattice points.

Point defect: 3 types

(i) Stoichiometric defects: Those defects which do not effect the formula or stoichiometry of the compound.

Types –in Non ionic solids

(a) Vacancy defect – When some atoms are missing from their positions or lattice points. It decreases density.

(b) Interstitial defect : When some constituent particles occupy interstitial sites. It increases the density of the crystal.

Types : In ionic solids

(c) **Schottky defect**	(d) **Frenkel defect**
* Occurs when equal no of cations and anions are missing from their lattice sites.	* It occurs, when ions are missing from lattice sites and found at other interstitial sites.
* Decreases crystal density	* No change in density
* Found in those ionic compounds which have similar size of cations and anions.	* Occurs when cations are smaller than anions (i.e. difference in size large)
* Found in those compound which have high co-ordination. number	* In those compound which have low coordination number
	* Called Dislocation defect
* eg. NaCl, CsCl, CsBr, $AlCl_3$, AgBr	* eq. $ZnCl_2$ AgCl, CuCl, AgBr.

Impurity defect (Cation replacement type defect).

The defect in which a new cation or anion from outside replaces the existing ones such that electrical neutrality is maintained. eg. NaCl having $SrCl_2$ as impurity.

Non-Stoichiometry defects : The defects in which the molecular formula or stoichiometry of the crystal is disturbed or altered.

2 types

(i) Metal excess defect - Cations are more than anions

(a) <u>Due to anionic vacency</u> - Some anions are missing from their lattice sites and their positions are occupied by electrons (Called F-centres or coloured centres-farbenzenter) It makes the crystal para-magnetic and imparts colour to the crystal.

It makes

NaCl	→	Yellow
KCl	→	Violet
LiCl	→	Pink

(b) <u>Due to extra cations at interstitial sites</u> - When ZnO is heated it turns yellow. $ZnO \xrightarrow{Heat} Zn^{+2} + \frac{1}{2}O_2 + 2e$, there will be excess of Zn^{+2} ions in the crystal which occupy interstitial sites and the electrons lost by oxide ions occupy neighbouring interstitial sties.

(ii) <u>Metal deficiency defect.</u> - It occurs in those crystals in which their cations show variable oxidation states. The charge of missing cations is taken by neighbouring cations. In FeO, some Fe^{+2} are missing. Electrical neutrality is maintained by oxidation of Fe^{+2} to Fe^{+3} which leads to change in stoichiometry.

eq. [$Fe_{0.93}$ $O_{1.0}$, $Ni_{0.98}$ $O_{1.8}$]

Types of solids on the basis of electrical conductivity

	Conductivity (k)	Forbidden	Zone	Examples
Conductors	10^7	$ohm^{-1}m^{-1}$	Over lapped	Metal
Insulators	10^{-20} to 10^{-10}	$ohm^{-1}m^{-1}$	large	MnO, CaO, NiO, CN, TiO_2, Fe_2O_3
Semiconductors	10^{-6} to 10^4	$ohm^{-1}m^{-1}$	small	Si, Ge

Pure semiconductors or Intrinsic semiconductors

- have low conductivity at room temperature

- Conductivity increases by adding impurity (Called doping)

<u>Doped Semiconductors :</u>Called Extrinsic semiconductors

* Possess high conductivity

2 Types

<u>n-Type semiconductors</u> - When Si crystal is doped with group 15 element such as P, As, Sb or Bi (Pentavalent impurity)

* The foreign atom (dopant) uses four of its electons for covalent bonding but 5th electron becomes delocalized and is thus free to contribute to electrical conduction

* 'n' stands for negative since electron are negatively charged and are responsible for semiconducting behavior

* **p-type semiconductors** -produced by doping Si with group 13 element such as B, Al, Ga (Trivalent impurity). The dopant atom has 3 valence electrons which are used for forming 3 covalent bonds with neighbouring Si atoms. The place where 4th valence electron is missing gives rise to an electron deficient site or positive hole. The movement of one electron into the vacancy leaves behind a hole at the neighbouring site which carries a positive charge. The movement of positivity charged holes is responsible for the conduction of current

Applications of n-type & p-type semiconductor

(1) for making anode used as rectifier.

