"Solid State Chemistry - I"

Topics :-

1. Crystal defect and Non - Stoichiometry - Perfect and imperfect ~~chemistry~~ Crystals.
2. Intrinsic and extrinsic defect - point defect.
3. line and plane defect
4. Vacancies :- Schottky and Frankel defect.
5. Thermodynamics of Schottky and Frankel defect.
6. Formation of Colour Centre
7. Non - Stoichiometry and defects.
8. Electronics properties and Band theory of Semiconductors

Solid State Chemistry

Date: / /

2014 * **Crystal Defect :-** Imperfaction of Solid means defect of solid or effect are crystal the arrangement of lattice point

OR

Imperfaction of Solid

Carrangement of atoms. molecule and ions) is affected by some factor and causes crystal effect.

Reasons of imperfaction of solid :-

(1) Due to the deffect of temprature.

(2) Due to the present of imperfaction

Imperfaction of Solid

↓

Point deffact

1) Stoichiometric deffect
   - i) Schottkey effect
   - ii) Frandle defect

2) Non-Stiochiometric deffect
   - i) due to exess of metal ion (due to exess of cation
   - ii) Due to vacancies of anion

3) Impurity deffect
   - i) due to nutral ion
     - 1) n-type Semi Conductor
     - (ii) P-type Semi Conductor
   - ii) due to ion

- **Point Defect :-** Point Defect causes due to imperfaction of Solid means lattic (molecule, atom or ions) show imperfaction due to the present of impurity and temprature

Point defect are of three type

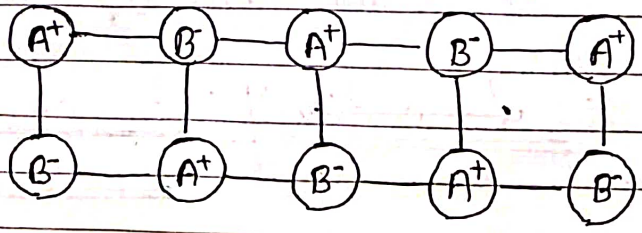
1.) Stoichiometric defect
2.) Non-Stiochiometric defect
3.) Impurity defect.

I) Stiochiometric defect :- In this type of defect the same ratio of chemical formula and structure formula of the same Constituent's particals which is known as Stoichiometric defect. its are of two types :-

1.) Schottkey defect 2) frankel defect

in other w means ratio of cation and anion are Same is called Stoichiometric defect.

1) Schottky defect :-



In this type of defect occure in pure alkali metals due to the absence of interstitial space so in this type of defect due to one cation and one anion missing from the Crystals and

due to this defect one +ve and one -ve place are vacant in this type of defect occurs in LiCl, NaCl, KCl, RbCl, CsCl. this defect is electrically nutral.

* **Due to this defect of the crystal :-**

||

1) **Density :-** In this defect density decreases due to missing of the cation and anion

2) **Dielectric Constant :-** It depend upon the medium in Schottkey defect due to absence of interstitial space dielectric Constant uneffected
there interstitial space is space is work as a midium so due to the absence of midium dielectric con^c is decreas as compair to frankel deffect.

3) **Conductivity :-** In this type of defect crystal are electrically nuetral because of same no. of +ve and -ve charge.

Que. * **Derivation** * **Explain physical property Schottkey and frankel defect** *

* Explain thermodynamics of schottkey and frankel defect.

* Why CsCl Crystal change into NaCl crystal on the basis of co-ordination number

1) Density
2) dielectric const.
3) Coductivity
4) Temprature

$$CsCl \xrightarrow[Temp]{\Delta} NaCl$$

Temprature 8:8 6:6 co-ordination no.

* In schottkey defect due to the effect of temprature co-ordination no. is changed
ex. - Csd in CsCl
Crystals after heating become change into NaCl due to the effect of temprature co-ordination no. will be decreases and change into 8:8 to 6:6 and 6:6 is the co-ordination no. of NaCl
So its considerd CsCl Crystal after heating change into NaCl Crystal.

