Unit-1

Chapter1: Crystal structure

A solid is a group of atoms, ions or molecules possessing definite shape and volume. When a solid is subjected to forces (shearing forces), it resists the forces and under goes deformation. After removing the forces it regains its shape and volume. Such properties are not exhibited by liquids or gases.

The properties and performance of every engineering material depends on internal structure. .mechanical properties determine the behavior of engineering materials under applied forces and loads. The response of the material to applied force depends on the type of bonding, structural arrangement of atoms or molecules and type of number of imperfections, sensitive to manufacturing process and operations. (Stress, strain, brittleness, ductility, fatigue, toughness)

The atoms in solids have two types of energies.i.e

- (a) Potential energy
- (b) Kinetic energy

When the atoms are in free state (separated by infinite distance) then the potential energy becomes zero. And the P.E is inversely related to some power of distance of separation.

$$P.E \propto \frac{1}{r^n}$$

The P.E due to attraction is -ve; as the atoms do work of attraction.

The P.E due to repulsion is + ve;as the external work is done to bring the atoms together.

BONDING: the process of holding the atoms together i.e the attractive and repulsive forces that tend to hold the adjacent atoms together at a particular distance in order to balance the opposite forces.

Nature of bonding forces:

To understand the nature of bonding forces, consider a system of two atoms. These two atoms exert attractive and repulsive forces on each other, such that the bonding force is 'F'

When the two atoms are present at distance of separation of 'r',

then the attractive force 'F_A' is given by

$$F_A = \frac{1}{r^M}$$

2

 $F_A = \frac{A}{r^M}$, where A is proportionality constant, M= 2 as per Coulomb's law

Repulsive force 'F_R'is given by

$$F_R = \frac{1}{r^N}$$

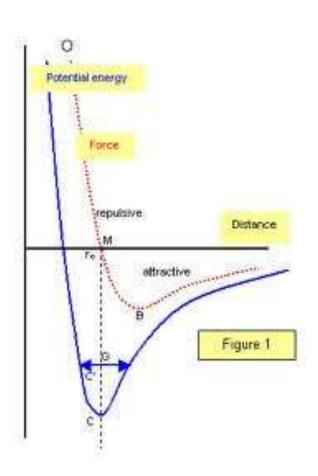
 $F_R = \frac{-B}{r^N}$, B is proportionality constant and N=7-10 as per Coulomb's law.

When two atoms are present at equilibrium distance r_0 , then magnitude of F_A and F_R are equal and opposite.

The sum of attractive and repulsive force is

$$F_{(r)}\!\!=F_A+F_R$$

$$F_{(r)} = \frac{A}{r^M} - \frac{B}{r^N}$$



Calculation of Cohesive energy of a solid:

"The amount of energy required to separate the atoms in a crystalline solid is known as cohesive energy also called as bonding cohesive energy

Or the amount of energy required to separate the atoms in a crystalline solid is known as cohesive energy or dissociation cohesive energy.

At equilibrium position the PE of either atom is given by

U= decrease in P.E due to F.A + increase in PE due to F.R

Since the work done on the system is stored as PE, it can be calculated by integrating the equation

$$F_{(r)} = \frac{A}{r^M} - \frac{B}{r^N}$$

$$U_{(r)} = \int F(r) dr...(1)$$

$$= A \int r^{-M} dr - B \int r^{-N} dr$$

$$= \frac{Ar^{-M+1}}{-M+1} - \frac{Br^{-N+1}}{-N+1} + C...(2)$$

Here
$$\frac{A}{M-1} = a$$
; $\frac{B}{N-1} = b$; $m = M - 1$; $n - N - 1$...(3) in (2)

$$U_{(r)} = \frac{-a}{r^m} + \frac{b}{r^n} + C...(4)$$

Here a and b are attractive and repulsive force constants and n are+ve integers and 'C' is a constant.

when
$$r \to \infty$$
, $V(r) = 0 \leftrightarrow C = 0$ in (4)

$$U_{(r)} = \frac{-a}{r^m} + \frac{b}{r^n}...(5)$$

The first term represents P.E due to force of attraction and second term represents P.E due to repulsion.