(2) Making n-p n and p-n-p transistors to amplify radio and audio signals

(3) Solar cell is photodiode used to convert light energy into electrical energy

13-15 compounds : In Sb, AlP, Ga As;

12-16 compounds : When solid state compound are obtained by combination of elements of group 12 and 16 eq. ZnS, Cds, CdSe, Hg Te

Transition metal oxides likes: TiO, CrO_2 ReO_3 behave like metals

*ReO_3 behaves like Cu in appearance as well as conductance

* VO, VO_2, VO_3, TiO_3 show electrical conductance depending upon temperature.

Magnetic properties:

Diamagnetic meterials: Those materials which are repelled by magnetic field. Occurs due to presence of paired electrons. eq. Cu^+, TiO_2, NaCl, C_6H_6 etc.

Ferromagnetic substances:

Those substances which are strongly attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field eq. Fe, Co, Ni etc.

* CrO_2 is used for making magnetic tapes of cassette recorders.

Antiferromagnetic substances:

The substances in which magnetic moments are aligned in such a way that net magnetic moment is zero eq. MnO ↑↓↑↓↑↓

Ferrimagnetism:

The substances in which magnetic moments are aligned in parallel and antiparallel directions in unequal numbers resulting in net dipole moment. eq. Fe_3O_4, $MgFe_2O_4$, $CuFe_2O_4$ ↑↓↑↓↑↑↓↑

* Glass objects recovered from ancient movements looks milky due to crystallization.

* Glass window panes of very old buildings are thick from bottom then at the top. (as glass is super - cooled liquid.

* AgBr shows both frenkel and schottky deffect.

* Coordination number (CN) of spheres with which one sphere is in contact is called its coordination number

SOLVED PROBLEMS

Q.1. Distinguish between :

(i) Hexagonal and monoclinic unit cell.

Sol.

S.No.	Point of Difference	Hexagonal	Monoclinic
1.	Type of unit cells	Primitive	Primitive and end centred
2.	Axial distances	$a = b \neq c$	$a \neq b \neq c$
3.	Axial angles	$\alpha = \beta = 90^o$ $\gamma = 120^o$	$\alpha = \gamma = 90^o$ $\beta \neq 90^o$

Q.2 A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it ? How many of these are tetrahedral volds ?

Sol. Number of close-pakced spheres, N = 0.5 ml

Now number of octahedral voids generated = N = 0.5 mol

Number of tetrahedral voids generated = 2N = 2× 0.5 mol = 1.0 mol

Total number of voids generated = 0.5 + 1.0 mol = 1.5 mol

Thus total number of voids = $1.5 = 6.023 = 10^{23} = 9.0345 \times 10^{23}$

Number of tetrahedral voids = $1 = 6.023 \times 10^{23} = 6.023 \times 10^{23}$.

Q.3 A compound is formed by two elements M and N. The element N forms ccp structure and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound ?

Sol. The number of tetrahedral voids formed is equal to twice thenumber of atoms of elements N and only 1/3rd of these are occupied by the atoms of element M.

Hence the ratio of number of atom M and N is $2 \times \frac{1}{3}$: 1 or 2 : 3 and the formula of the compound is $M_2 N_3$.

Q.4. An element with molar mass $2.7 \times 10.7 \times 10^{22}$ kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3 kgm^{-3}, what is the nature of the cubic unit cell ?

