Solid State

State of matter depends on.

(i) Tendency of relative motion at a particular temperature.

(ii) Intermolecular forces.

Table : 1

Properties	Solid	Liquid	Gases
(i) Motion of partical.	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 ($\sim$ zero)
(iii) Average separation (volume)	Average separation is fixed so volume is fix.	Average separation is almost constant so almost fixed volume.	No fixed volume.
(iv) Shape	Definate shape as location of partical are fixed.	Average separation is fixed but location of partical is not fixed so no definate 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 :

(1) Classification on the basis of forces among constituting particles

Table : 2

Type of solid	Constituent partical	Force of interaction	Example	Physical state	Melting point
(i) Molecular solid (non conducting) "Non conducting"	Molecules	(i) Non polar $\rightarrow$ dispersion force. (ii) Polar $\rightarrow$ dipole-dipole. (iii) Polar & H-bonding.	I_2, Xe(s), C_6H_6, CCl_4, H_2 HCl, SO_2, SF_4 H_2O (s), H_3BO_3(s)	Very soft Soft Hard	Very low Low Low
(ii) Ionic solid. solid $\rightarrow$ insulator Molten & aqueous $\rightarrow$ conducting.	Ions	Coulombic non directional 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, AIN, 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
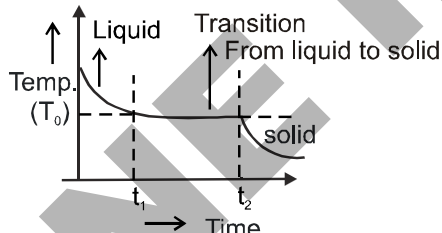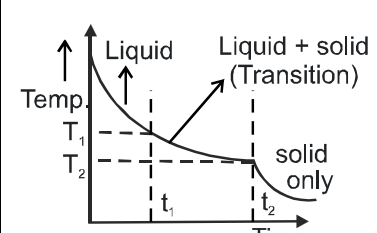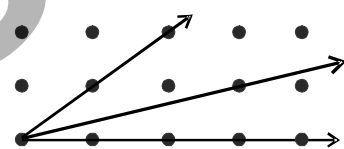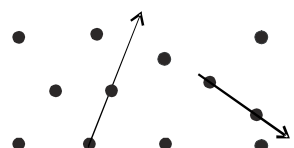
Ionic solid $\rightarrow$ Al_2O_3(s).

GENERAL CHARACTERISTICS OF SOLIDS :

(i) Solids have definite mass, shape and volume.
(ii) There is least intermolecular distances in solids as compared to liquids and gases.
(iii) There is strong intermolecular forces of attraction between particles in solids.
(iv) The particles of a substance cannot flow in its 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 translational motions only.
(vi) They are rigid and incompressible.

(2) Types of SOLIDS on the basis of arrangement of particles :

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

Table : 3

	Crystalline solid		Amorphous solids
	True solid		Pseudo solids, super cooled liquid [In between solid & liquid]
1	The constituent partical (atoms, molecule, ion) follow a definite repetiting arrangement.	1	No particular pattern is followed partical 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 :**	4	These have a range of temperature in which they melts as. There melting point and enthalpy of fusion is not fixed.
5	These are anisotropic : Physical properties will have different values in different direction. Ex. : Ag, Fe, Cu, NaCl, H_2O (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.

Internal arrangement of partical in crystalline solid :

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

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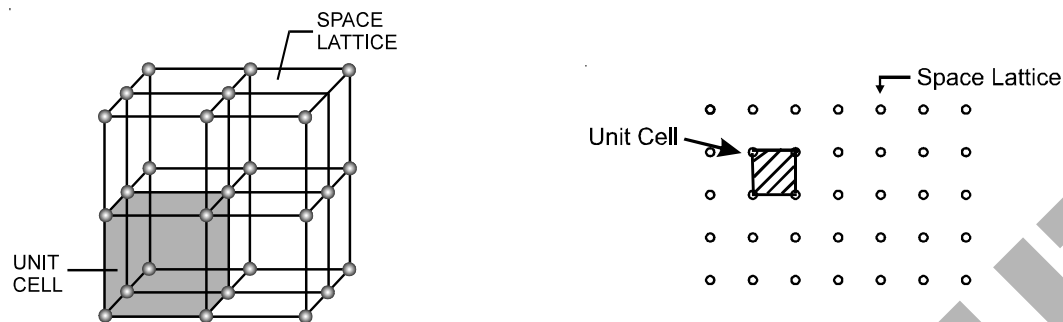
Figure

Unit Cell :

The group of the lattice point (generally the smallest one) which on repetition parallel to its edges & equal to its edge length generates whole of the lattice is called unit cell of the lattice.

or

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

CHARACTERISTICES 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.
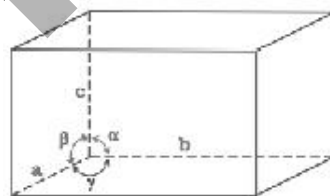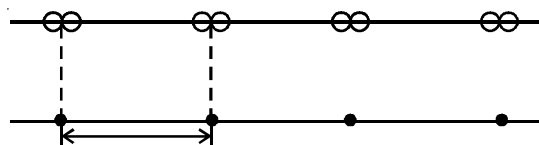

Illustration of parameters of a unit cell

A unti cell may also be defined as a1D, 2D, 3D three dimensional group of lattice points that generates the whole lattice by repetation or stacking.

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

1-Dimensional space lattice :
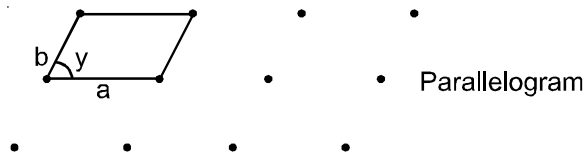
Uniformly separated lattice point in 1-D

Figure

only one parameter is required $\rightarrow$ distance between two lattice point.

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2-D Lattice :

Regular arrangement of point in plane 3 parameter required $\rightarrow$ Two edge lengths & angle between these two edge.
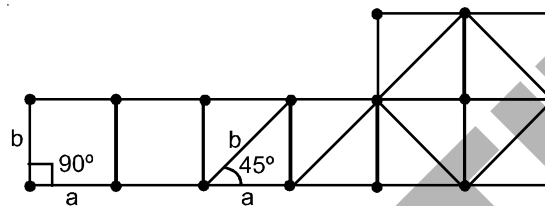

Parallelogram

Figure

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

(i) Square unit cell $\rightarrow$ a = b, $\gamma = 90^{0}$
(ii) Rectangle unit cell $\rightarrow$ a $\neq$ b, $\gamma = 90^{0}$
(iii) Hexagonal unit cell $\rightarrow$ a = b, $\gamma = 60^{0}$
(iv) Rhombic unit cell $\rightarrow$ a = b, $\gamma \neq 90^{0}$ & $\gamma \neq 60^{0}$
(v) Parallelogram $\rightarrow$ a $\neq$ b, $\gamma \neq 90^{0}$