i.e when $r \rightarrow r_0$, at equilibrium distance of separation

$$U_{(r_0)} = \frac{-a}{r_0^m} + \frac{b}{r_0^n}...(6)$$

By differentiating eqn(6)

$$\left(\frac{du}{dr}\right)_{r=r_0} = (-a)(-m)r_0^{-m-1} + b(-n)r_0^{-n-1}$$

$$= \frac{ma}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

$$= ma \qquad bn$$

$$= \frac{ma}{r_0^{m+1}} = \frac{bn}{r_0^{n+1}}$$
$$= \frac{ma}{r_0^m} = \frac{bn}{r_0^n}$$

$$r_0^n = \frac{n}{m} \frac{b}{a} r_0^m \dots (7) \text{ in } (6)$$

$$U_{min} = \frac{-a}{r_0^m} + \frac{b}{\frac{n}{m} \frac{b}{a} r_0^m}$$
$$= \frac{-a}{r_0^m} + \frac{m}{n} \frac{a}{b} \frac{b}{r_0^m}$$
$$= \frac{-a}{r_0^m} + \frac{m}{n} \frac{a}{r_0^m}$$

$$U_{min} = \frac{-a}{r_0^m} \left(1 - \frac{m}{n} \right)$$

This is the expression for cohesive energy of a molecule containing two atoms in a solid. The energy U_{min} is called Bonding energy or dissociation energy or cohesive energy.

Calculation of Lattice energy of Ionic crystals:

The lattice energy of an ionic solid will differ from the bond energy of diatomic soilds.in the former case there will be interactions between more atoms.

"The cohesive energy of an ionic crystal is the energy that would be liberated by the formation of the crystal from individual neutral atoms

In case of NaCl crystal, each sodium ion is subjected to attractive potential due to 6 chloride ions each at a distance 'r'.thus the attractive potential at the sodium ion by the chloride ion is

$$U_1 = -6\frac{e^2}{4\pi\epsilon_0 r}$$

The next nearest neighbors are 12 sodium ions at a distance of $\sqrt{2}r$.thus

$$U_2 = 12 \frac{e^2}{4\pi\epsilon_0 r(\sqrt{2})}$$
 ans so on

Thus the total potential energy is

$$U_{attraction} = -6\frac{e^2}{4\pi\epsilon_0 r} + 12\frac{e^2}{4\pi\epsilon_0 r(\sqrt{2})} - 8\frac{e^2}{4\pi\epsilon_0 r(\sqrt{3})} + \cdots \dots$$

$$= -\frac{e^2}{4\pi\epsilon_0 r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots \right)$$

Let $\propto = \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots\right) = 1.75$ is called Madelung constant

Thus
$$U_{att} = -\frac{\propto e^2}{4\pi\epsilon_0 r}$$

The P.E due to short range repulsive forces can be expressed as

$$U_{rep} = \frac{B}{r^n}$$

Where B is a constant and U_{rep} is positive which increases rapidly with decreasing internuclear distance 'r'.thus the total P.E 'U' of each ion due to its interaction with all other ions in the crystal is

$$U_{(r)} = -\frac{\propto e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n} \dots (1)$$

At the equilibrium spacing 'r₀', U is min and hence $\frac{du}{dr} = 0$

$$\begin{aligned} \left[\frac{du}{dr}\right]_{r=r_0} &= -\frac{\propto e^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0\\ &\frac{\propto e^2}{4\pi\epsilon_0 r_0} = \frac{nB}{r_0^n} \end{aligned}$$

$$B = \frac{\propto e^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$
...(2) in (1) with r=r₀, we get

$$U_{min} = -\frac{\propto e^2}{4\pi\epsilon_0 r_0} + \frac{\propto e^2 r_0^{n-1}}{4\pi\epsilon_0 n r_0^{n}}$$

$$=-\frac{\propto e^2}{4\pi\epsilon_0 r_0}+\frac{\propto e^2}{4\pi\epsilon_0 n r_0}$$

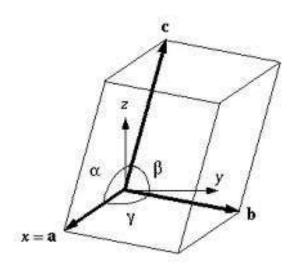
$$U_{min} = -\frac{\propto e^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{1}{n} \right]$$

Thus for one KMol of the crystal, the energy is

$$U_{min} = -\frac{\propto e^2 N_A}{4\pi\epsilon_0 r_0} \left[1 - \frac{1}{n} \right]$$

Unit cell: is a minimum volume cell which on repetition gives actual crystal structure.