Sol. Here,

$\rho = 2.7 \times 10^3$ kmg^{-3}

$M = 2.7 \times 10^{-3}$ kg mol^{-1}

$a = 405$ pm $= 405 \times 10^{-12}$ m

We know that

$$\text{Density,} \quad \rho = \frac{ZM}{a^3 N_A}$$

$$\text{or} \qquad Z = \frac{\rho . a^2 . N_A}{M}$$

$$= \frac{2.7 \times 10^3 \times (405 \times 10^{-12})^3 \times 6.022 \times 10^{23}}{2.7 \times 10^{-2}} = 4$$

Thus, value of Z(= 4) suggests that the lattice is cop.

Q.5 Calculate the efficiency of packing in case of metal crystal for -

(a) simple cubic

(b) body-centred cubic

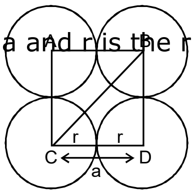
(c) face-centred cubic

(with the assumption that atoms are touching each other)

Sol.(a) In simple cubic :

Suppose the length of the unit cell edge is a and r is the radius of the sphere.

Therefore, cell edge become equal to 2r.



$\therefore \quad a = 2r$

We know that a simple cube has effectively one sphere because the spheres at the corners of the cube are shared by eight unit cells (8 × 1/8 = 1).

$\therefore$ Volume of one sphere = $\frac{4}{3}\pi r^3$

Volume of the unit cell = $(a^3) = (2r)^3 = 8r^3$

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

$$= \frac{(4/3)\pi r^3}{8r^3} = 100 = \frac{\pi}{6} \times 100$$

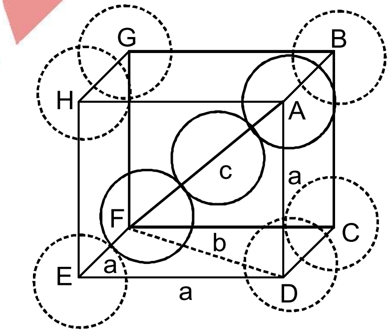
$$= \frac{3.1416}{6} \times 100 = 52.4\ \%$$

(b) In body-centred cubic :

In ΔEFD, $FD^2 = EF^2 + ED^2$

$b^2 = a^2 + a^a = 2a^2$

$b = \sqrt{2}\,a$



Now, in ΔAFD, $AF^2 = AD^2 + FD^2$

$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$

$c = \sqrt{3}\ a$

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere, therefore, c = 4r, as all the three sphere along the diagonal touch each other.

Therefore, $\sqrt{3}\,a = 4r$; $a = \frac{4r}{\sqrt{3}}$ ....(i)

$$a^3 = \left[\frac{4}{\sqrt{3}}r\right]^3 \qquad ....(ii)$$

We know, per unit cell in bcc structure, has effectively 2 spheres and total volume of two spheres is 2 × (4/3) πr^3 and volume of the cube is a^3 is $(4/\sqrt{3}\,r)^3$

Therefore,

$$\text{Pacing efficiency} = \frac{\text{Volume occupied to two sphers in the unit cell} \times 100}{\text{Total volume of the unit cell}}$$

$$= \frac{2 \times 4/3\pi r^3 \times 100\%}{[(4/\sqrt{3})r]^3} = \frac{8/3\pi r^3 \times 100}{[64/(3/\sqrt{3})r^3]} = 68\ \%$$

(c) In face-centred cubic :

In ΔABC, $AC^2 = BC^2 + AB^2$

$b^2 = a^2 + a^2 = 2a^2$

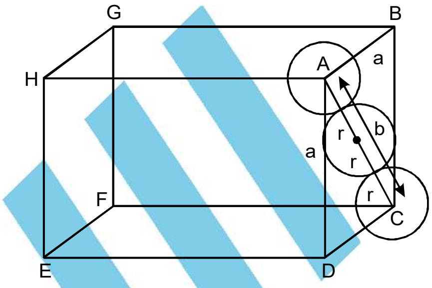
or $b = \sqrt{2}\,a$

if r is the radius of the sphere, we find

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

or $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$ ....(i)

$a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \text{or } a^3 = (2\sqrt{r})^3$