Most symmetrical $\grave{E}$ square unit cell.
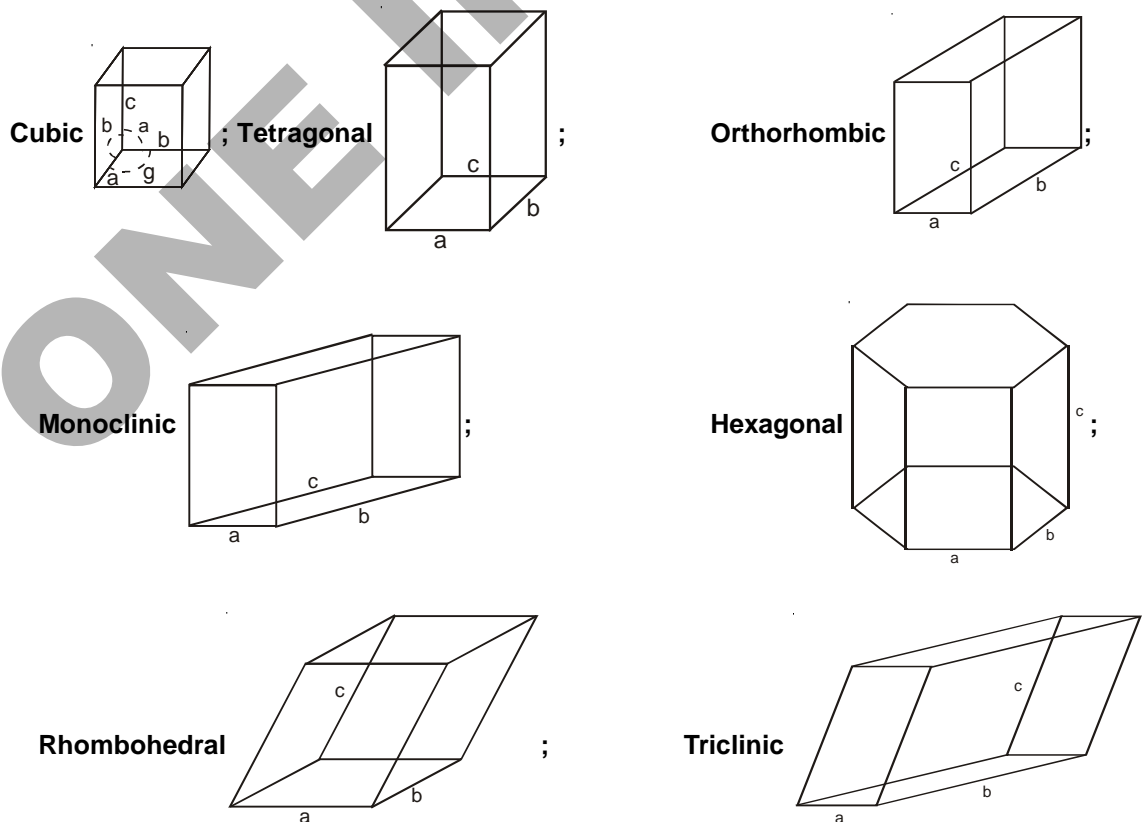
Square unit cell :

Figure

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

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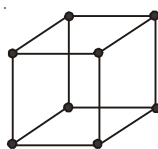
3-D-Lattice :

Seven Primitive unit cells in crystals

Cubic ; **Tetragonal** ; **Orthorhombic** ;

Monoclinic ; **Hexagonal** ;

Rhombohedral ; **Triclinic**

Figure

SOLID STATE # 4

The type of unit cells found in different types of crystals.
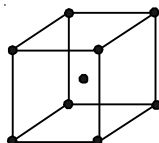
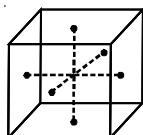1.   **Primitive /simple unit cell :**

SC → Simple cubic.

2.   **Non primitive :**
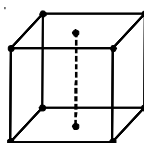
(a) Body centered (B.C.) :   B.C.C → Body centered cubic.

(b) Face centered (F.C.) :   F.C.C

(c) End centered (E.C.) :   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.

→   3-egde length (a,b,c) and 3-angle between these. (α, β, γ), [a–b→γ], b–c→α], [c–a–β].

Seven Crystal System
Table : 4

Crystal System	Features	Unit cell found	Examples
Cubic	$a = b = c$ $= = = 90°$	SC, BCC, FCC	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, CaF_2, Na_2O, KCl, Pb, Alum.
Tetragonal	$a = b \neq c$ $= = = 90°$	S, BC	Sn (white tin), SnO_2, TiO_2, ZnO_2, $NiSO_4$, urea.
Orthorhombic	$a \neq b \neq c$ $= = = 90°$	S, BC, FC, EC	Rhombic sulphur, $BaSO_4$, KNO_3, $PbCO_3$, $CaCO_3$ (aragonite)
Rhombohedral or Trigonal	$a = b = c$ $= = \neq 90°$	S	$CaCO_3$(Calcite), HgS(Cinnabar), $NaNO_3$, ICl.
Monoclinic	$a \neq b \neq c$ $= = 90°$; $\neq 120°, \neq 90°, \neq 60°$	S, EC	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$.
Hexagonal	$a = b \neq c$ $= = 90°, = 120°$	S	Graphite, ZnO, CdS, Mg, PbI_2, SiC.
Triclinic	$a \neq b \neq c$ $\neq \neq \neq 90°$	S	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3.

Note :   In 3-D 14 different types of unit cell are found and these are also known as 14 **Bravais lattice**.

SOLID STATE # 5

Contribution of different Lattice point in one Cubical unit cell :

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

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

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

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

Solved Examples

Ex.2 The lattice parameters of a given crystal are a = 5.62 Å, b = 7.41 Å and c = 9.48 Å. The three coordinate axes are mutually perpendicular to each other. The crystal is :
(A) tetragonal   (B) orthorhombic   (C) monoclinic   (D) trigonal.

Ans. (B)

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

Ex.3 Tetragonal crystal system has the following unit cell dimensions:
(A) a = b = c and $\alpha = \beta = \gamma = 90°$ (B) a = b ≠ c and $\alpha = \beta = \gamma = 90°$
(C) a ≠ b ≠ c and $\alpha = \beta = \gamma = 90°$ (D) a = b ≠ c and $\alpha = \beta = 90°$, $\gamma = 120°$

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

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.

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

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

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

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

(ii)   1 amu = 1.67×10^{-24} gram

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

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

Some Definations

Coordination number : *The number of nearest neighbours sphere in a packing is called coordination number.*

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 = $\dfrac{z \times M}{a^3 \times N_A \times 10^{-30}}$ gcm^{-3}

Packing efficiency : *The perecentage of total space filled by the particles is called packing efficiency. Different types of packing arrangements have different packing efficiency.*
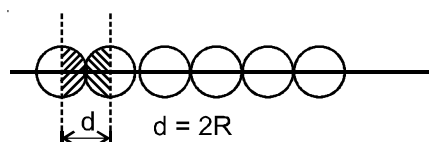
Packing efficiency = $\dfrac{\text{Volume of atoms in a unit cell}}{\text{Total volume of a unit cell}} \times 100$

Structure of Solids :

1-D Lattice :

(d > 2R) → not close packing

Figure

d = 2R
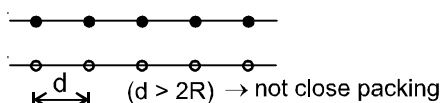
Figure

→ Arrangement of maximum stability. → Arrangement of minimum P.E.
→ Arrangement of closet packing. → Arrangement of maximum efficiency (100%).