Lattice parameters: the primitives (a,b,c) and interfacial angles $(\alpha,\beta,\gamma,)$ are the basic lattice parameters which determine the actual size of unit cell.

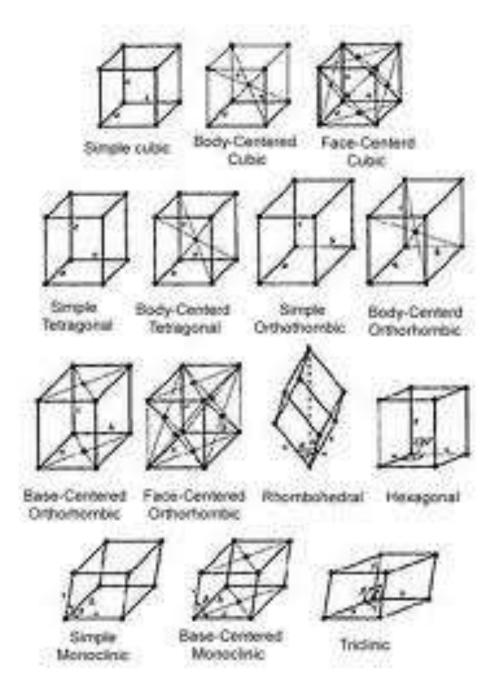


Seven crystal systems with 14 Bravais points

S	S:no	Name of the crystal	Primitives	Interfacial angles	Bravais Lattice
		systems			points

1	Cubic	a= b= c	α=β=γ=90°	3(P,I,F)
2	Tetragonal	a= b≠ c	$\alpha=\beta=\gamma=90^{\circ}$	2(P,I)
3	Orthorhombic	a≠ b≠ c	$\alpha=\beta=\gamma=90^{\circ}$	4(P,C,I,F)
4	Monoclinic	a≠ b≠ c	α=β=90°≠γ	2(P,C)
5	Triclinic	a≠ b≠ c	α≠β≠γ≠90°	1(P)
6	Trigonal	a=b=c	α=β=γ≠90°	1(P)
7	Hexagonal	a= b≠ c	α = β = 90° and γ = 120°	1(P)

P= simple, C= base centered , I= body centered, F= face centered



Atomic radius (\mathbf{r}) – The atomic radius is defined as the half the distance between neighboring atoms in a crystal of pure element.

Co-ordination number-defined as the no: of equidistant neighbors that an atom has the given structure .Greater the co-ordination no: the atom are said to be closely packed.

Packing factor (PF)-It is the ratio of volume occupied by the atoms or molecule in unit cell to the total volume of the unit cell

Simple crystal structure

- 1. Simple cubic structure (SC)
- 2. Body centered structure (BCC)
- 3. Face centered structure (FCC)