We know, per unit cell in fcc (or ccp) structure, has effectively 4 spheres and total volumes of four spheres is equal to 4 × (4/3) pr^3 and volume of the cube is a^3 or $(2\sqrt{2r})^3$ using eq. Therefore,

$$\text{Packing efficienty} = \frac{4 \times (4/3)\pi r^3 \times 100\%}{(2\sqrt{2}r)^3} = \frac{(16/3)\pi r^3 \times 100\%}{16\sqrt{2}r^3} = 74\ \%$$

Q.6 Silver crystallises in fcc lattice. If edge legnth of thecell is 4.07 × 10^{-8} cm and density in 10.5 g cm^{-3}, calculate the atomic mass of silver.

Sol. Edge length, $a = 4.07 \times 10^{-8}$ cm

$\therefore$ Volume of unit cell, $a^3 = (4.07 \times 10^{-8})^3$

$= 67.41 \times 10^{-24}\ cm^3$

Atoms per unit cell of fcc, Z = 4

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

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

$$= \frac{10.5 \times 6.023 \times 10^{23} \times 67.41 \times 10^{-24}}{4} = 106.57\ g\ mol^{-1}$$

Q.7 A cubic solid is made of two elements PO and Q are at the corners of the cube and P at the body-centre. What is the formula of the compound ? What are the coordiantion number of P and Q ?

Sol. We know that in simple cubic number of atoms at corner 1/8 = 8 = 1, and in body centre it is also 1. So the formula of compound is PQ. The structure of the compound formed by P and Q resembles CsCl structure. Thus coordination number of PO and Q is 8 each.

Q.8 **Nobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 92.90 u.**

Sol. According to question,

$$Z = 2$$
$$\rho = 8.55 \text{ gm cm}^{-3}$$
$$M = 92.90 \text{ u}$$

We know that

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

$$a^3 = \frac{2 \times 92.90}{8.55 \times 6.023 \times 10^{23}}$$

$$a^3 = 36.09 \times 10^{-24} \text{ cm}^3$$

$$a = 3.3 \times 10^{-8} \text{ cm}$$

or 3.3×10^{-10} m

We know for bcc structure

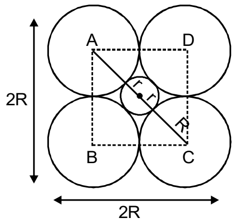
$$r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 3.3 \times 10^{-10}$$

$$r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 3.3 \times 10^{-10}$$

$$r = 1.43 \times 10^{-10} \text{ m}$$

Q.9 **If the radius of the octahedral void is r and radius of the atoms in close-packing is R, derive relation between r and R.**

Sol. An octahedral void is represented by the shaded protion. Suppose the length of the each arm of the square is 2R (R is radius of atom). Let r be the radius of void. For right angled trangle ABC



$$AC = \sqrt{(AB)^2 + (BC)^2} = \sqrt{(2B)^2 + (2R)^2} = \sqrt{8}\,R$$

Also $AC = R + R + 2r$

$= 2r + 2R = 2\,(r + R)$

or $\sqrt{(g)}\,R = 2\sqrt{2}\,R = 2\,(r + R)$

or $r = \sqrt{2}\,R - R$

$r = (\sqrt{2} - 1)\,R = 0.414 \times R$

Q.10 **Non-stoichlometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you acount for the fact that this substance is p-type semiconductor ?**

Sol. Cu_2O having Cu : O ratio less than 2 : 1 shows metal deficiency due to cation vacanicies. Metal deficient compounds conduct electricity through positive holes conduction mechanism therefore, it is a p-type semiconductor.

Q.11 **Calssify each of the following as being eiother a p-type of an n-type semiconductor :**

(i) Ge doped with In.

(ii) B doped with Si.

Sol. (i) p-type semicoinductor

(ii) n-type semicoinductor

Q.12 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

(a) What is the length of the unit cell ?

