

Ionic Bond. Directionality.

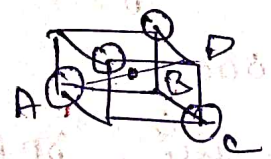
- ① High m.p & B.P due to strong electrostatic force between the ions.
- ② Hardness. Electrostatic force make the crystal hard.
- ③ Solubility. Dissolved easily in polar solvents of high dielectric constant.
- ④ Conductance. In solid state low conductance. In solution - conductance.

Cations & anion are present in ionic solids. Properties are different from covalent solids. Maximum cation-anion attraction & minimum cation-cation & anion-anion repulsion. It is called ionic solids.

Radius Ratio rule. Cations & anions of an ionic crystal try to arrange themselves in geometrical shapes. The geometry & C.N of ions is dependent upon relative size of the ions. It is called Radius Ratio Rule.

$$= \frac{r^+ \text{ (Radius of cation)}}{r^- \text{ ( " " anion)}}$$

To predict the C.N & shape of ionic crystals determining the C.N & shape of the ionic crystal is known as Radius ratio effect. Calculation of radius ratio!  
Tetrahedral.



a - length of each side

The face diagonal  $AC = \sqrt{BC^2 + AB^2}$

$$= \sqrt{a^2 + a^2} = \sqrt{2}a \quad \text{--- (1)}$$

Anions are touching one another

$$AC = r^- + r^- = 2r^- \quad \text{--- (2)}$$

Compare (1) & (2)

$$2r^- = \sqrt{2}a \quad \Rightarrow \quad r^- = \frac{1}{\sqrt{2}} a \quad \text{--- (3)}$$

Body diagonal.

$$AD = \sqrt{AC^2 + CD^2}$$

$$\sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a \quad \text{--- (1)}$$

$\frac{1}{2} AD = r^+ + r^-$  Cation present at the centre of the body AD

Compare (1) & (2) (3)

$$\frac{\sqrt{3}a}{2} = r^+ + r^- \quad \text{--- (6)}$$

Dividing (6) by (3)

$$\frac{\sqrt{3}a}{2} = r^+ + r^-$$

$$r^- = \frac{1}{\sqrt{2}} a$$

$$\frac{r^+ + r^-}{r^-} = \frac{\sqrt{3}a}{\frac{a}{\sqrt{2}}} \times \frac{\sqrt{2}}{a} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = 0.225 \text{ for } \text{Fd.}$$

Ionic crystals.

Stability of Ionic Crystals

Maxi Cat-an<sup>o</sup> attracts

Mini Cat-Cat an-an - repulsive.

Oppo, charged ions close to one another

Same " " far away " "

AX type.

depends upon size of Ions

Ions are same

C.N also same.

AlaCl.

fcc

Cl<sup>-</sup> ions Face centered cubic arrangement.

Na<sup>+</sup> occupy all oh sites

Only one oh site per atom. closed packed lattice

Each Na<sup>+</sup> ion is surrounded by six Cl<sup>-</sup>

Each Cl<sup>-</sup> " " " " six Na<sup>+</sup>

Therefore CN is same.

Radius ratio 0.524 for Na<sup>+</sup>

" " 0.95 for Cl<sup>-</sup>

ZnS.

Cubical close packing

S<sup>2-</sup> ions are arranged CCP.

Ions are present at corner & faces of cube

S<sup>2-</sup> has two td sites.

Zn<sup>2+</sup> occupy 1 half of the td site

4:4 arrang. (W) Each ion surrounded by four

Radius ratio 0.40 for Zn<sup>2+</sup>

" " 0.74 for S<sup>2-</sup>

Wurtzite

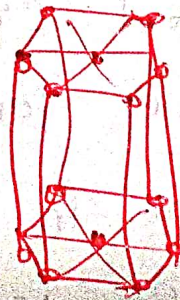
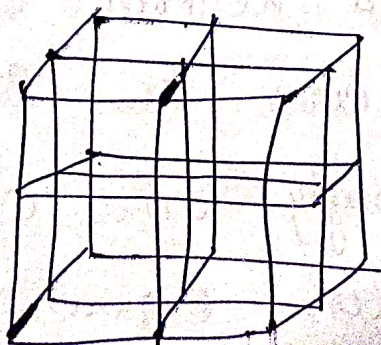
S<sup>2-</sup> hcp hexagonal close packing.

Ions are present in corner & jaw of hexagon

S<sup>2-</sup> has two td site

Zn<sup>2+</sup> one half of the td site.

4:4



Rutile str. distributed.  
 1.  $Ti^{4+}$  surrounded by  $6 O^{2-}$   
 2.  $O^{2-}$  " " by  $3 Ti^{4+}$   
 6:3

Fluorite str.

$Ca^{2+}$  ions CCP arrange  
 Ions present at corners of face of a cube  
 $Ca^{2+}$  has two fd sites.  
 $F^-$  occupy all fd sites.  $Ca^{2+} : F^- = 1:2$   
 $4 : 8$  arrange.  
 $Ca^{2+}$  surrounded by  $8 F^-$   
 $F^-$  " "  $4 Ca^{2+}$ .

Lattice. egn.

$CaCl_2$  similar to NaCl

$Ca^{2+} \rightarrow$  hcp Layered lattice.  
 $Cl^- \rightarrow$  lie on oh sites

Boon - Lande egn.

$I^-$  at  $Ca^{2+}$  surround by  $I^-$  ions  $I^-$  has 8 oct

Importance of Boon - Lande.

I year book.

Wander Wald's or London force.

Crystal defect

- 1 Schottky 2 Frenkel.

Schottky

\* Some of lattice points are unoccupied  
 It is called Lattice vacancies or holes

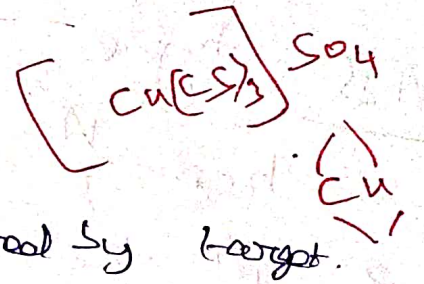
existence two holes one - missing +ve ion  
 - " -ve ion.

It not a crystal neutral. bcoz  
 +ve & -ve ions are the same.

It appears in strongly ionic cpds having  
 C.N no. of  $Ca^{2+}$  ions are equal, size.

Ex: NaCl & CsCl

Geiger Muller Counter  
Radio active tractors.

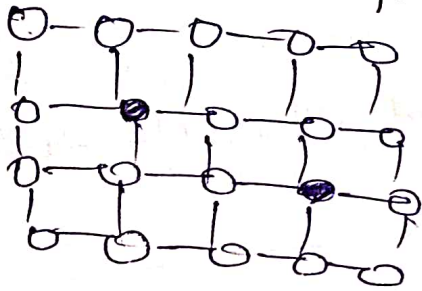


Scattering.

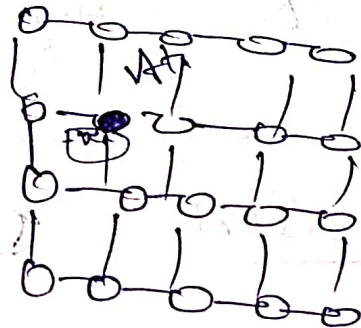
Projectile particles are scattered by target.  
Elasticum

Exchange of kinetic energy

Stoichi.



Interstitial.



hole in the network

Interstitial.

It occupies interstitial +ve b/w lattice points.

+ve ion in interstitial space

It appears less ionic Cpds. -ve ions larger than +ve ions.

Ex. AgBr, Zn.

Intrinsic Semiconductors.

Si, Ge  $\rightarrow 4 e^-$

Extrinsic

As added to Ge.

Remaining one  $e^-$  to produce electron. It is n-type Semiconductor.

In added to Ge

D-type electron vacant site is known as the hole.

1. hcp  
 2. all the d holes occupied by Ni  
 3. Ni

Surrounded by 6 As

4. As

6:6

β - Cristobalite  
 High temp form of silical. like Zn blende  
 Si-O-Si

Layered Struc-

$CdI_2$

1) hcp

$Cd^{2+}$

ion lie in Oh site

$Cd^{2+}$

Surrounded by six  $I^-$

$I^-$

6:3

Super conductivity.  $T_c$  defined as transition temp.

~~Transition temp~~  
 Critical temp

Ex: Ag, Pb below 2.2 K

## Rutile. ( $\text{TiO}_2$ )

1. Distorted bcc
2. Ions present at all corners ~~and~~ body centre of the distorted cube.
3.  $\text{Ti}^{4+}$  surrounded by six  $\text{O}^{2-}$  ions  
 $\text{O}^{2-}$  " " " Three  $\text{Ti}^{4+}$
4. CN of Ti & O are 6 & 3

CaF<sub>2</sub> Similar to NaCl

Na replaced by  $\text{Ca}$   
Cl " "  $\text{F}$

## $\text{CdI}_2$

$\text{I}^-$  ion hcp arrangement

$\text{Cd}^{2+}$  surrounded by six  $\text{I}^-$

$\text{I}^-$  has 3  $\text{Cd}^{2+}$

Arrangement  $\text{I} - \text{Cd} - \text{I}$   $\text{I} - \text{Cd} - \text{I}$