Packing factor of SC.BCC, FCC

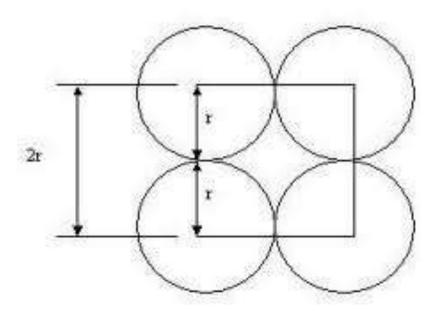
1. Simple cubic

Packing fraction = volume of all the atoms in unit cell

Volume of unit cell

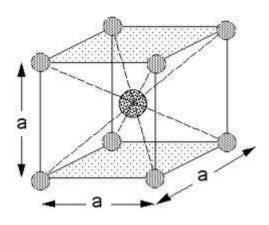
$$= 1 \times 4/3\pi r^{3} = 56\%$$

$$= 3$$



2. Body centered structure (BCC)

Packing fraction =
$$\frac{2 \times 4/3\pi}{a^3}$$
 = 68%



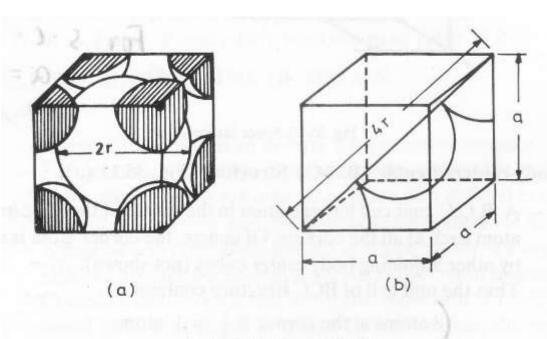
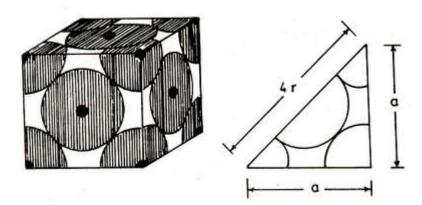


Fig. 35.12. Unit cell of BCC.

3. Face centerd structure(FCC)

Packing fraction= $4 \times (\pi a^3 \sqrt{2}/24)$ = 74%



Chapter 2 **DEFECTS IN CRYSTALS**

In a perfect crystal:

- 1. Atoms exist only in lattice sites.
- 2. Periodicity of lattice extends up to infinity.
- 3. Atoms do not loose electrons, no free electrons are present.
- 4. Atoms would be stationary.

Any deviation from the above four properties is known as defect.

The properties of crystal are divided into two categories based on the presence of imperfections.

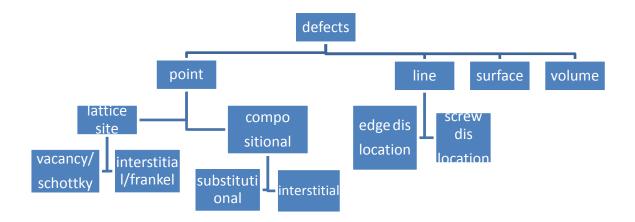
- 1. **Structure sensitive properties:** which are affected by the presence of imperfections. Ex: mechanical strength, electrical conductivity in semi conductors, magnetic hysteresis, dielectric strength.
- 2. **Structure insensitive properties:** which are not affected by the presence of imperfections.

Ex: stiffness.

Defects are produced by various methods:

- 1. by heating
- 2. Rapid cooling
- 3. By applying external strength
- 4. By bombarding with high energy particles like neutrons or particles from cyclotron.

Defects are broadly classified into



Point defects: (zero dimensional defects) arises when an atom is absent from the regular position, presence of impurity atom or atom in the wrong place during crystallization.. These are small defects which extends its influence in all directions but limited to a specific region of small order (two or three atomic orders).

Point defects are:

Vacancy: missing of an atom from its original lattice site. Generally arises due to thermal vibrations during crystallization and influenced by external parameters. Vacancies may be single, two or more depending on crystal type. For most of the crystals, in order to create one vacancy thermal energy of 1.1 ev is required.

Interstitial: this defect arises when an atom of same kind or different kind occupies the void space between the regular atomic sites.

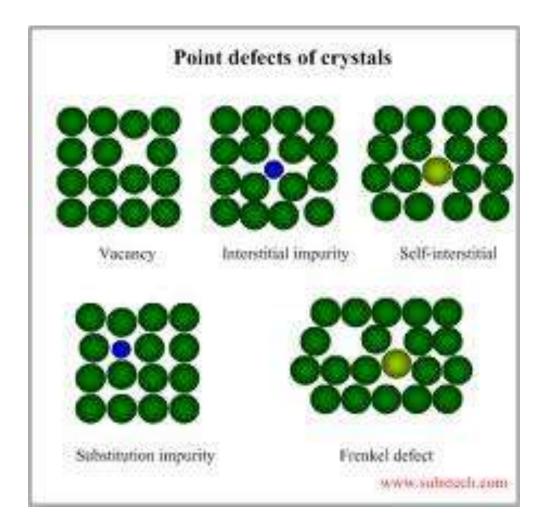
Impurity atom: an atom that does not belong to the parent lattice (original crystal).

Substitutional defects: this defect arises when an impurity atom replaces or substitutes parent atom.

Ex: in brass, zinc is a substitutional atom in a copper lattice

Interstitial impurity: this defect arises when an impurity atom which is small in size is placed between the regular atomic sites.