(b) How many unit cells are there in 1.00 cm^3 of aluminium ?

Sol. (a) For ccp structure, radius of atom

$$= \frac{\text{edge length}}{2\sqrt{2}} \quad \text{or} \quad r = \frac{a}{2\sqrt{2}} \quad \text{or} \quad a = 2\sqrt{2}\, r$$

Edge length (a) = $125 \times 2\sqrt{2} = 354$ pm

(b) Volume of one unit cell (a^3) = $(354 \times 10^{-12})^3$

$a^3 = 4.436 \times 10^{-29} = 4.435 \times 10^{-23}\ cm^3$

Number of unit cells of aluminium in 1 cm^3 = $\frac{1}{4.436 \times 10^{-23}} = 3.25 \times 10^{22}$ units cells

Q.13 If NaCl is doped with 10^{-3} mol % of $SrCl_2$, What is the concentration of cation vacancies ?

Sol. We know that, doping of $SrCl_2$ to NaC brings in replacement of two Na^+ ions by each Sr^{2+} ions, but each Sr^{2+} occupis only one lattice point. This produces one cation valencey. Thus, doping of 10^{-3} mole of $SrCl_2$ in 100 moles of NaCl will produce cation vacancies = 10^{-3} mol.

or 1.00 mole of NaCl will have cation vacancies after doping = $\frac{10^{-3}}{100} = 10^{-5}$ mol

OR

The addition of $SrCl_2$ to NaCl procues cation vacancies equal in number to that of Sr^{2+} ions.
Number of moles of $SrCl_2$ added to 1 mol of

NaCl = $\frac{10^{-3}}{100} = 10^{-5}$ mol

Number of Sr^{2+} added to 1 mol of

NaCl = $10^{-5} \times 6.02 \times 10^{23}$ ions

= 6.02×10^{18} ions

Concentration of cation vacancies = 6.02×10^{18}

Q.14 In a closed packed structure of oxides, one eighth of the tetrahedral voids are occupied by bivalent cations A and half of the octahedral holes are occupied by trivalent cations B. Calculate the molecular formula of oxide.

Sol. No. of bivalent cations A = $\frac{1}{8} \times 2 = \frac{1}{4}$

No. of trivalent cation B = $\frac{1}{2} \times 1 = \frac{1}{2}$

Hence, the formula of the compound is $A_{1/4}\, B_{1/2}O$

or AB_2O_4

Q.15 Define F-centres, Mention some properties of solids which have F-centres in the crystals.

Sol. When anions are missing from their lattice sites, leaving holes which are occupied by the electrons to maintain the electrical balance, the vacant sites occupied by electrons are called F–centres.

Properties due to F–centre are as follows:

(i) The crystals having F–centres are coloured.

(ii) When the crystals are exposed to light, they become photoconductors.

(iii) The crystals having F-centre are paramagnetic due to the presence of unpaired electrons

Q.16 CsCl forms a bcc lattice. Cs^+ and Cl^- ions are in contact with each other long the body diagonal. The radius of Cl^- ions is 181 pm and unit cell edge length is 412 pm. Calculatate radius of Cs^+.

Sol. In right-angled ΔABC

$$AC = \sqrt{AB^2 + AC^2}$$
$$= \sqrt{a^2 + a^2}$$
$$= \sqrt{2}\,a$$

In right-angled ΔACD

$$CD = \sqrt{AB^2 + AC^2} \qquad = \sqrt{\left(\sqrt{2a}\right)^2 + a^2}$$
$$= \sqrt{3}\,a$$

$$\therefore \quad 2(r_{Cs^+} + r_{Cl^-}) = \sqrt{3}\,a \qquad 2(r_{Cs^+} + 2 \times 181) = 1.732 \times 412$$

$$2r_{Ca^+} = (1.732 \times 412) - (2 \times 181) \qquad = 351.584$$

$$r_{Ca^+} = \frac{351.584}{2} = 175.792 \text{ pm}$$

Q.17 Examine the illustration of a portion of the defective crystal given below and answer the following questions:

⊕ ⊖ □ ⊖ ⊕ ⊖ ⊕ ⊖
⊖ ⊕ ⊖ ⊕ □ ⊕ ⊖ ⊕
⊕ ⊖ ⊕ ⊖ ⊕ ⊖ □ ⊖
⊖ ⊕ □ ⊕ ⊖ ⊕ ⊖ ⊕
⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖

(i) What are these type of vacancy defects called ?
(ii) How is the density of a crystal affected by these defects?
(iii) Name one ionic compound which can show this type of defect in the crystalline state.
(iv) How is the stoichiometry of the compound affected?

Sol. (i) Schottky defects (ii) decreases (iii) Sodium chloride (iv) No effect

Q.17 (a) Why ice has porous structure?
(b) How does conductivity of superconductors vary with temperature?
(c) What is the effect of Frenkel defect on the electrical conductivity of crystalline solids ?

Sol. (a) Due to cage like structure on account of intermolecular H-bonding among H_2O molecules.
(b) It decreases with rise in temperature.
(c) Conductivity increases because vacancies are created.

Q.18 Analysis shows that Nickes oxide has formula $Ni_{0.98}\,O_{1.00}$. What fractions of the nickel exist as Ni^{+2} and Ni^{+3} ions.

Sol. Let Ni^{+3} be x mol
Ni^{+2} be 0.98 – x
(Sum of O. N. of all atoms in a compound is equal to zero)
So $3x + 2(0.98 - x) + (-2)$
$x = 0.04$

$$\% \text{ of } Ni^{3+} = \frac{0.04 \times 100}{0.98} = 4.08 \qquad \% \text{ of } Ni^{+2} = 100 - 4.08 = 95.92$$

EXERCISE – I UNSOLVED PROBLEMS

Q.1 (i) What is meant by the term coordination number?
(ii) What is the coordination number of atoms:
(a) in a cubic close - packed structure?
(b) in a body-centred cubic structure?

Q.2 How will you distinguish between the following pairs of terms:
(i) Hexagonal close -packing and cubic close -packing?
(ii) crystal lattice and unit cell?
(iii) Tetrahedral void and octahedral void?

Q.3 How many lattice points are there in one unit cell of each of the following lattice?
(i) Face-centred cubic
(ii) Face-centred tetragonal
(iii) Body-centred

Q.4 Calculate the efficiency of packing in case of a metal crystal for
(i) simple cubic
(ii) body-centred cubic
(iii) face-centred cubic (with the assumptions that atoms are touching each other).

Q.5 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Q.6 Analysis shows that nickel oxide has the formula $NiO_{98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions ?

Q.7 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Q.8 Gold (atomic radius = 0.144 nm) crystallises in a face -centred unit cell. What is the length of a side of the cell?

Q.9 In terms of band theory, what is the difference between
(i) a conductor and an insulator
(ii)a conductor and semiconductor?

Q.10 Explain the following terms with suitable examples:
(i) Schottky defect (ii) Frenkel defect (iii) Intersititials and (iv) F-centres

Q.11 Explain the following with suitable examples
(i) Ferromagnetism (ii) Paramagnetism
(iii) Ferrimagnetism (iv) Antiferromagnetism
(v) 12-16 and 13-15 group compounds.

EXERCISE – II

BOARD PROBLEMS

Q.1 Name a substance which on addition to AgCl causes cation vacancy in it.

Q.2 Calculate the density of silver which crystallises in the fcc structure. The distance between the nearest silver atoms in this structure is 287 pm. (Molar mass of Ag = 107.87 g/mol)

Q.3 What makes alkali metal halids sometimes coloured, which are otherwise colourless?

Q.4 Define the term amorphous.

