

## Mathematical analysis of Cubic system.

Simplest crystal system is to be studied in cubic system. Three types of cubic systems are following

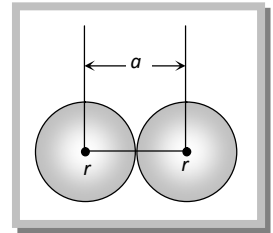
- Simple cubic (sc): Atoms are arranged only at the corners.
- Body centered cubic (bcc): Atoms are arranged at the corners and at the center of the cube.
- Face centered cubic (fcc): Atoms are arranged at the corners and at the center of each faces.

(1) Atomic radius: It is defined as the half of the distance between nearest neighboring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.

(i) Simple cubic structure (sc): Radius of atom 'r' =  $\frac{a}{2}$

(ii) Face centered cubic structure (fcc): 'r' =  $\frac{a}{2\sqrt{2}}$

(iii) Body centered cubic structure (bcc): 'r' =  $\frac{\sqrt{3}a}{4}$



(2) Number of atoms per unit cell/Unit cell contents: The total number of atoms contained in the unit cell for a simple cubic called the unit cell content.

(i) Simple cubic structure (sc): Each corner atom is shared by eight surrounding cubes.

Therefore, it contributes for  $\frac{1}{8}$  of an atom.  $\therefore Z = 8 \times \frac{1}{8} = 1$  Atom per unit cell in crystalline solid.

(ii) Face centered cubic structure (fcc): The eight corners atoms contribute for  $\frac{1}{8}$  of an atom and thus one atom per unit cell. Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centered atom contribute half of its share.

$\therefore Z = 6 \times \frac{1}{2} = 3$  Atom per unit cell.

So, total  $Z = 3 + 1 = 4$  atoms per unit cell.

(iii) Body centered cubic structure (bcc): Eight corner atoms contribute one atom per unit cell.

Centre atom contribute one atom per unit cell. So, total  $1 + 1 = 2$  atoms

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

per unit cells.

$$= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$$

Note: Number of atoms in unit cell: It can be determined by the simplest relation

Where  $n_c =$  Number of atoms at the corners of the cube = 8

$n_f =$  Number of atoms at six faces of the cube = 6

$n_i =$  Number of atoms inside the cube = 1

Cubic unit cell	nc	nf	ni	Total atom in per unit cell
Simple cubic (sc)	8	0	0	1
body centered cubic (bcc)	8	0	1	2
Face centered cubic (fcc)	8	6	0	4

(3) Co-ordination number (C.N.) : It is defined as the number of nearest neighbours or touching particles with other particle present in a crystal is called its co-ordination number. It depends upon structure of the crystal.

(i) For simple cubic system C.N. = 6.

(ii) For body centered cubic system C.N. = 8

(iii) For face centered cubic system C.N. = 12.

(4) Density of the unit cell: It is defined as the ratio of mass per unit cell to the total volume of unit cell.

$$\text{Density of unit cell } (\rho) = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}; \rho = \frac{\text{Number of particles} \times \text{mass of each particle}}{\text{volume of the unit cell}}$$

$$\text{or } \frac{Z \times M}{a^3 \times N_0}$$

Where Z = Number of particles per unit cell, M = Atomic mass or molecular mass,  $N_0$  = Avogadro number ( $6.023 \times 10^{23} \text{ mol}^{-1}$ ),  $a$  = Edge length of the unit cell =  $a \text{ pm} = a \times 10^{-10} \text{ cm}$ ,  $a^3$  = volume of the unit cell

i.e. 
$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} \text{ g/cm}^3$$

The density of the substance is same as the density of the unit cell.

(5) Packing fraction (P.F.): It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

Let radius of the atom in the packing =  $r$

Edge length of the cube =  $a$

Volume of the cube  $V = a^3$

Volume of the atom (spherical)  $v = \frac{4}{3} \pi r^3$ , then packing density  $= \frac{vZ}{V} = \frac{\frac{4}{3} \pi r^3 Z}{a^3}$

(i) Simple cubic unit cell: Let the radius of atom in packing is  $r$ . Atoms are present at the corner of the cube, each of the eight atom present at the eight corners shared amongst eight unit cells.

Hence number of atoms per unit cell  $= 8 \times \frac{1}{8} = 1$ , again  $r = \frac{a}{2}$

$\therefore$  P.F.  $= \frac{\frac{4}{3} \pi r^3}{(2r)^3} = 0.52$ ; % P.F. = 52%, then % of void =  $100 - 52 = 48\%$

(ii) Body centered cubic unit cell: Number of atoms per unit cell  $= 8 \times \frac{1}{8} + 1 = 2$ ,  $r = \frac{\sqrt{3}a}{4}$

$$\text{P.F.} = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$$

; % P.F. = 68%, then % of void = 100 – 68 = 32%

(iii) Face centered cubic unit cell: Number of atoms per unit cell = 4,  $r = \frac{\sqrt{2}a}{4}$

$$\text{P.F.} = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74$$

; % P.F. = 74%, then % of void = 100 – 74 = 26%

Structure	r related to a	Volume of the atom (v)	Packing density
Simple cubic	$r = \frac{a}{2}$	$\frac{4}{3} \pi \left(\frac{a}{2}\right)^3$	$\frac{\pi}{6} = 0.52$
Face-centered cubic	$r = \frac{a}{2\sqrt{2}}$	$\frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3$	$\frac{\sqrt{2}\pi}{6} = 0.74$
Body-centered cubic	$r = \frac{\sqrt{3}a}{4}$	$\frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3$	$\frac{\sqrt{3}\pi}{8} = 0.68$

(6) Ionic radii: X-ray diffraction or electron diffraction techniques provides the necessary information regarding unit cell. From the dimensions of the unit cell, it is possible to calculate ionic radii.

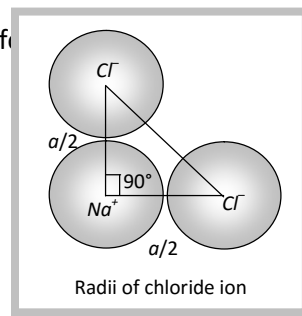
Let, cube of edge length 'a' having cations and anions say  $\text{NaCl}$  structure.

Then,  $r_c + r_a = a/2$

Where  $r_c$  and  $r_a$  are radius of cation and anion.

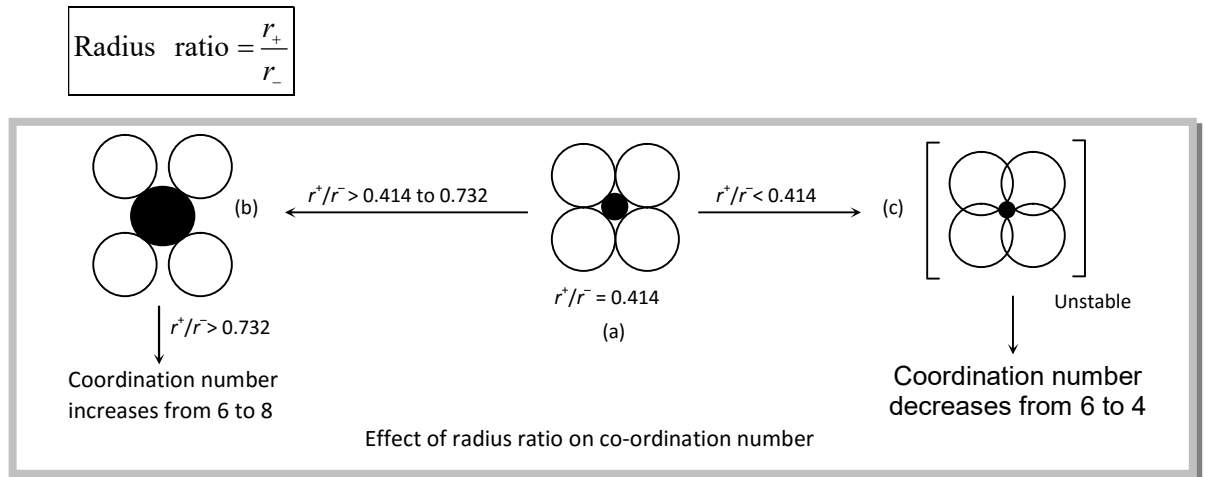
Radius of  $\text{Cl}^- = \sqrt{\frac{(a/2)^2 + (a/2)^2}{2}} = \frac{a}{4}$

For body centered lattice say  $\text{CsCl}$ .  $r_c + r_a = \frac{\sqrt{3}a}{2}$



Radius ratio: Ionic compounds occur in crystalline forms. Ionic compounds are made of cations and anions. These ions are arranged in three dimensional array to form an aggregate of the type  $(A+B)^{-n}$ . Since, the Coulombic

forces are non-directional, hence the structures of such crystals are mainly governed by the ratio of the radius of cation ( $r_+$ ) to that of anion ( $r_-$ ). the ratio  $r_+$  to  $r_-$  ( $r_+ / r_-$ ) is called as radius ratio.



The influence of radius ratio on co-ordination number may be explained as follows: Consider an ideal case of octahedral voids in close packing of anions with radius ratio 0.414 and co-ordination number six. An increase in size of cation increases the radius ratio from 0.414, then the anions move apart so as to accommodate the larger cation. As the radius ratio increases more and more beyond 0.732, the anions move further and further apart till a stage is obtained when more anions can be accommodated and this cation occupies a bigger void i.e., cubic void with co-ordination number eight.

When the radius ratio decreases from 0.414, the six anions would not be able to touch the smaller cation and in doing so, they overlap each other. This causes the cation to occupy a smaller void i.e., tetrahedral void leading to co-ordination number four

#### Limiting Radius ratios and Structure

Limiting radius ratio ( $r_+/r_-$ )	C.N.	Shape
< 0.155	2	Linear
0.155 – 0.225	3	Planar triangle
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral

0.732 – 0.999 or 1	8	Body-centered cubic
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### Characteristics of Some Typical Crystal Structure

Crystal	Type of unit cell	Example	$\frac{r_+}{r_-}$	C.N.	Number of formula units of (AB, or AB <sub>2</sub> ) per unit cell
CsBr	Body-centered	CsBr, TiCl	0.93	8 – 8	1
NaCl	Face-centered	AgCl, MgO	0.52	6 – 6	4
ZnS	Face-centered	ZnS	0.40	4 – 4	4
CaF <sub>2</sub>	Face-centered	CaF <sub>2</sub> , SrF <sub>2</sub> , CdF <sub>2</sub> , ThO <sub>2</sub>	0.73	8 – 4	4

Note: The ionic radius increases as we move from top to bottom in a group of periodic table for example:



Along a period, usually iso-electronic ions are obtained e.g.  $Na^+, Mg^{2+}, Al^{3+}$  (greater the nuclear charge, smaller the size,  $Al^{3+} < Mg^{2+} < Na^+$ )