Ex: when pentavalent and trivalent impurities are added to pure Si or Ge, we get n-type and P-type semiconductors.



Imperfections in ionic crystals: in case of ionic crystals imperfections appear in crystals while maintaining the electrical neutrality. two types of defects (point defects) occur in ionic crystals.

- 1. Frenkel defect
- 2. Schottky defect.

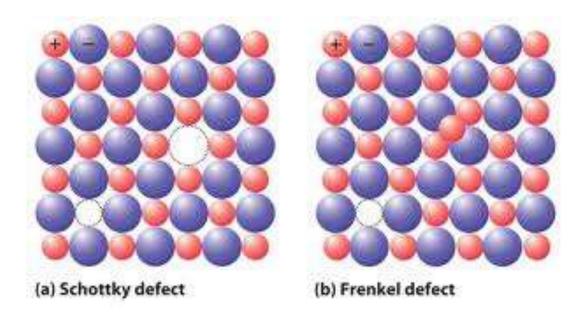
Frenkel defect:

When an ion is displaced from a regular lattice site to an interstitial site is called Frenkel defect. Generally cations which are small in size are displaced to an interstitial site as the interstitial space is small.

A Frenkel imperfection does not change the overall electrical neutrality of the crystal.

Schottky defect:

A pair of one cation and one anion missing from the original lattice site on to the surface of the crystal so that charge neutrality is maintained in the crystal is called Schottky defect.



Line defects (or) dislocations (one dimensional defect) dislocation is defined as the disturbed region between the two perfect parts of the crystal and these defects are formed in the process of deformation.

Edge dislocation:

A perfect crystal is composed of several parallel vertical planes which are extended from top to bottom completely and parallel to side faces. The atoms are in equilibrium positions and the bond lengths are in equilibrium value.

If one of the vertical planes does not extend from top to bottom face of the crystal, but ends in midway within the crystal, then crystal suffers with a dislocation called edge dislocation.

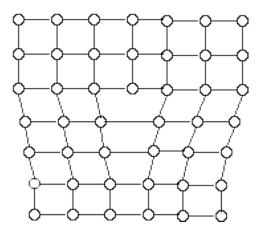
In imperfect crystal all the atoms above the dislocation plane are squeezed together and compressed there by the bond length decreases. And all the atoms below the dislocation plane are elongated by subjecting to the tension and thereby the bond length increases.

There are two types of edge dislocation. They are

- 1. Positive edge dislocation
- 2. Negative edge dislocation.

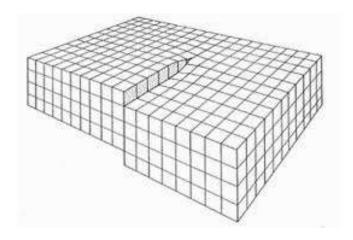
Positive edge dislocation: if the vertical plane starts from top of the crystal and never reaches to the bottom .

Negative edge dislocation: if the vertical plane starts from bottom of the crystal and never reaches top.



Screw dislocation; atoms are displaced in two separate planes perpendicular to each other or defects forming a spiral around the dislocation line.

A screw dislocation marks the boundary between slipped and unslipped parts of the crystal, that can be produced by cutting the crystal partway and then sheering down one part relative to the other by atomic spacing horizontally.



Burger's vector: gives the magnitude and direction of dislocation line.

Construction of Burger,s vector:

Starting from a point 'p' move same number of steps left, right, up and down in the clockwise direction.

If the starting point 'p' and ending point 'p' coincide, then the region enclosed in the Burger's circuit is free from imperfection.

If the starting point and ending point do not coincide i.e. $pp^{l} = b$. b is the quantity indicating magnitude.

Burgers' vector is perpendicular to edge dislocation plane and parallel to screw dislocation plane.

Surface defects: (two dimensional defects) ,grain, twin, twilt and stacking defects come under surface defects

Volume defects: (three dimensional defects) when group of atoms are missing and cracks arise in the crystal.

Expression for the number of vacancies at any temperature. Or energy of formation of vacancy.

Let 'N' be the number of atoms in a crystal, 'E_v' is the energy required to create 'n' vacancies.