Q.5 Calculate the value of Avogadro's constant from the following data:
Density of NaCl = 2.165 g/cm^3
Distance between Na^+ and Cl^- in NaCl = 281 pm
(Molar mass of NaCl = 58.5 g/mol)

Q.6 Which point defect lowers the density of a crystal?

Q.7 What is meant by coordination number in an ionic crystal?

Q.8 What is the maximum possible coordination number of an atom in an hcp crystal structure of an element ?

Q.9 Aluminium metal forms a cubic close packed crystal structure. Its atomic radius is 125×10^{-12} m
(a) calculate the length of the side of the unit cell.
(b) How many such unit cells are there in 1.00 m^3 of aluminium?

Q.10 A cubic solid is made of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound?

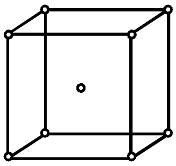
Q.11 An element has a body-centred cubic ctructure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. Calculate the number of atoms present in 208 g of the element.

Q.12 Name the non-stoichiometric point defect responsible for colour in alkyl halides.

Q.13 Calculate the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 g/cm^3. [Molar mass of NaCl = 58.5 g/mol]

Q.14 Assign reasons for the following :
(i) Phosphorus doped silicon is a semiconductor.
(ii) Schollky defect lowers the density of a solid.
(iii) Some of very old glass objects appear slightly milky instead of being transparent.

Q.15 What is the number of atoms per unit cell in a body -centred cubic structure?



Q.16 What is a semiconductor? Describe the two main types of semiconductors and explain mechanism of their conduction.

Q.17 What is the total number of atoms per unit cell in a face centred cubic structure?

Q.18 How do you account for the following?
(i) Frenkel defects are not found in alkali metal halides.
(ii) Schottky defects lower the density of related solids.
(iii) Impurity doped silicon is a semiconductor.

Q.19 Explain the following properties giving suitable examples
(i) Ferromagnetism (ii) Paramagnetism (iii) Ferrimagnetism

Q.20 Silver crystallises in a fcc lattice. The edge length of its unit cell is 4.077×10^{-8} cm and its density is 10.5 g cm^{-3}. Calculate on this basis the atomic mass of silver.

Q.21 What are F-centres ?

Q.22 Account for the following:
(i) Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K.
(ii) Zinc oxide on heating becomes yellow.
(iii) Frenkel defect does not change the density of AgCl crystals.

Q.23 With the help of suitable diagrams on the basis of bond theory explain the difference between.
(i) A conductor and an insulator. (ii) A conductor and a semiconductor.

Q.24 Why is glass considered a supercooled liquid?

Q.25 The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom be 137.8 pm, is the copper unit cell simple cubic, body/centred cubic or face-centred cubic?

Q.26 What is the number of atoms in a unit cell of a face- centred cubic crystal ?

Q.27 Silver crystalises with face-centred cubic unit cells. Each side of the unit cell has a length of 409 pm. What is the radius of an atom of silver?
(Assume that each face atom is touching the four corner atoms.)

Q.28 Calculate the packing efficiency of a metal crystal for a simple cubic lattice.

Q.29 Explain how you can determine the atomic mass of an unknown metal if you know its mass density and the dimensions of unit cell of its crystal.

Q.30 What are n-type semiconductors ?

Q.31 Copper crystallises with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal.
(Atomic mass of Cu = 63.55 u and Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1})

OR

Iron has a body centred cubic unit cell with the cell dimension of 286.65 pm. Density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number. (Atomic mass of Fe = 56.0 u)

Q.32 The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom be 127.8 pm, is the copper unit cell simple cubic, body centred cubic or face-centred cubic ?
(given : atomic mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})

Q.33 (a) What change occurs when AgCl is doped with $CdCl_2$?
(b) What type of semiconductor is produced when silicon is doped with boron ?

Q.34 Aluminium crystallizes in an fcc structure. Atomic radius of the metal is 125 pm. What is the length of the side of the unit cell of the metal ?