* 2) In Frankel Defect :- In this types of defect occure. Some d-block element

* In frankel defect :- due to effect of temprature co-ordination no. is not change because in this type of deffect +ve ion presence on the Interstitial Space.

*	Co-ordination no.	Geometry	Example
1)	6:6	octahedral / Cubic	NaCl
2)	8:8	Hexagonal	CsCl / CsBr
3)	4:4	Tetrahedrall	ZnS (Zn blend)
4)	8.4	Tetrahedrall	CaF_2
5)	3:3	Trigonal	B_2O_3 (Boreze anhydride)

* Derivation of Schottkey :-

$$\left[\frac{N!}{(N-n)!\,n!}\right]^2$$

the different way in which Schottkey defect can be formed is then (each type of ion)

$$\left[\frac{N!}{(N-n)!\,n!}\right] \times \left[\frac{N!}{(N-n)!\,n!}\right]$$

So according to Boltezmann rea^n

$$S = k \ln \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

or

$$\log \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

due to thermodynamically according to helmholtz free energy consider H

$$f = E - Ts$$

$$F = {}^{n}E_p - kT \ln \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

K = Boltezmann Constant

Ep = energy Required for Removel of cation and anion

Page: 6
Date: / /

Starling give a formula for Schottkey defect

$$\left[\frac{\partial F}{\partial n}\right]_T = 0 \quad \text{At equilibrium}$$

So $$E_p = 2KT\left[\ln (N-n) - \ln n\right]$$

or

$$0 = E_p - 2KT \ln\left(\frac{N-n}{n}\right)$$

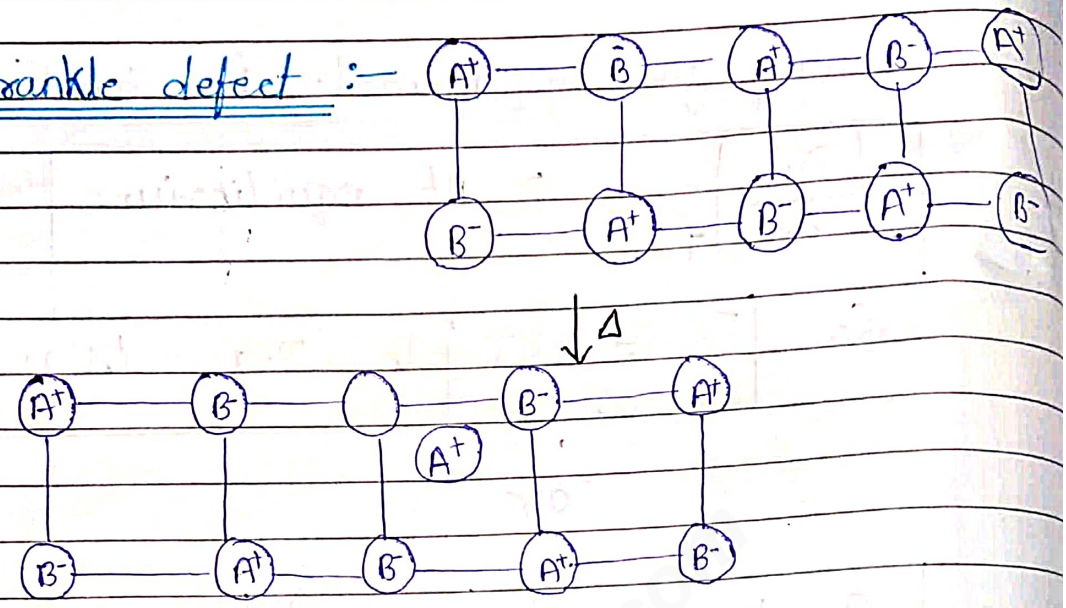
$$E_p = 2KT \ln\left(\frac{N-n}{n}\right) \quad \text{---(1)}$$

$$\frac{N-n}{n} = e^{-E_p/2KT}$$

$$\frac{N}{n} = e^{-E_p/2KT}$$

$$n = N \cdot e^{-E_p/2KT}$$

2.) **Frankle defect :-**



In this type of defect occure in some d-block elements and this defect due to the Presence of intersticial defect in this defect one cation present on the intersticial space so cation present in intersticial space causes frankle defect ex - ZnS, AgCl, AgI,

this type of defect not found in pure alkali metals because in pure alkali metal intersticial space absence and due to the absence of intersticial space frankle defect not takes place

* Effect of Crystal due to frankle defect :-

1) **Density :-** Density uneffected in frankle defect due because no. of cation and anion are same.

KT/n

KT II

Page : 8
Date : / /

2.) **Dielectric Constant** :- It is deffected because the presence of interstitial space. So in the presence of medium it will be effected.

3) **Conductivity** :- Conductivity least due to vacant space of cation.

* **Derivation** :- In a frankle defect energy required for displacement of cation from its proper position to an interstitial space. So position is E_i and N is atom in the crystal. Ni is interstitial position in the crytal shown below.

$$\frac{Ni}{(N-n)!n!} \quad \frac{Ni!}{(Ni-n)!n!} \qquad \text{---(1)}$$

where n frankle defect can be formed and according to helmhootdz free energy produced by the certain of n frankle defect is

$$f = nE_i - kT\ln\left[\frac{N!}{(N-n)!n!} \quad \frac{Ni!}{(Ni-n)!n!}\right] \qquad \text{---(2)}$$

Starlling gave formula for the frankle defect is shown below —

$$\left[\frac{\partial f}{\partial n}\right]_T = E_i - kT \ln \frac{(N-n)(N_i-n)}{n^2} \quad \text{---(3)}$$

* at equilibrium — $\left(\frac{\partial f}{\partial n}\right)_T = 0$

So $N \gg n$, $N_i \gg n$, So equⁿ (3) is given below —

So $$E_i = kT \ln \frac{N N_i}{n^2}$$

$$\frac{E_i}{kT} = \ln N N_i - 2 \ln n$$

$$\ln n = \tfrac{1}{2} \ln N N_i = \frac{E_i}{2kT}$$

$$\therefore n = (N N_i)^{1/2} e^{-E_i/2kT}$$

Que. AgBr have both type of defect shottkey defect as well as frankle defect?

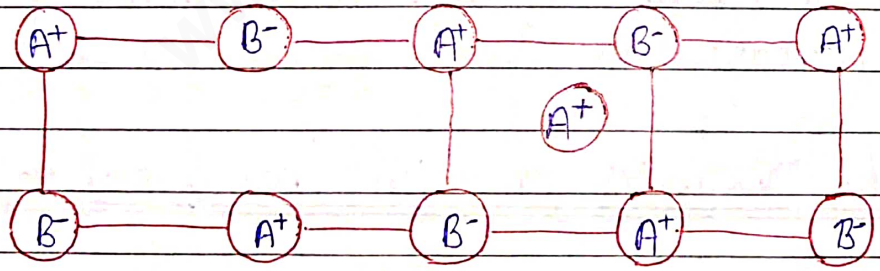
Ans. AgBr show both type of defect due ~~to~~ to behaviour behaves like schottkey defect crystals and frankel defect crystals both because it ionic in nature and it

have arise due to missing of ions from there Crystal lattic its same as that Schotkey defect because Size of Ag ion is more then Size of Br

in frankle defect always Size of cation ions is more and Size of anion is least so it is behaves a frankle defect Crystal and they have interstitial space.

(II) Non - Stoichiometric defect — In this type of defect chemical formula and structural formula can not be same means no. of anion and cation is unbalanced so non - stiochiometric are of two type

1) Due to exess of metal ion / cation
2) Due to vacancies of anion



$ZnO \rightleftharpoons^{heat} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$

white crystal yellow crystal

In this type of defect extra +ve charge present on the interstitial space. this defect due to present of interstitial space. this defect called Excess of metal ion

Due to this defect cation is more then anion so produce colour of the crystal in this type of defect occure same as that frankle defect.

* **Effect of the crystal :-**

* **Density :-** Density of the crystal increases due to presence of extra cation.

* **Dielectric Constant :-** In this defect dielectric Constant will be increase due to presence of the interstitial space because ~~due to the~~ it is work as a medium. ~~of the~~

* **Conductivity :-** In this types of defect Conductivity is present due to the present of extra cationc. so Conductivity is Increase.

* **Due to Vacancies of anion (non-metal deficiency)**

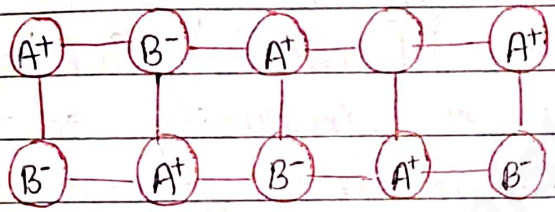
It is known as due to non-metal ion and also known as colour center

In this type of defect anion missing from the crystal due to the absence of interstitial and causes vacancies of anion due to vacant of anion e^- are free and due

to free e^- form of f-center takes Place. and f-Center is germed german word and meaning of f-Center form means colour formation takes place.

due to colour formation which is known as colour center. in this type of defect cation is more than anion.

example :-



LiCl - Pink
KCl - Purple
NaCl - yellow
KI - yellow

:- Effect of Crystal :-

1) **Density** :- In this type of defect density decrease due to missing of anion.

2) **Di-electric Constant** :- Di electrics constant decreas du to absence of interstitial space and interstitial space react as a medium.

3.) **Conductivity** :- In this type of defect Conductivity increas due to vacant space of anion.

3) **Impurity Defect** :- In this type of defect due to the emv Present of Impurity. which is known as Impurity

:- **Impurity defect are of two type** :-

1) Due to the neutral ion
2) Due to the ion

* **Dopping** :- In this type of process when the addition of another substance or another elements as a impurity so this is known as dopping. in this process group 14th elements added with group 15th elements and group 14th element added with group 13th elements and gives semi conductor

* **Uses of dopping** :- formation of trangister
formation of Semiconductor

1) **Due to the neutral ion** :- its devied into two type.

(A.) N type Semiconductor (N-P-N Semiconductor)
(B.) P type Semiconductor (P-N-P —u—)

(A) **N-type Semiconductor** :-

group 14th element's (Si, Ge)

$_{14}Si$ - 2, 8, 4

group 15th elements (P, As)

$_{15}P$ - 2, 8, 5

$_{14}Si - 2, 8, 4$ $_{15}P - 2, 8, 5$

↓

N-type Semiconductor

↓

due to the presence of unpaired e^-

↓

It is excited into lower energy to high energy level

↓

Conductivity

In this types of semiconductor from due to addition of 14th elements with addition of group 15th elements Such as group 14th elements Si, Gre added group 15th P, As due to this types of impurity defect one extra electron is present and excitation of e^- from lower energy level to higher energy level.

So due to the transmition of e^- Conductivity takes place

(b) P-type Semiconductor :- In this types of Semiconductor form by addition of group 14th element's with group 13th element the group 14th element Such as Si, Gre and group 13th element Such as Al, Gra.

Page : 15
Date : / /

So due to the addition of group 14^{th} element's with group 13^{th} element the group 14^{th} element. Such as Si Ge

due to the present of 2^{nd} electron formation of hole take place and Conductivity increase So due to the formation of hole Conductivity of P-types semiconductor increase as compair to N-types Semiconductor.

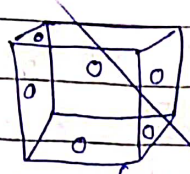
group 14^{th} element + group 13^{th} element

(Si, Ge) + (Al, Ga)

$Si_{14} = 2, 8, 4$ $\quad$ $_{13}Al - 2, 8, 3$

2) **Due to ion :-** In this type of impurity defect causes due to ion if heating of Nacl Crystale and in Nacl Crystal added $CaCl_2$ or $SeCl_2$ takes place So melting of Crystal takes place and chlorine is easily vaporate and due to the vaporisation of chlorine from $CaCl_2$ or $SrCl_2$ crystal So after cooling form Nacl Crystal and it Consist impurity of Ca and Sr ions with is known as impurity due to ion.

Page: 12
Date: / /



So total no. of atoms in fcc

$8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

4 Atoms

$Z = 4$

ex- NaCl

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* **Electric properties :-** Electronic properties the Crystal Consisting Conductivity solids are classified into categoryies

* **Condactores :-** In this type of properties solid have the Conductivity range 10^4 to 10^7 per om per meter ($ohm^{-1} m^{-1}$) are called good Conductor or mettice Conductor of electricity.

they are furthur classified as mettice Conductor and non- mettic Conductor in the mettice Conductor the flow of electricity is due to flow of electron without any out in chemical change the Conductivity of metallic depend upon the no. of valance electrons in the case of electrolyte Conductor like NaCl, KCl, and other electrolite so in the electrolylic conductor flow of electricity due to the flow of ions

Thus whereas metal Conduct electricity in the solid as a motion state

Conductivity of Crystal in motion State due to freely freely movable ions at the room temprature

① Increase the Conductivity if increase the room temprature. in this case the electron Grape b/w the valance band and the Conducton band is low so e^- easily jump into valance to Conduction band

2) Insulator :- In this case the energy gape the valance band and the Conduction is more so it very difficult to jumping of e^- from the valance band to Conduction band which is known as insulator the range of Insulator is 10^8 to 10^{20} Ω m

So the Solid which have extreamly low conductivity which is known as insulator

ex:- plastic, Rubber, wood etc.

3) Semi-Conductor :- The energy Grape between valance band and Conduction band is in between that of a Conductor and insulator which is known as Semi-Conductor.

we know that semiconductor mainly form by dopping and Semiconductor are of two type -

Date / /

Doping add करना है —

1) N-type Semiconductor or Extransic

2) P-type Semiconductor or Intransic

* Band theory * (band model)

Intro :- its valid for explanation of matllic bond this model prepared by the Concept of molecular orbital and its based on LCAO

Defi :- According to this theory crystline matllic solid is a single macro molecules and its valid for molecular orbital and overlaping of bands takes Place. and form bonding and anti-bonding molecular orbitals and due to many more no. of bonding and anti bonding molecular orbital and form continevous band this is band model and this theory is called model

Explanation :- Late us discus formation metal in electronic Configuration of Li metal $1s^2, 2s^1$ and form three type energy band

* 1st band :- In Li $2e^-$ present in 1st orbital and form 1st band and total electron is 2n for $1^{st} \Rightarrow n = 1$

$2 \times 1 \Rightarrow 2e^-$

* **2nd band :-** In 2s band of Li Consist only one e^- due the present of 1 e^- overlapping form 2s band which is called Valance band and it half field orbital and in half a common tempo another e^- field in half field orbital which is called Conduction band.

Forbidden Zone :- In between 1s and 2s orbital takes place. and due to the presence of energy differen e^- presence in 1s band it not transfer into 2s band energy difference in betwee 1s band and 2s band is called forbidden zone.

* Bond theory for Semiconductor. *

Semiconductor have more Conduct in between Conductor it is made up of by dopping process.

Dopping add करना है।

We know that No energy Gape in b/w Valan band and Conduction bond which is knowen as Conductor

if the energy gape in b/w Valance bond and Conduction band so which is known as Semiconductor

If energy gape in b/tw valance band and Conduction band is more so which is known as insulator

* Semi-Conductor are of two type * 1) Intrinsic 2) Impurity

1.) Intrinsic :- In this type of Semiconductor the energy gape in b/w is least Valance band and empty Conduction band so due to the excitation of valance cell e⁻ field in Conduction band which is called intrinsic type Semiconductor
ex :- Si, Ge

$$\sigma = \sigma^{\circ} e^{-E/kT}$$

σ = electrical Conductivity
σ° = Constant
K = Boltzmann Constant
T = Temprature
ε = degree of band or stright ltg line on the slop

In the case of Semi-conductor property is increased so mobality of charge is given by -

$$\sigma = Ne\mu$$

N = no. of charge Carrier
e = Charge
μ = mobality of ions.

☆2) Impu Extrinsic :—

Impurity Semiconductor / N and P-type :— In this type of semi-Conductor the energy gape in b/w valance and Conduction band is large. so its possible the imperfaction of Solid such as impurity defect and in this type of crystal Conduction band is fille so the impurity leval the Conductor of charge mobile e⁻ dependent

Ex:- Ge, As

this phenomena As has been dopped in Ge so N type of semiconductor takes place and Ge dopped in In so p-type is of semiconductor takes place and P-type semiconductor hole formation takes place.

Que 2016 Electrical properties of Solid ?

Ans. 1) Conductor – 1) Metalic Conductor
2) Electrical Conductor

2) Insulator

3) Semiconductor – 1) Imperfect Crystal (Point defect आयेगा)
2) Perfect Crystal.

Perfect Crystal :- In this type of crystal show no effect of tem. and impurity and no effected latice poin. It is hypothetical.

In other words a perfect Crystal is not Contant point defect no line defect no imperfaction of Solid impurity defect.

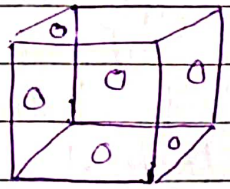
* Plane defect OR Surface imperfaction *

In this types of defect Surface imperfaction take place and the structural imperfaction the change may be one of the orientation of the 7.17 Sequence of the plane.

1) **Grain boundary :-** Grain boundary are those Surface imperfaction with saparate the Crystal of different orientation the boundary atom can not have perfact ~~arrangement of~~ arrangement of the Constituent partical

2) **Stacking fault** :- It is a surface imperfaction that result from the stacking of the one atomic plane out of sequence on another while the lattice on other side of the fault is perfect is for crystal.

In fcc crystal may be define as constituent particals present on the corner and faces



So total no. of atoms in fcc

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2}$$

4 atoms

$Z = 4$

Ex:- NaCl

* V-Center *

V-center studied by Kazing the ESR spectro in a NaCl crystal when heating in Chloride glass so it also become colourled and this type of Center is called V-center and due to V-center identified the chroride ion co-valent bond and according to x-ray studies chloride ion and chloride atom form V-ceters so in a perfactly normal NaCl crystal that no have vacancy. so it is form chloride ion to chloride ion

Page : 24
Date: / /

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^- Na^+ ← Schottky defect

Cl^- Na^+ □ Na^+ Cl^- □ Cl^-

Na^+ Cl^- Na^+ Cl^- □ Cl^- Na^+

Na^+ ← frankle

Cl^- Na^+ Cl^- Na^+ Cl^- Na^+ Cl^- defect

Na^+ Cl^- Na^+ Cl^- Na^+ ⊖ Na^+ ← f-center

Cl^- Na^+ Cl^- Na^+ Cl^- Na^+ Cl^- ← V-center

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^- Na^+

H-centre

Cl^- Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-

* Line Defect or Dislocation *

Line defect due to the imperfaction of solid and due to dislocation of ion two type of line defect takes place.

1) Edge line defect 2) Screw line defect.

Edge line defect :- In this types of dislocation or line defect ~~along the line perpandicular~~ dislocation a long the line perpendicular to the plane of the paper this type of dislocation is also known as paylor पायलर dislocation and it is also known as paylor orwan ओरवान dislocation

In this type of dislocation no. of
Eg Edges not in perpendicular in manner.

is other method this type
of edge dislocation ordinary crystal not in
direction of the plane depending upon the
dislocation motion

3) Screw line deffect :- In this type of dislocation
introdues buergur so which
is called ~~bue~~ buerger dislocation
According to dislocation 1
Part of the crystal run around dislocation
of crystal line. when in a atomic plane
dislocation takes place and disaption of cell
takes place.

Que. HBr have both types of defect shottkey and frankle why?

Ans. HBr have both types of deffect shottky and frankle because shottky deffect occure in ionic solid and due to the size of cation is more (size of silliver ion) and size of anion is small (Br) so it have shaw frenkle deffect.