The total energy required for the creation of 'n' number of vacancies is called enthalpy and is given as

$$u=nE_v$$
....(1)

The number of ways of selecting 'N' atoms to create 'n' vacancies is p

$$p = Nc_n = \frac{N!}{n!(N-n)!}$$
 -----(2)

Here 'p' is disorder parameter

In stastistical mechanics, the relation between disorder parameter 'p' and entropy's' is

free energy (F) of the atoms in the crystal is given by

$$f = u - Ts$$
....(4)

$$f = nE_V - KT \log p \dots (5)$$
 from 1 and 3

$$f = nE_v - KT \log \frac{n!}{(N-n)!n!} \dots (6)$$
 substitute 2 in 5

By applying stirling's approximation, to eqn (6)

$$logx! = xlogx - x$$

$$f = nE_V - KT(logN! - \log(N - n)! - logn!)$$

$$f = nE_v = KT(NlogN - N - (N - n)\log(N - n) + (N - N) - nlogn + n)$$

$$F = nE_V - KT(NlogN - (N - n)\log(N - n) - nlogn)....(7)$$

At thermal equilibrium, the free energy is minimum and constant.i.e.

$$\frac{dF}{dn} = 0 \text{ in } (7)$$

$$\frac{dF}{dn} = E_v - KT(0 - (N - n)\frac{1}{(N - n)}(-1) - \log(N - n)(-1) - n\frac{1}{n} - \log n)$$

$$0 = E_v - KT(1 + \log(N - n) - 1 - \log n)$$

$$0 = E_v - KT\left[\log\left(\frac{N - n}{n}\right)\right]$$

$$E_v = KT\log\left(\frac{N - n}{n}\right)$$

$$\frac{E_v}{KT} = \log\left(\frac{N - n}{n}\right)$$

Taking exponential on both sides

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

The number of vacancies in a crystal is very small when compared with the number of atoms. $N \gg n$

$$N-n\cong N$$

Therefore $e^{-E_v/KT} \frac{n}{N}$

$$n = Nexp^{-E_v/KT}....(8)$$

FRENKEL DEFECT:

Let 'N' be the number of atoms, 'N_i'be the number of interstitial atoms, let 'E_i 's the energy required to create 'n' number of vacancies and the total energy required is $u = nE_i....(1)$

The total number of ways in which Frenkel defects can be formed is given by $p = N_n^c \times N_{i_n}^c$

$$p = \frac{N!}{(N-n)!n!} \times \frac{N_i!}{(N_i-n)!n!}$$
.....(2)

The increase in entropy (s) due to Frenkel defect is given by $s = K \log p$

$$S = Klog \left[\frac{N!}{n!(N-n)!} \times \frac{N_i!}{(N_i-n)!n!} \right] \dots (3)$$

This increase in entropy produces change in Free energy F = u - TS....(4)

Substitute (1),(3) in (4)

$$F = nE_i - KTlog \left[\frac{N!}{n! (N-n)!} \times \frac{N_i!}{(N_i - n)! n!} \right]$$

Using Strling's approximation, logx! = xlogx - x

$$F = nE_{i} - KT \left[log \frac{N!}{n! (N-n)!} + log \frac{N_{i}!}{(N_{I} - n)! n!} \right]$$

$$F = nE_i - KT[logN! - logn! - log(N - n)! + logN_i! - log(N_i - n)! - logn!]$$

$$\begin{split} F = nE_i - KT[(NlogN-N) - (nlogn-n) - [(N-n)log(N-n) - (N-n)] + N_ilogN_i \\ - N_I - [(N_i-n)log(N_i-n) - (N_i-n)] - (nlogn-n)] \end{split}$$

$$\begin{aligned} F &= nE_i - KT[NlogN - N - nlogn + n - (N - n)log(N - n) + (N - n) + N_ilogN_I - N_i \\ &- (N_i - n)log(N_i - n) + (N_i - n) - nlogn + n] \end{aligned}$$

$$F = nE_I - KT[NlogN + N_ilogN_i - (N - n)log(N - n) - (N_i - n)log(N_i - n) - 2nlogn]$$

