The Solid State

Crystal Lattice

A regular arrangement of the constituent particles of a crystal in the three dimensional space is called crystal lattice or space lattice.

Unit Cell

The smallest three dimensional portion of the space lattice which when repeated over and again in different directions produces the complete space lattice is called the unit cell.

Types of unit cells

(i) **Simple:** Here the particles are present only on the corners.

(ii) **Face centred:** Here in addition to the particles on the corners, there is one particle present on the centre of every face.

(iii) **End face centred:** Here in addition to the particles on the corners, there is one particle in the centre of two opposite faces.

(iv) **Body centred:** Here in addition to the particles on the corners, there is one particle present within the body of the unit cell.

Relation between the nearest neighbour distance (d), atomic radii (r) and the edge (a) of the unit cell

Co-ordination number: Of any particle is the number of its nearest neighbours.

Simple	Body-centred	Face centred
$d = a$	$d = \dfrac{\sqrt{3}}{2}a$	$d = \dfrac{a}{\sqrt{2}}$
	(It is half of the body diagonal)	(It is half of the face diagonal)
$r = \dfrac{a}{2}$	$r = \dfrac{\sqrt{3}}{4}a$	$r = \dfrac{a}{2\sqrt{2}}$

Expression of density for cubic lattice

$$d = \frac{Z \times M}{a^3 \times N_A} \, g/cm^3$$

where Z = Number of atoms present per unit cell; M = Atomic mass of the element

a = Edge of the cubic crystal in cm; N_A = Avogadro's number

Type of close packed structures

There are three ways in which atoms in a crystal are packed:

(i) **Hexagonal close packing (hcp)** i.e. ABAB... pattern e.g. in Be, Mg, Ca, Cr, Mo, V, Zn.

(ii) **Cubic close packing (ccp)** i.e. ABC ABC... pattern e.g. in Fe, Cu, Ag, Au, Pt, Al and Ni.

Space occupied = 74%, space unoccupied = 26%. The space occupied by spheres in one layer of the hexagonal close packing is 60.4%.

(iii) **Body centred cubic (bcc)** i.e. in alkali metals, space occupied = 68%, empty space = 32%. This is not a close packed arrangement.

Voids

Types of Voids

Tetrahedral void: It is a triangular void surrounded by four sphere arranged tetrahedrally around it.

Octahedral void: It is a combination of two triangular voids surrounded by six spheres.

Number of Voids

Number of octahedral voids = Number of atoms in the close packed arrangement.

Number of tetrahedral voids = 2 × Number of atoms in the close packed arrangement.

Location of Voids

In ccp or fcc, there are 4 atoms per unit cell, therefore, there are 4 octahedral & 8 tetrahedral voids.

Octahedral voids are 12 at the edge centres and 1 at the body centre. Distance of octahedral void from the corner is a/2 and at the body centre from the corner is $\dfrac{\sqrt{3} \times a}{2}$.

Tetrahedral voids are 8 at the corner as each spheres at the corner touches the three spheres present on the face centres of three adjoining faces, giving rise to a tetrahedral void. Distance of tetrahedral void from corner is $\dfrac{\sqrt{3} \times a}{4}$.

Relation between radius ratio, co-ordination number and structural arrangement:

Limiting ratio = r^+/r^-	Co-ordination Number of cation	Structural Arrangement (Geometry of voids)
0.155 –0.225	3	Plane Trigonal
0.225–0.414	4	Tetrahedral
0.414–0.732	4	Square planar
0.414–0.732	6	Octahedral
0.732–1	8	Body centred cubic

Main features of NaCl, CsCl, ZnS, AB$_2$ type structure

(*i*) **NaCl:** It has FCC arrangement of ions where Cl^- creates FCC unit and Na^+ ion is present in octahedral voids. Here, Na^+ and Cl^- ions have 6 : 6 co-ordination and each unit cell has 4 NaCl units.

Examples: Halides of alkali metals (except those of Cs) and those of NH_4^+, oxides and sulphides of alkaline earths (except BeS), halides of Ag (except AgI).

(*ii*) **CsCl:** It has BCC arrangement of ions where Cs^+ and Cl^- ions have 8 : 8 co-ordination number. Each unit cell has only one CsCl unit.

Examples: CsBr, CsCl, CsCN, TlCl, TlBr and TiCN.

(*iii*) **ZnS (sphalerite type):** It has FCC arrangement of ions, where S^{2-} creates FCC and Zn^{2+} ions are present at $1/4^{th}$ of the distance along each body diagonal.

Zn^{2+} and S^{2-} ions have 4 : 4 co-ordination.

Examples: CuCl, CuBr, CuI, AgI, BeS

(*iv*) **AB$_2$:** Calcium fluorite (CaF_2) type, it has CCP/FCC arrangement of Ca^{2+} ions Ca^{2+} and F^- ions have 8 : 4 co-ordination.

Defects in Solids

Schottky defect: Is that in which equal number of cations and anions are missing form their lattice sites. As a result, density decreases. Schottky defect arises where cation and anions are of nearly equal size (radius ratio high).

Frenkel defect: Is that in which cations are missing from their lattice sites and occupy interstitial sites. As a result density remains unchanged, where size of cation is small as compared to size of anion.

F-centres: Are the sites where anions are missing by leaving behind electrons. They are responsible for colour (F = Farbe [Colour]).

Doping

It means incorporating small amount of foreign impurity. Doping of group 14 elements with group 15 elements gives rise to excess electrons whereas with group 13 elements give rise to holes. Both make group 14 elements semi-conductors. The former are called n-type (as negative charge flows) and the latter are called p-type (as holes move like positive charge i.e. in a direction opposite to the flow of electrons).