2-D Lattice :

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

Table : 5

| (i) Square arrangement (poor arrangement)	Hexagonal Arrangement (Better arrangement)
Array are arranged such that sphere of one array are exactly above the sphere of another array	One dimensional array are arranged such that sphere of one array occupy the depression of other array.
A–A–A type packing	AB–AB type packing
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) = $\dfrac{1 \times \pi R^2}{4R^2} = \dfrac{\pi}{4} = 78.5\%$ (iv) Co-ordination no. (CN) = 4.	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) = $\dfrac{3(\pi R^2)}{6 \times \frac{\sqrt{3}}{4}(2R)^2} = 90.6\%$ (iv) Co-ordination no. (CN) = 6.

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 :

(i) Square packed sheets are kept on another such that -
atoms / spheres of one sheet are exactly above spheres of other sheet.

→ A A A A .... pattern repeat.

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

Simple
cubic
Figure

$a = b = c$
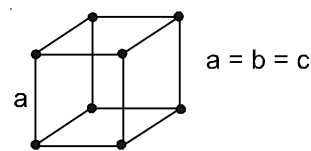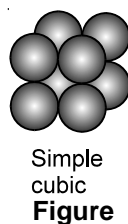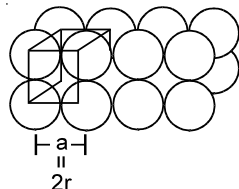
(i) Relation between a & R.

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

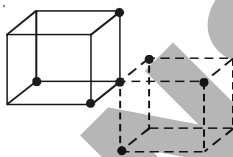**(ii) Effective no. of atom (Z) (per unit cell).**

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

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

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

(v) Co-ordination number :

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

Figure

Table : 6

	Type of neighbour	Distance	No. of neighbours	
(i)	Nearest	a	6	$\left\{\dfrac{3 \times 8}{4} = 6\right\}$
(ii)	(next)[1]	$\sqrt{2}\,a$	12	$\left\{\dfrac{3 \times 8}{2} = 12\right\}$
(iii)	(next)[2]	$\sqrt{3}\,a$	8	$\left\{\dfrac{1 \times 8}{1} = 8\right\}$
(iv)	(next)[3]	$2\,a$	6	
(v)	(next)[4]	$\sqrt{5}\,a$	24	

(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.

$a = b = 2R$
$c = 2\sqrt{2}\ R$
R

Figure

SOLID STATE # 8
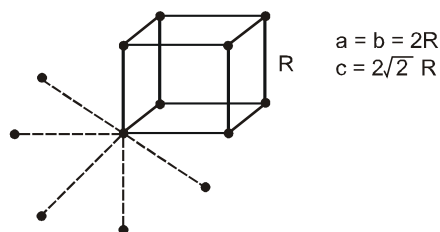
Body centered cubic (BCC) :

$$\leftarrow a \rightarrow = \frac{4R}{\sqrt{3}}$$
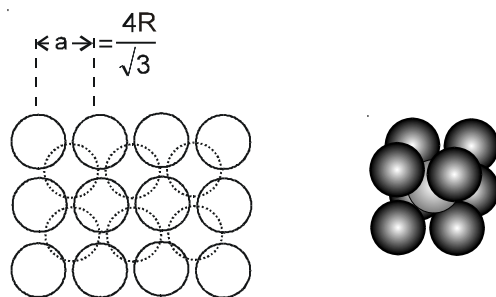
Figure

$\rightarrow$ Not so close pack arrangement.

$\rightarrow$ 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.

$\rightarrow$ 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 : (a $\neq$ 2 R)

Sphere are not touching along edge they touching along the body diagonal. So $\sqrt{3}\,a = 4R$.

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

(iii) Packing fraction

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

(iv) Co-ordination No. (CN) = 8.

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

Table : 7

	Type of neighbour	Distance	No. of neighbours
(i)	Nearest	$\dfrac{\sqrt{3}a}{2} = 2R$	8
(ii)	(next)[1]	a	6
(iii)	(next)[2]	$\sqrt{2}a$	12
(iv)	(next)[3]	$\dfrac{\sqrt{11}a}{2}$	24
(v)	(next)[4]	$\sqrt{3}\,a$	8

Note : In bcc crystal structure, the co-ordination no. is 8 because each atom touches four atom 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)

SOLID STATE # 9

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 Å

(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 have

(E) What is calculated density of crystalline K.

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

(A) $2r = \dfrac{\sqrt{3}\,a}{2} = \dfrac{\sqrt{3} \times 5.2}{2} = 4.5$ Å   (B) distance = a = 5.2 Å

(C) 8   (D) 6

(E) $d = \dfrac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92$ g/ml
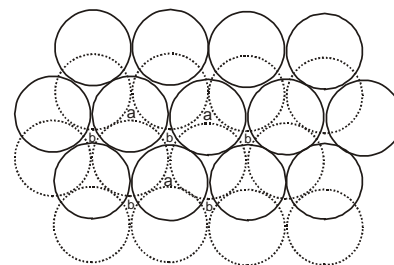

(B) Arrangement of hexagonal closed packed sheets :

$\rightarrow$ To generate close packing two dimensions arrangement must be hexagonal.

$\rightarrow$ Sheet are arranged such that void or depressions of one sheet are occupied by sphere of other sheet.

$\rightarrow$ Only 50% void of one layer can be occupied by sphere of other layer (II layer).

$\rightarrow$ Now there will be two method to place III layer on the II layer.

Figure

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

$\rightarrow$ 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.
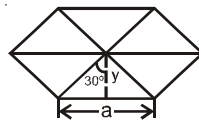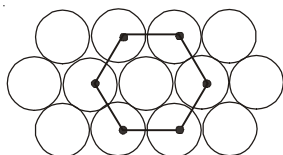
One type of void always remain on occupied.

Exploded view

Hexagonal closest-packed
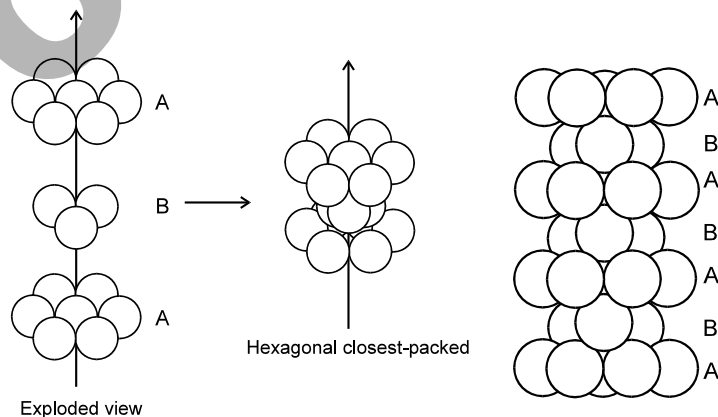
Unit cell : a = 2r = b; $\gamma = 120^0$

Figure

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

$$a = b = 2R$$

Figure

$$\tan 30 = \frac{a}{2 \times y} \quad \text{So} \quad y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$$

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

calculation of c.
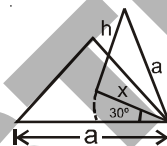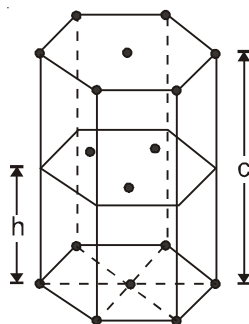
Figure

$$\cos 30^0 = \frac{a}{2 \times x} \qquad x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$$

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

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

$$h = \sqrt{\frac{2}{3}} \, a$$

so $\quad c = 2h = 2\sqrt{\dfrac{2}{3}} \, a$

so volume of hexagon = area of base × height

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

(ii) Effective no. of atoms (Z) :

$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6.$$

(iii) Packing efficiency :

$$= \frac{6 \times \frac{4}{3} \pi R^3}{24\sqrt{2} \, R^3} = \frac{\pi}{3\sqrt{2}} = 74\%.$$

SOLID STATE # 11

(iv) Coordination number, (CN) = 12
    (Each sphere touch 6 sphere in its layer 3 above and 3 below)

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

(2) ABC–ABC arrangement (Cubic close packing (FCC))

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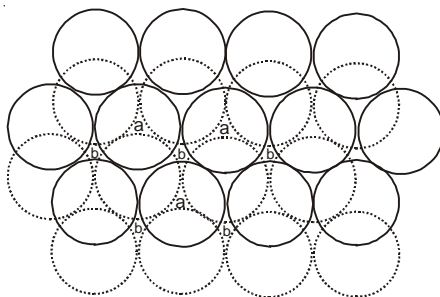
Figure

→   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).

Cubical closest-packed structure

Exploded view

Figure

planes of closest packing ≡

Figure

Figure

SOLID STATE # 12
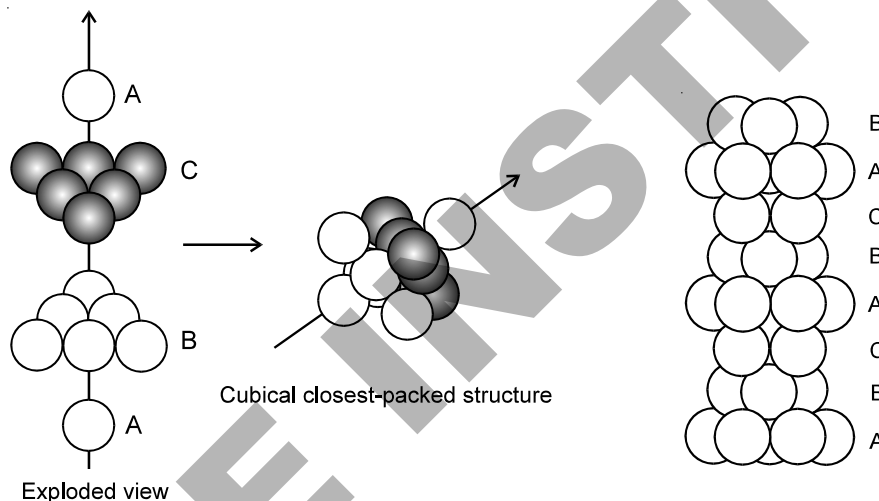
(i) Relation between 'a' and 'R' :

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

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

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

(iv) Coordination number, (CN) = 12

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

Table : 8

Type of neighbour	Distance	No. of neighbours
Nearest	$\dfrac{a}{\sqrt{2}}$	12
(Next)[1]	a	6
(Next)[2]	$\sqrt{\dfrac{3}{2}}\,a$	24
(Next)[3]	$\sqrt{2}\,a$	12
(Next)[4]	$\sqrt{\dfrac{5}{2}}\,a$	24

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 :
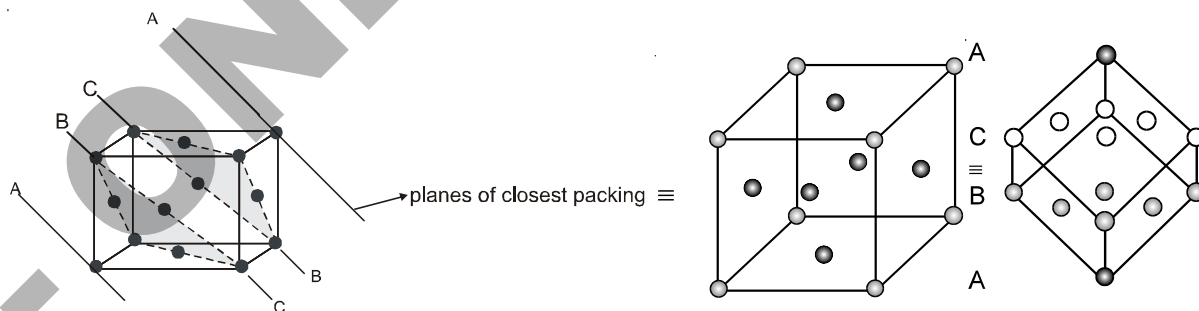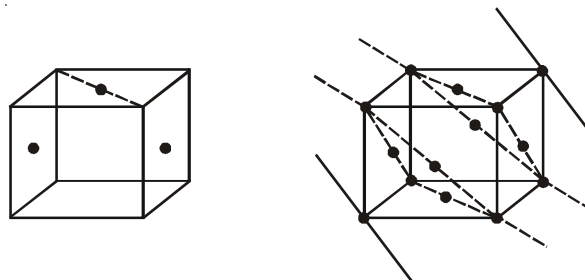
(A) 3.12   (B) 2.04   (C) 1.26   (D) 0.72

Ans. (C)

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

Ex.10 In a ccp structure, the :

(A) first and third layers are repeated   (B) first and fourth layers are repeated

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

Ans. (B)

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.

Ans. (A)

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

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

Ans. (D)

Sol. Volume of 4 atoms = $a^3 = (4 \times 10^{-8})^3 \text{ cm}^3$

volume of N_A atoms $= \dfrac{(4 \times 10^{-8})}{4} \times 6.023 \times 10^{23} = 9.6 \text{ ml.}$

Types of voids found in close packings :

$\rightarrow$ Although the close packed structure have maximum packings efficiency, but there are some empty space left in arrangement.

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.*

$\rightarrow$ Maximum size of sphere which can be place in void space is depends on size of void.

R $\rightarrow$ Radius of sphere

r $\rightarrow$ Radius of sphere placed in void.

2-Dimensions void :

(i) Triangular void [2D–3 coordinate void]

$\rightarrow$ This type of void found in close packed structure of plane when three sphere are in contact.
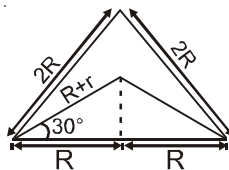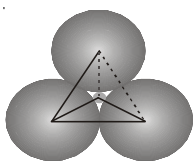
Figure

$$\cos 30° = \left(\frac{R}{R+r}\right) \qquad \left[\frac{R+r}{R}\right] = \frac{1}{\cos 30°}$$

$$\frac{r}{R} = 0.155.$$

3-Dimensions void :

(i) Tetrahedral void [3D-4 coordinate void]

$\rightarrow$ If IInd layer sphere are placed over a triangular void then new void is tetrahedral.
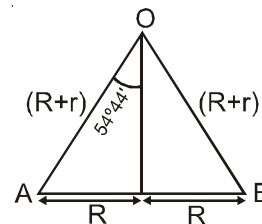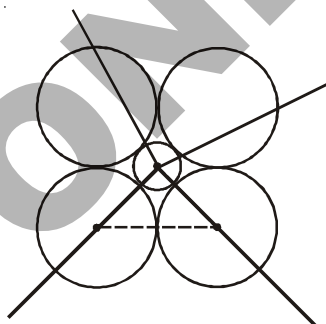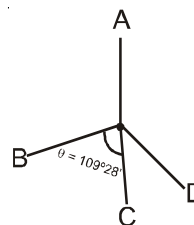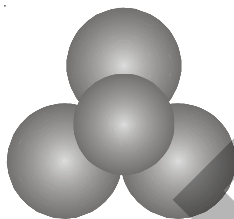
Figure

$$\sin 54°44' = \left(\frac{R}{R+r}\right) \qquad \frac{r}{R} = 0.225$$

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.

SOLID STATE # 14
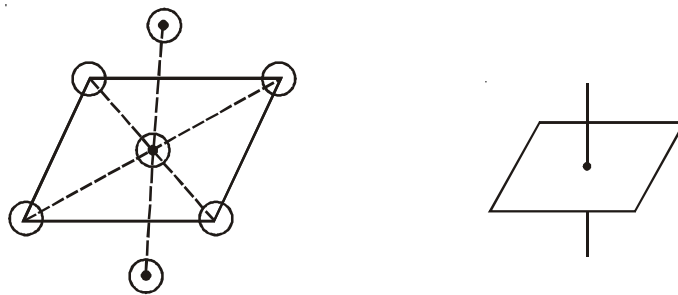
Figure

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

a = 2R
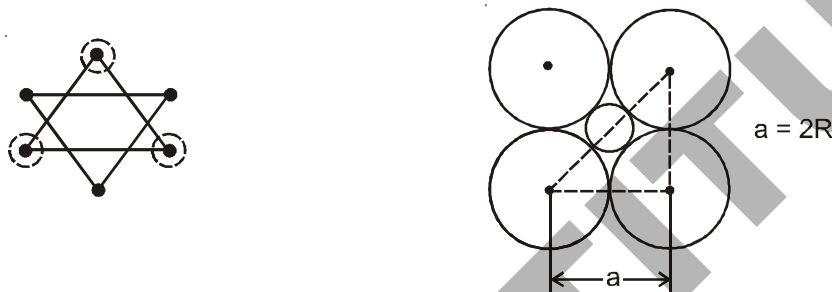
Figure

$$\sqrt{2}\, a = 2[R + r] \; ; \qquad 2\sqrt{2}\, R = 2[R + r]. \qquad \frac{r}{R} = 0.414$$

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

Sphere are touch along body diagonal :

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

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

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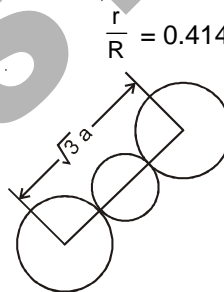
Figure

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 form 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) :

→ 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.

SOLID STATE # 15

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.

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

For HCP unit cell (Z) = 6.
So tetrahedral void = (Z × 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 :

Table : 9

Unit cell	Z	Tetrahedral void = Z × 2	Octahedral void = Z × 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. $\dfrac{r_{tetrahedral}}{r_{octahedral}} = \dfrac{0.225R}{0.414R} = 0.543.$

(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 3.61Å. What is the size of the largest atom which could fit into the interstices of the copper lattice without distorting it?
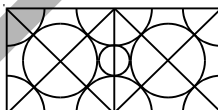
Figure
(**Hint. :** Calculate the radius of the smallest circle in the figure)
Ans. 0.53Å
Sol. $r_{octahedral} = 0.414\ R$

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

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

$r = \dfrac{0.414\sqrt{2}\ a}{4} = \dfrac{0.414\sqrt{2} \times 3.61}{4} = 0.53\ \text{Å}$

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.

SOLID STATE # 16

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 = $\left(\dfrac{r_+}{r_-} \right)$,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	
$0.155 \le r_+/r_- < 0.225$	triangular void	3	Boron oxide
$0.225 \le r_+/r_- < 0.414$	tetrahedral void	4	Zinc sulphide
$0.414 \le r_+/r_- < 0.732$	octahedral void	6	Sodium chloride
$0.732 \le r_+/r_- < 1$	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

$\Rightarrow$ 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
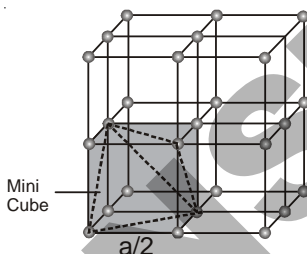
Mini
Cube
a/2

Figure

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

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

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

$$\boxed{a_{fcc} = \dfrac{4}{\sqrt{3}}(r_+ + r_-)}$$

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

$$6 \quad : \quad 6$$

"coordination number   "coordination number
of cation"   of anion"
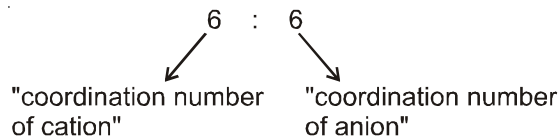
Figure

$\rightarrow$ Experimental $\dfrac{r_{Na^+}}{r_{Cl^-}} = 0.51$.

(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) = $\dfrac{Z \times M}{N_A \times a^3}$

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

→ $2[r_{Cl^-} + r_{Na^+}] = a$

(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].

O—→ Anion   ●—→ Cation
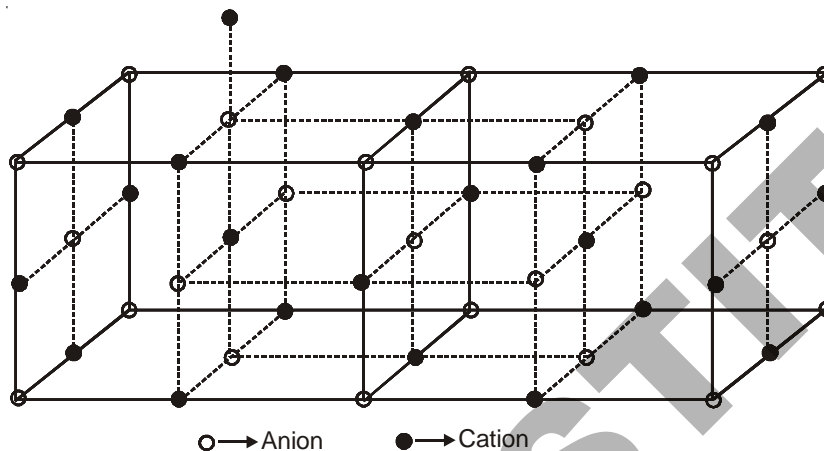
Figure

For Cl^- :

Table : 11

Type of neighbour	Distance	No. of neighbours
Nearest	Na^+, $\dfrac{a}{2}$	6
(Next)[1]	Cl^-, $\dfrac{a}{\sqrt{2}}$	12
(Next)[2]	Na^+ (B.C.), $\sqrt{\dfrac{3}{2}}\,a$	8
(Next)[3]	Cl^-, a	6

Example : Halide of Li, Na, K and Rb, AgCl, AgBr, NH_4Cl.

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) :

ZnS $\Bigg\langle$
Zinc blende → FCC
Wurtzite → HCP

Figure

SOLID STATE # 18
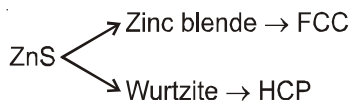
Zinc blende type :

(i) S^{2-} ion form the FCC lattice.

$\rightarrow$ Zn^{2+} ion occupy alternate (non adjacent) four tetrahedral void.
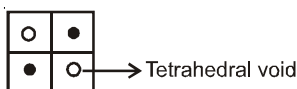
Figure

(ii) Effective number of ion

$\rightarrow$ Effective number of S^{2-} ion per unit cell = 4.

$\rightarrow$ Effective number of Zn^{2+} ion per unit cell = 4.

(iii) Formula of unit cell = Zn_4S_4

Formula of ionic compound = ZnS

(iv) $\dfrac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.3$

so anion–anion contact is not there.

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

(v) Density (d) $= \left[\dfrac{Z \times M}{N_A \times a^3} \right]$ M = 97 gram/mole.

(vi) Coordination number :

Coordination number of Zn^{2+} ions = 4.

Coordination number of S^{2-} ions = 4.

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

For S^{2-}

Table : 12

Type of neighbour	Distance	No. of neighbours	Ions
Nearest	$\dfrac{\sqrt{3}}{4} a_{FCC}$	4	Zn^{2+}
(Next)[1]	$\dfrac{a}{\sqrt{2}}$	12	S^{2-}
(Next)[2]	$\dfrac{\sqrt{11}}{4} a$	12	Zn^{2+}
(Next)[3]	a	6	S^{2-}
(Next)[4]	$\dfrac{\sqrt{19}}{11} a_{FCC}$	12	Zn^{2+}

(3) CaF_2 [Flourite structure] [AB_2 type]

Coordination number of compound

8 : 4

"coordination number of cation"   "coordination number of anion"

Figure
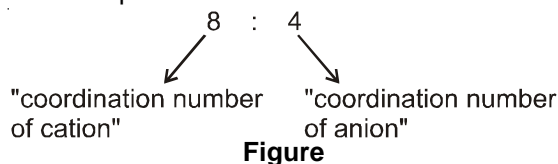
(i) Ca^{2+} ion form the FCC lattice.

$\rightarrow$ F^- ion occupy all tetrahedral voids.

(ii) Coordination number of F^- ion = 4 $\because$ It occupy tetrahedral void.

$\rightarrow$ Coordination number of Ca^{2+} ion = 8

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

$\rightarrow$ Effective number of F^- ion = 8.

(iv) Formula of unit cell = Ca_4F_8

$\rightarrow$ Formula of ionic compound = CaF_2.

Solid State # 19

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

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

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

   Other examples : CaF_2 , SrF_2 , BaF_2, $BaCl_2$.

For Ca²⁺

Table : 13

Type of neighbour	Distance	No. of neighbours	Ions
Nearest	$\dfrac{\sqrt{3}}{4}$	8	F^-
(Next)[1]	$\dfrac{a}{\sqrt{2}}$	12	Ca^{2+}
(Next)[2]	$\sqrt{\dfrac{11}{16}}$	24	F^-
(Next)[3]	a	6	Ca^{2+}

For F⁻

Table : 14

Type of neighbour	Distance	No. of neighbours	Ions
Nearest	$\dfrac{\sqrt{3}}{4}$	4	Ca^{2+}
(Next)[1]	$\dfrac{a}{2}$	6	F^-
(Next)[2]	$\dfrac{a}{\sqrt{2}}$	12	F^-
(Next)[3]	$\sqrt{\dfrac{11}{16}}$	–	Ca^{2+}

(4) Na₂O [Sodium oxide] [A₂B type]

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

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

(i) Cl⁻ form simple cubic lattice.
   $\rightarrow Cs^+$ ion occupies cubical void.

(ii) Effective number of ion :
   $\rightarrow$ Effective number of Cs^+ ion = 1. $\Rightarrow$ $\rightarrow$ Effective number of Cl^- ion = 1.

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

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

   $\rightarrow$ anion–anion contact is not there so,

   $2[r_{Cl^-} + r_{Cs^+}] = \sqrt{3}\, a_{Sc}$

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

   Other example : CsCl, CsBr, CsI.

Note : **On increasing pressure Ė Coordination number tends to increase.**
   On increasing temperature Ė Coordination number tends to decrease.

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

SOLID STATE # 20

Other important structure :

(1) Spinel structure [AB$_2$O$_4$] : Spinel is an oxide consisting of two type of metal ions with the oxides ion arranged in CCP layers in normal spinel one eight 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.

Ex : A spinel is formed by Zn^{2+}, Al^{3+} and O^{2-} with Zn^{2+} ion in the tetrahedral holes. The formula of the spinel is $ZnAl_2O_4$.

(2) Perovskite structure [ABO$_3$] : 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.
Ex : $BaTiO_3$ or $MgTiO_3$.
(3) Lattice of diamond :
$\rightarrow$ 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

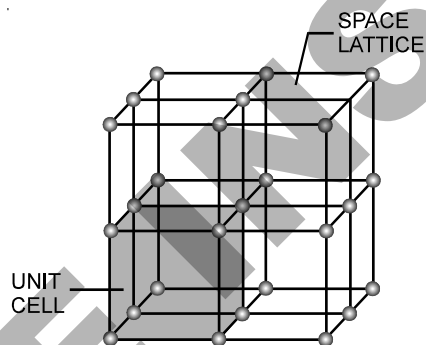$$a_{FCC} = \frac{4}{\sqrt{3}} [d_{c-c}]$$

$d_{c-c} = 2r_{c-c}$ 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.

e.g.

Figure

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 A. 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)

Sol. $r_+ + r_- = \dfrac{\sqrt{3}\,a}{2} = \dfrac{\sqrt{3} \times 4.3}{2} = 3.72$ Å .

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Crystal imperfections / defects

Imperfections can be because of :-

- Conditions under which crystals have been developed,

- Impurities,

- Temp (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.

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

Schottky defect   Frenkel defect   Interstitial defect
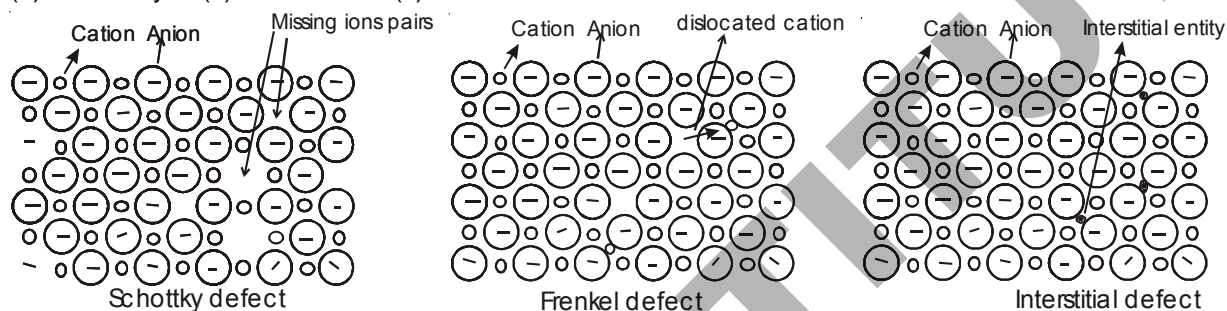
Figure

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

net density of crystal will get decreased

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

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

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

Interstitial :

When some small foreign atoms are trapped in interstitial voids of the lattice without any chemical reaction.

Formula remains the same $\rho_{exp} > \rho_{theortical}$

(ii) Non-stoichiometric defects :

(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 e⁻ the electrical and optical (colour) properties of the compound get modified.

So these locations of e⁻s are also known as color centres (F - centres) .

ZnO - white in color 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 color.

(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.

Metal excess   Cation Vacancy
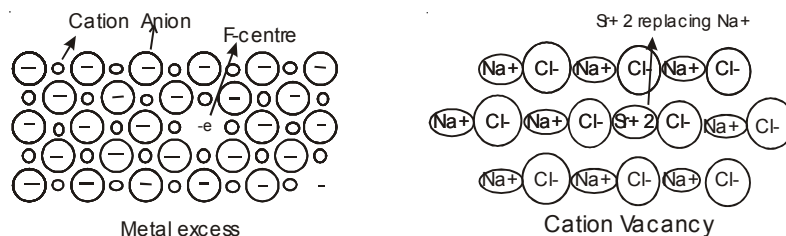
Figure

Solved Examples

Ex.17 Which of the following is incorrect

$$\begin{array}{cccccccc}
\oplus & \ominus & \square & \ominus & \oplus & \ominus & \oplus & \ominus \\
\ominus & \oplus & \ominus & \oplus & \square & \oplus & \ominus & \oplus \\
\oplus & \ominus & \oplus & \ominus & \oplus & \ominus & \square & \ominus \\
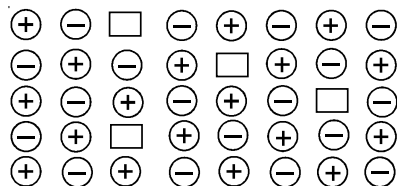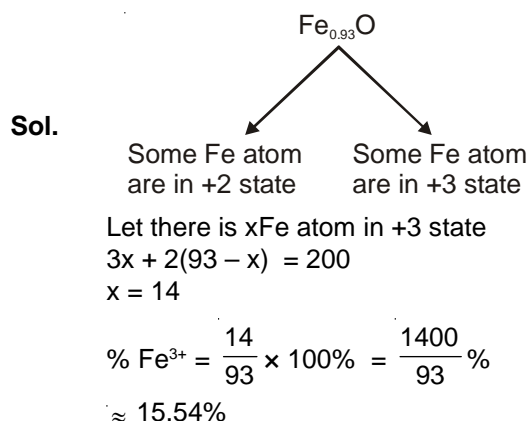\ominus & \oplus & \square & \oplus & \ominus & \oplus & \ominus & \oplus \\
\oplus & \ominus & \oplus & \ominus & \oplus & \ominus & \oplus & \ominus
\end{array}$$

(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.

$$Fe_{0.93}O$$

Sol.

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

Let there is xFe atom in +3 state
$3x + 2(93 – x) = 200$
$x = 14$

$\% Fe^{3+} = \dfrac{14}{93} \times 100\% = \dfrac{1400}{93}\%$

$\approx 15.54\%$

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 ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(1) Conductors : *Metals are goods condcutors and have conductiveites in the order 10^7 $(\hbar m)^{-1}$.*

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

(3) Semicondutors : *Those solids which have intermideidate conductivities generally from 10^{-6} to 10^4 $(\hbar m)^{-1}$ are termed as semicondcutors.*

Intrinsic Semicondcutors : *The conduction by pure subtances such as silicon and germanium is called intrisic conduction and these pure substances exhibiting electrical condcutivity are called intrinsic semicodcutors.*

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 moleuclar orbitals which are too close in energy to each other so as to form a band.
5. If conduciton 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 interinsic semiconductors.

9. For partical purpose, the conductivity of pure silicon and germanium is too low at room temperature, therefore, there is need to increase the conductance by doping.
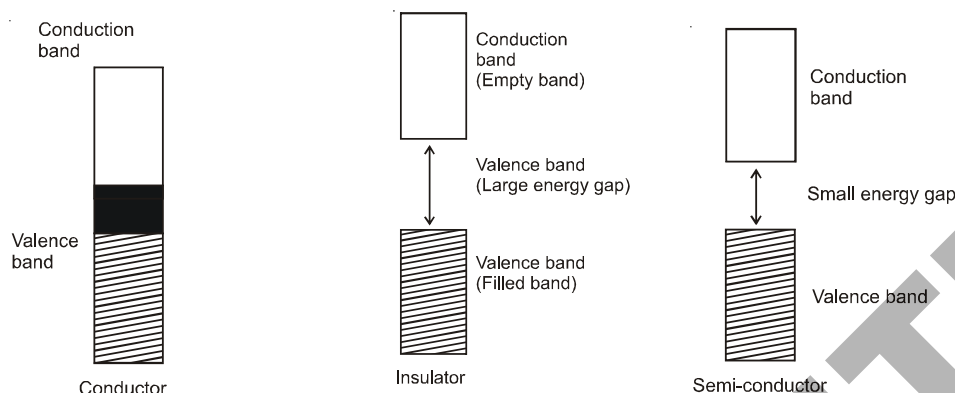

Figure

Doping : *The conductivity of silicon and germanium can be increases by adding apporpirate amount of suitable impurity. The process is called doping.*

Type of Semiconductors :

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

Creation n-Type Semicondcutor :

1. When siliconk is doped with small amont of group -15 elements such as P, As or Sb, its electrical condcutivity increass sharply.

2. In pure silicon each silocn atom uses its four valence electrons for the formation of four covalent bonds with the neighbouring silicon atoms.

3. When silcon is doped with some group-15 element, the some of the positions in the lattice are substituted by atoms fo groups -15 elements have five valence electrons. After forming the four covalent bonds with silicon (or anyother group-14 element such as germanium). one excess electron is left on them.

4. Since this electron is not involed in bonding it becomes delocalized and contributre to electrical conduction. Silicon dped with group 15 element behaves as a n-type semconductor.

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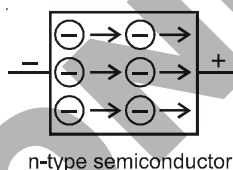
(2) p-Type Semiconductors : *Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore p-type semiconductors.*

Creation p-Type Semiconductor :

1. Electrical conductivity of silicon or germinum can alos be increases by doping with some group-13 element such as B, Al or Ga.

2. Goup-13 elements have only three valence electrons. The combine with group-14 elements to form an electron deficient bond or electron vacancy or a hole. These holes can move sthough the crystal like a positve charge giving rise to electrical condcutivity.

3. Gorup-14 elements doped with group-13 elements behave as p-type semicondcutors. In the presence of electricl field the holes move in direction opposite to that of electrons.

p-type semiconductor
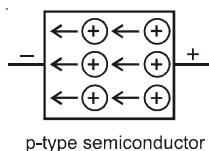
Application of n-type and p-type semicondcutiors.

1. Diode is a combination of n-type and p-type semicondcutors used as rectifier.

2. They are used for making transitors which contains n-p-n and p-n-p junctions to amplify radio and audio singnals.

3. The solar cell is photo-diode used to convert light energy into electrical energy.

13-15 Compouds : *The solid state materials are porduced by combination of elements of goups 13 and 15 the compounds thus obtianed are called 13-15 compouds* e.g. InSb, AIP GaAs.

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

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 phenonmenon of superconductivity was first discovered by kammerlingh Onners in 1913 when he found that mercury becomes superconducting at 4.0 K temperature.

Transition Temperature : *The temperature at which a substance starts behaving as super-condcutor is called transition temperature.*

(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.

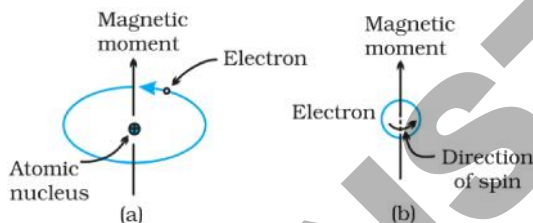(i) its orbital motion around the nucleus. (ii) its spin around its own axis.

Figure : 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.

(1) **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.

(2) **Diamagnetic materials :** *Those materials which are repelled by magnetic field are called diamagnetic materials* e.g. Cu^+, TiO_2, NaCl and C_6H_6. They do not have unpaired electrons.

(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 CrO_2.
This type of magnetism arise due to the spontaneous alignment of magnetic moments due to unpaired electron in the same direction.
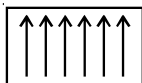
(4) **Anti Ferro Magnetism** : *Substances which are expected to possess paramagnetism or ferro magnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called Anti-ferromatic substances and the phenomenon is called as Anti-ferromagnetism.* eg. MnO, Anti-ferromagnetism is due to the presence equal number of magnetic moments in the opposite direction.
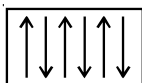
(5) . . . . *Substances which are expected to possess large magnetism on the basis of unpaired electrons, but actually have small magnetic momentum are called ferrimagnetic substances* eg. Fe_3O_4, ferrites of the formula M^{2+}, Fe_2O_4 where M = Mg, Cu, Zn etc. Ferrimagnetism arises due to the unequal moments in opposite direction resulting in same net magnetic moment. On heating these substance loss their magnetism and convert in to paramagentic substance

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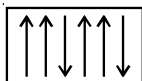
Curie Temperature : *The temperature at which a ferromagnetic substance loses its ferromagnetism and becomes only paramagnetic.* For iron the curie temperature is 1033 K and for nickel 629 K, for Fe_3O_4 850 K. Below this temperature paramagnetic solid becomes ferromagnetic.

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 :

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 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 porudced by combination of elements of goups 13 and 15 the compounds thus obtianed are called 13-15 compouds* e.g. InSb, AlP GaAs.

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

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 AB_2 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/cm^3 and an edge length of 412.6 pm. In what cubic unit cell does titanium crystallise? (Ti = 48)

Sol. $$\text{Density } d = \frac{zM}{a^3N_0}$$

   d = 4.54 g/cm^3 , M = 48g mol^{-1} , Z = ? $N_0 = 6.023 \times 10^{23}$ mol^{-1}
   If value of z is known, structure can be decided

   $$z = \frac{dN_0a^3}{M} = \frac{4.54 \times 6.023 \times 10^{23} \times (412.6 \times 10^{-10})^3}{48} = 4$$

   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 Mg^{2+} is also = **6**
   and   that of O^{--} or O^{2-} = **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

   $$\frac{r_{A^+}}{r_{B^-}} = 0.414$$

   $$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = \textbf{290 pm.}$$

7. The C.N. of the barium ion Ba^{2+}, in BaF$_2$ 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 × (−1) = − 8). In order to balance out the eight negative charges, we need four barium ion (charge 4 × (+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 $\dfrac{r_+}{r_-} = \dfrac{94}{146} = 0.644$

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

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

$\therefore \qquad 4 \times r_{Na} = \sqrt{3} \times 4.29$

$r_{Na} = \dfrac{\sqrt{3}}{4} \times 4.29 = $ **1.86 Å**

10. CsCl crystallises in a cubic that has a Cl^- at each corner and Cs^+ at the centre of the unit cell. If $(r_{Cs^+}) = 1.69$ Å and $r_{Cl^-} = 1.81$ 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 $Cl^\ominus$.

= 1.69 + 1.81 = 3.50 Å

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

$\therefore \qquad \dfrac{a\sqrt{3}}{2} = 3.50$ Å $\qquad \therefore \qquad$ a = **4.04 Å**

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. $r = \dfrac{a}{2\sqrt{2}}$ (for fcc), a = $2\sqrt{2}$ r = 3.9 Å

density = $\dfrac{ZM}{a^3 N_0} = \dfrac{4 \times 195}{(3.9 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 21.83$ g/cm^3 .

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 $\qquad$ density d = $\dfrac{zM}{a^3 N_0}$

where $\quad$ a = length of the unit cell

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

a = 5.64×10^{-10} m

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

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

14. In a CPS (close packed structure) of mixed oxides, it is found that lattice has O^{2-} (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A^{3+}) and one-eighth of tetrahedral voids are occupied by divalent cations (B^{2+}). Derive formula of the mixed oxide.

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

Hence, number of trivalent cations (A^{3+}) = $1 \times \dfrac{1}{2} = \dfrac{1}{2}$

number of tetrahedral voids per ion in lattice = 2

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

Thus, formula is $A_{1/2}B_{1/4}O$ or   **A_2BO_4.**

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 g/cm³

a = 300 pm = 3×10^{-8} cm

$\therefore$ $a^3 = 27 \times 10^{-24}$ cm³

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

$\therefore$ $M = \dfrac{dN_0 a^3}{z} = \dfrac{5.20\,g/cm^3 \times 6.02 \times 10^{23}\,mol^{-1} \times 27 \times 10^{-24}\,cm^3}{4}$ = 21.13 g mol⁻¹

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

$\therefore$ 3.01×10^{24} atoms have = $\dfrac{21.13}{6.02 \times 10^{23}} \times 3.01 \times 10^{24}$ g = **105.65 g**

16. Calcium crystallises in a face-centred cubic unit cell with a = 0.556 nm. Calculate the density if it contained 0.1% Vaccancy defects.

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

d(with Vaccance defect) = $\dfrac{3.996 \times 40}{(0.556 \times 10^{-7})^3 \times 6.02 \times 10^{23}}$ = 1.5448 g/cm³