Differentiating w.r.to 'n', and equating to 0, we get

$$\begin{split} \frac{dF}{dn} &= E_i - KT \left[0 + 0 - \left[(N-n) \frac{1}{(N-n)} (-1) \right] + \log(N-n) (-1) \right] \\ &- \left[(N_i - n) \frac{1}{(N_i - n)} (-1) + \log(N_i - n) (-1) \right] - 2 \left[n \times \frac{1}{n} + \log n \right] \right] \\ &0 &= E_i - KT [1 + \log(N-n) + 1 + \log(N_i - n) - 2 - 2 \log n] \\ &0 &= E_i - KT \left[\log \frac{(N-n)(N_i - n)}{n^2} \right] \end{split}$$

$$E_{i} = KT \left[log \frac{(N-n)(N_{i}-n)}{n^{2}} \right]$$

As $n \ll N$, $N-n \cong N$, similarly $N_i-n \cong N_i$

$$E_{i} = KTlog\left(\frac{NN_{i}}{n^{2}}\right)$$

Thus $E_i = KT[logNN_i - 2logn]$

$$\frac{E_i}{KT} = \log(NN_i) - 2\log n$$

$$2\log n = \log(NN_i) - \frac{E_i}{KT}$$

$$logn = \frac{1}{2}log(NN_i) - \frac{E_i}{2KT}$$

Taking exponentials on both sides

$$n = (NN_i)^{\frac{1}{2}} exp^{\frac{-E_i}{2KT}}$$

SCHOTTKY DEFECT:

In ionic crystals, the formation of paired vacancy is most favoured.i.e an equal number of positive and negative vacancy pairs are produced.

Let 'N' be the number of atoms, 'E_p' is the energy required to create a pair of vacancies and 'n'be number of vacancies created. The total energy required to create vacancies is

$$U = nE_{p....(1)}$$

The number of ways in which 'n' vacancies created is

$$p = N_n^c \times N_n^c = (N_n^c)^2$$

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

The relation between the disorder parameter 'p' and entropy 's' is given by

$$s = Klogp = klog \left[\frac{N!}{(N-n)!n!}\right]^2$$
....(2)

By applying Striling's approximation

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

$$= 2[N\log N - N - ((N-n)\log(N-n) - (N-n)) - (n\log n - n)]$$

$$= 2[N\log N - N - (N-n)\log(N-n) + N - n - n\log n + n]$$

$$= 2[N\log N - (N-n)\log(N-n) - n\log n]$$

There fore s = 2K[NlogN - (N - n)log(N - n) - nlogn]....(3)

Free energy of the atoms in the crystal is given by F = U - TS....(4)

Substitute (1),(3) in (4)

$$F = nE_p - 2KT[NlogN - (N - n)log(N - n) - nlogn]$$

Differentiating above equation w.r.to 'n' and equating it to zero ,we get

$$\begin{split} \frac{dF}{dn} &= E_p - 2KT[log(N-n) + 1 - logn - 1 = 0] \\ &E_p - 2KTlog\Big(\frac{N-n}{n}\Big) = 0 \\ &\frac{E_p}{2KT} = log\Big(\frac{N-n}{n}\Big) \end{split}$$

Taking exponentials on both sides

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

As nn \ll N, N = $nexp^{\frac{E_p}{2KT}}$

$$n = Nexp^{\frac{-E_p}{2KT}}$$

Chapter 3: PRINCIPLES OF QUANTUM MECHANICS

De-Broglie Hypothesis –Matter waves: An electromagnetic wave behaves like particles, particles like electrons behave like waves called matter waves, also called de-Broglie matter waves.

The wave length of matter waves is derived on the analogy of radiation.

Based on Planck's theory of radiation, the energy of a photon is given by

$$E = h\vartheta = \frac{hc}{\lambda}....(1)$$

c =Velocity of light

 λ = Wavelength of the photon

h= Planck's constant

According to Einstein's mass energy relation

$$E = mc^2 \dots (2)$$

m= mass of the photon

Equating equations (1) and (2)

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{mc^2} = \frac{h}{mc} = \frac{h}{p}.....(3)$$

P = momentum of photon

de-Broglie proposed the concept of matter waves, according to which a material particle of mass'm', moving with a velocity's' should have an associated wavelength ' λ ' called de-Broglie wavelength.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$
... (4) is called de-Broglie's wave equation.

Properties of matter waves:

- 1. Wavelength is associated with moving particle and independent of charge of the particle
- 2. Greater the mass, velocity of the particle, lesser will be the wavelength.

de-Broglie wavelength associated with an electron: