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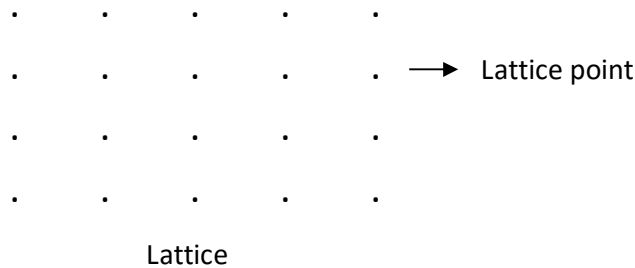


**UNIT - I**  
**CRYSTAL LATTICES**

**Lattice:**

A regular arrangement of point is called a lattice.

**Diagram:**



In the above diagram the points are called lattice points. Here the lattice is called the plane lattice.

Two types,

- (i) Two dimensional Lattice (Plane Lattice)
- (ii) Three dimensional Lattice (Space Lattice)

**Translation Vectors:**

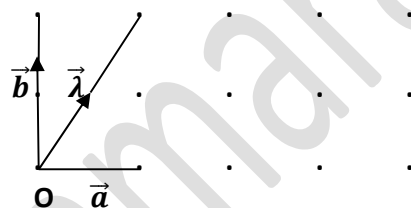
Translation vectors are used to define lattice point. They are classified into

- (i) Two dimensional translation vectors
- (ii) Three dimensional translation vectors

**Two dimensional translation vectors:**

Two dimensional translation are used to locate define lattice point in a plane lattice.

**Diagram:**



The above diagram its points are called lattice points

$\vec{a}, \vec{b}$  are primitives.

For plane lattice, the translation vector

$$\vec{T} = \mu\vec{a} + \nu\vec{b}$$

Where  $\mu, \nu$  are integers.

In the above diagram.

$$\mu=1$$

$$\nu=2$$

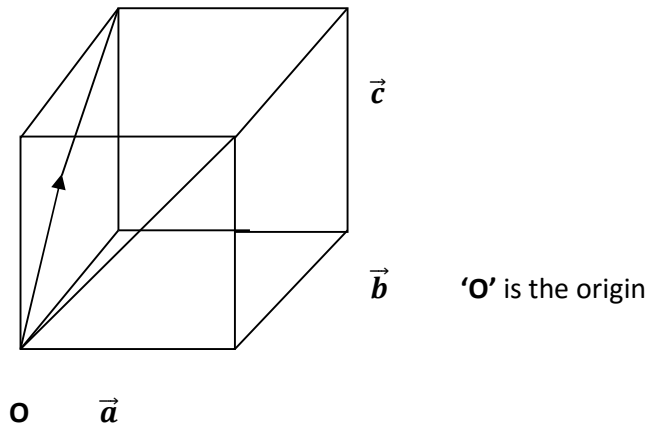
$$\vec{T} = 1 \cdot \vec{a} + 2 \cdot \vec{b}$$

**Three dimensional translation vector:**

Three dimensional translation vector are used to define lattice point in a space lattice.



Diagram:



In the above diagram

$\vec{a}, \vec{b}, \vec{c}$  is a primitives.

$\vec{T}$  is the Translation vector.

For a space lattice the translation vector is

$$T = \mu \vec{a} + v \vec{b} + w \vec{c}$$

Where,

$u, v, w$  are integers.

In the above diagram

$$\mu=1$$

$$v=1$$

$$w=1$$

$$T = 1 \cdot \vec{a} + 1 \cdot \vec{b} + 1 \cdot \vec{c}$$

### Two dimensional lattices:

A two dimensional lattice is called as a plane lattice.

A plane lattice is defined by two primitives  $a, b$

The translation vector for a plane lattice is

$$\vec{T} = \mu \vec{a} + v \vec{b}$$

Where,  $\mu, v$  are integers.

### Types:

There are five types of two – dimensional lattices, (plane lattices)

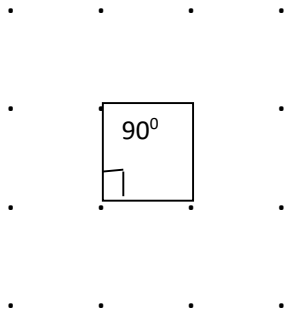
1. Square lattice.
2. Rectangle lattice.
3. Centered Rectangle lattice.
4. Hexagonal lattice.
5. Oblique lattice.

### (i) Square lattice:

For Square lattice the lattice constants are  $a=b, \phi=90^\circ$



Diagram:



The above diagram the points are called lattice points.

$\vec{a}, \vec{b}$  are called primitives.

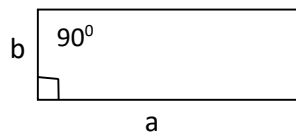
The unit cell is square.

**(ii) Rectangular lattice:**

In the rectangular lattice the lattice constants are  $a \neq b, \phi = 90^\circ$

Diagram:

The diagram is given below.



The above diagram a, b are primitives.

**(iii) Centered rectangular lattice:**

In the centered Rectangular lattice constants are  $a \neq b, \phi = 90^\circ$

Diagram:

The diagram is given below.



It is a non – primitive lattice.

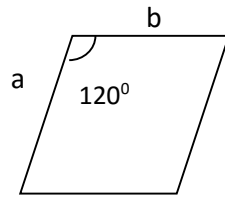
**(iv) Hexagonal lattice:**

For Hexagonal lattice the lattice constants are

$a = b, \phi = 120^\circ$



**Diagram:**

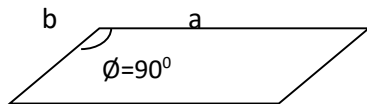


In the above diagram the points are called lattice points.  
 It is a primitive lattice.

**(V). Oblique Lattice:**

For oblique lattice the lattice constants are  $a \neq b, \phi = 90^\circ$

**Diagram:**



It is a primitive lattice.

The two dimensional Bravais lattices are given in the following table:

Plane Lattices	Lattice Constants	Point group
(1) Square lattice	$a=b, \phi=90^\circ$	4, 4 mm
(2) Rectangle lattice	$a \neq b, \phi=90^\circ$	1m; 2mm
(3) Centered rectangle lattice	$a \neq b, \phi=90^\circ$	1m, 2mm
(4) Hexagonal lattice	$a=b, \phi=120^\circ$	6, 6mm
(5) Oblique lattice	$a \neq b, \phi \neq 90^\circ$	1, 2
M → Mirror plane		

**Three dimensional lattices (Space lattices):**

A three dimensional lattice is called as a space lattice. They are also called as Bravais lattice.

A Space lattice is defined by three primitives  $\vec{a}, \vec{b}, \vec{c}$

The translation vector for a space lattice is

$$\vec{T} = u \vec{a} + v \vec{b} + w \vec{c}$$

Where,

u,v,w are integers.

There are 14 Bravais lattices



They are,

- (i) Simple Cubic (SC)
- (ii) Body Centered Cubic (BCC)
- (iii) Face Centered Cubic (FCC)
- (iv) Simple tetragonal
- (v) Body Centered tetragonal
- (vi) Simple orthorhombic
- (vii) Body Centered orthorhombic
- (viii) Face Centered orthorhombic
- (ix) Base Centered orthorhombic
- (x) Simple monoclinic
- (xi) Base Centered monoclinic
- (xii) Simple triclinic
- (xiii) Simple rhombohedral (or) trigonal
- (xiv) Simple hexagonal

There are 7 Crystal Systems.

The lattice constants, lattice types and crystal systems are given below.

Crystal System	Lattice Constants	Bravais Lattices
(i) Cubic	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	P,I,F
(ii) Tetragonal	$a\neq b=c$ $\alpha=\beta=\gamma=90^\circ$	P,I
(iii) Orthorhombic	$a\neq b\neq c$ $\alpha=\beta=\gamma=90^\circ$	P,I,F,C
(iv) Mono Clinic	$a\neq b\neq c$ $\alpha\neq\beta=\gamma=90^\circ$	P,C
(v) Triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma\neq 90^\circ$	P
(vi) Trigonal	$a=b=c$ $\alpha=\beta=\gamma\neq 90^\circ$	P
(vii) Hexagonal	$a=b\neq c$ $\alpha=\beta=90^\circ$ $\gamma=120^\circ$	P

In the above table

P → Primitive lattice

I → Body centered

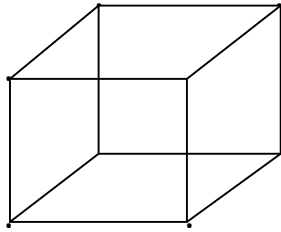
F → Face centered

↔ Base centered



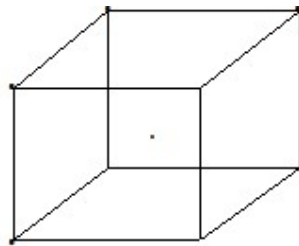
Diagrams:

(i) Simple Cubic (SC)



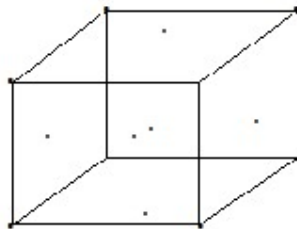
$$a=b=c$$
$$\alpha=\beta=\gamma=90^\circ$$

(ii) Body Centered Cubic:



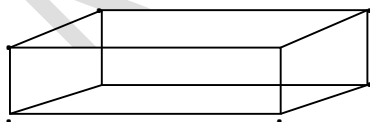
$$a=b=c$$
$$\alpha=\beta=\gamma=90^\circ$$

(iii) Face Centered Cubic:



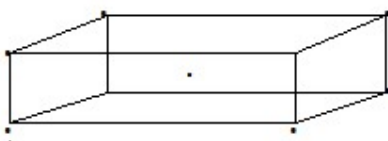
$$a=b=c$$
$$\alpha=\beta=\gamma=90^\circ$$

(iv) Simple Tetragonal:



$$a \neq b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$

(V) Body Centered tetragonal:



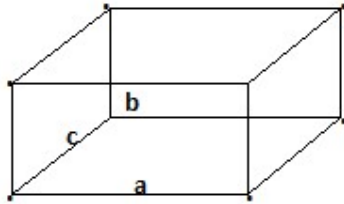
$$a \neq b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$



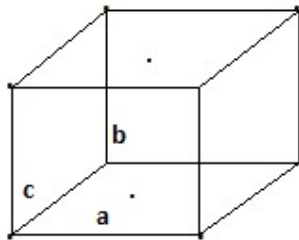
(Vi) Simple Orthorhombic:

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

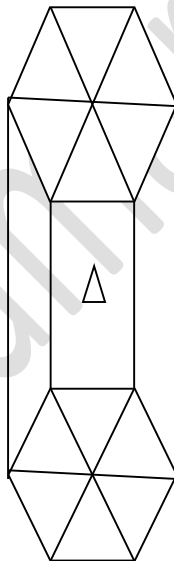


(Vii) Body Centered Orthorhombic:

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



(Viii) Simple Hexagonal:



Explain the following:

(1) Lattice:

A regular arrangement of point is called a lattice.

(2) Basis:

A basis is an atom or a molecule.



**Example:**

For a sodium chloride (NaCl) Crystal basis is NaCl molecule.  
 Here the basis consists of two atoms.

**Another Example:**

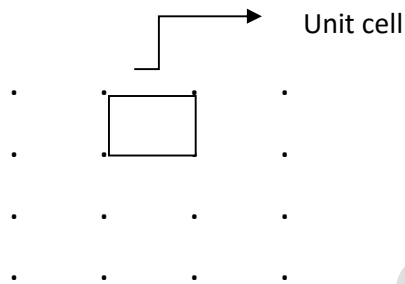
For KCl crystals, basis is KCl molecule.

**(3) Unit Cell:**

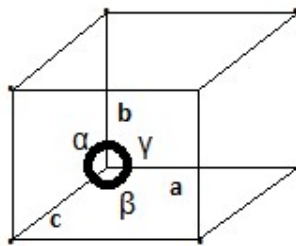
The smallest repeating pattern in a crystal is called a unit cell.

**Diagram:**

For a two dimensional unit cell.



In the above the points are lattice points. The unit cell is square unit cell.  
 For a three dimensional unit cell.



$$a=b=c$$

$$\alpha=\beta=\gamma=90^\circ.$$

**(4) Crystal Structure:**

A crystal structure is formed by adding the basis to each lattice point.

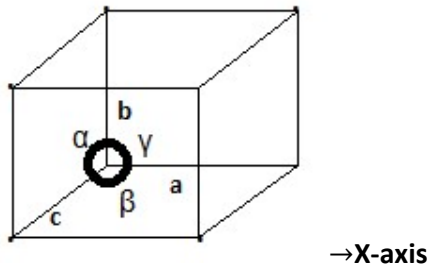
$$\text{Crystal Structure} = \text{Lattice} + \text{basis}$$

**(5) Lattice Parameters**

Lattice Parameters are  $a, b, c$  and  $\alpha, \beta, \gamma$   
 Axial parameters are  $a, b, c$   
 Angular parameters are  $\alpha, \beta, \gamma$



Diagram:



(6) Give lattice parameters to the seven crystal system:

(Tabulation) Previous page.

(7) Space lattice: (5 mark)

Three dimensional lattice (Previous page)

(8) Index System for crystal planes:

**Miller Indices:**

Miller indices are used for indexing crystal planes. The symbol for miller indices is (hkl)

**Examples:**

(111), (001), (100), (213) etc.

**Procedure: For Finding miller indices:**

**Steps:**

(i) Find the intercepts Example:  $pa, qb, rc$  (or)  $2a, 2b, c$ .

(ii) Divide by  $a, b, c$  →  $2, 2, 1$  Separately

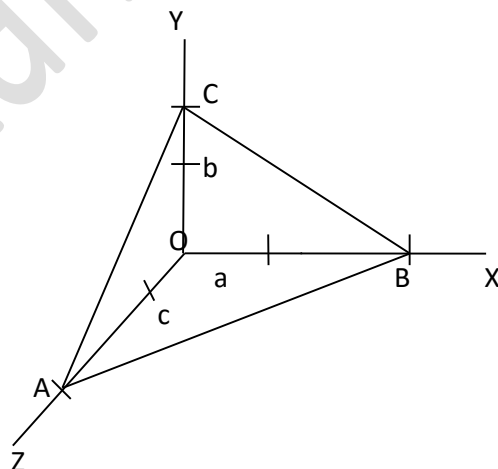
(iii) Find the reciprocals →  $1/2, 1/2, 1/1$

(iv) Clear the fractions by multiplying with Lcm → (112)

LCM → Least Common Multiple

**Diagram:**

Consider a crystal plate ABC as given below.



In the above diagram,  $a, b, c$  are primitives. The intercepts are  $2a, 2b, c$ . The miller indices are (112)



**Important features:**

- (1) If a plane is parallel to an axis, the intercept is infinity ( $\infty$ )
- (2) All the parallel planes have same miller indices.
- (3) The relation between the intercept, lattice constant and miller indices are  
 Intercepts along X – axis =  $a/h$   
 Intercepts along Y – axis =  $b/k$   
 Intercepts along Z – axis =  $c/l$

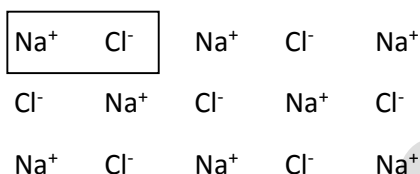
**Uses:**

- (i) Miller indices are used to denote crystal planes.
- (ii) Miller indices are used to find lattice parameters.
- (iii) Miller indices are used the crystal structure.

**Sodium Chloride Structure:**

Sodium Chloride is an ionic crystal. It consist of sodium ions and chloride ions.  $\text{Na}^+$  ions are positive ions and  $\text{Cl}^-$  ions are negative ions.

The diagram for NaCl. Crystal is given below.



In the above diagram basis is NaCl molecule.

Sodium Chloride structure consists of two FCC sub lattices.

In one FCC lattice, the chlorine ion ( $\text{Cl}^-$ ) is at the origin.

In another FCC lattice the sodium ion ( $\text{Na}^+$ ) is at the origin.

There is a attractive force between  $\text{Na}^+$  ions and  $\text{Cl}^-$  ions.

**Explanation:**

In the above diagram  $\text{Cl}^-$  are at corners.  $\text{Na}^+$  ion is at the centre of the unit cell.

Position of  $\text{Na}^+$  ions:  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Position of  $\text{Cl}^-$  ions:  $(0,0,0)$

Number of  $\text{Na}^+$  ions per unit cell = 1

Number of  $\text{Cl}^-$  ions per unit cell =  $8 \times \frac{1}{8} = 1$

The Number of sodium chloride molecule per unit cell = 1

Co-ordination number is 8

**Examples:**

$\text{CsCl}$ ,  $\text{CsBr}$ ,  $\text{CsI}$  etc

**Primitive unit cell:**

The smallest repeating pattern in a crystal is called a unit cell. In the atoms are only at the corners, of the unit cell, It is called a primitive unit cell.

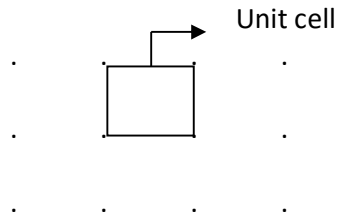
**Features:**

- (1) Primitive unit cell has atoms only at the corners.
- (2) Number of atoms per unit cell is one.



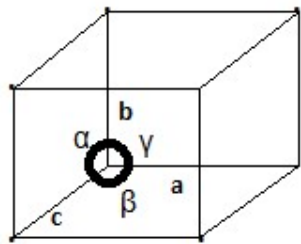
Diagram:

Two dimensional primitive unit cell.



For a two dimensional primitive unit cell.

For a three dimensional primitive unit cell.



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**UNIT – II**  
**TYPES OF MAGNETIC MATERIALS**

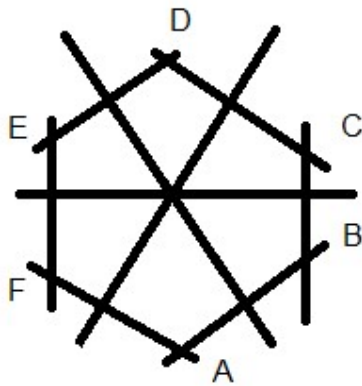
**Wigner –Seitz primitive cell**

It is a primitive unit cell and the number of atoms per unit cell is one.

**Procedure to draw Wigner –Seitz primitive cell:**

**Steps:**

- (1) Select a lattice point
- (2) Draw lines to connect the selected lattice point
- (3) Draw perpendicular lines at the midwg
- (4) The unit cell enclosed is called the Wigner – Seitz cell.



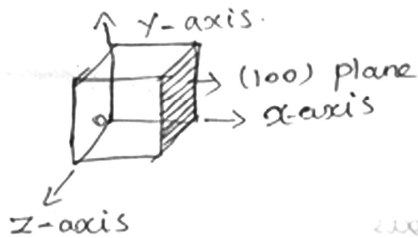
In the above diagram ABCDEF is the Weigner - Seitz primitive cell.

**Sketch the following planes:**

- (a) (100) plane
- (b) (010) plane
- (c) (001) plane
- (d) (111) plane

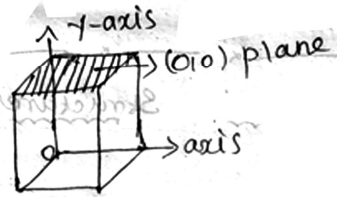
**Diagrams:**

(a) (100) plane:-

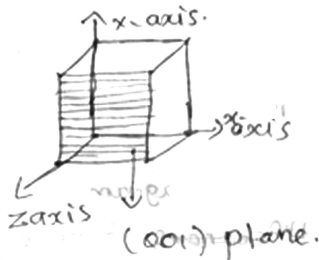




(b) (010) plane:



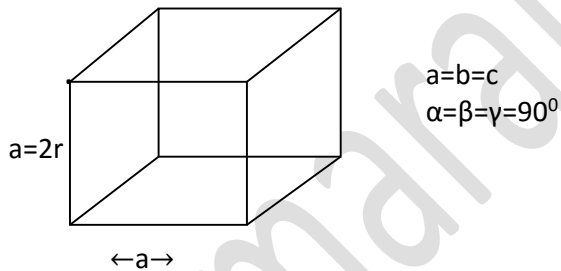
(c) (001) plane:



### Some Important Crystal Structures:

#### (1) Simple Cubic (Sc)

The diagram for simple cubic structure is given below.



In the above diagram atoms are points are at the centre of faces.

The number of atoms per unit cell =  $8 \times 1/8 = 1$

Co-ordination Number = 6

Atomic radius =  $r = a/2$ .

Where 'a' is the lattice parameter.

#### Packing density or packing

Fraction = 52%

= 0.52

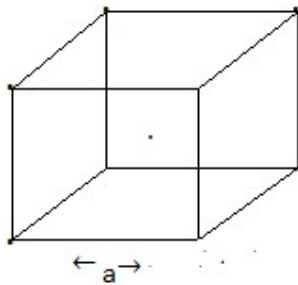
#### Example:

Polonium.



## (2) Body Centered Cubic (BCC)

The diagram for Body Centered Cubic structure is given below.



$$a=b=c$$

$$\alpha=\beta=\gamma=90^\circ$$

In the above diagram the atoms are at the corners and also 1 atom is at the centre of unit cell.

The number of atoms per unit cell.

$$= (8 \times 1/8) + 1 = 2$$

Co-ordination number = 8

$$\text{Atomic radius} = (4r)^2 = 3a^2$$

$$16r^2 = 3a^2$$

$$r^2 = \frac{3a^2}{16}$$

$$r = \frac{\sqrt{3}a}{4}$$

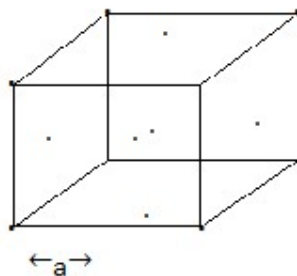
Packing density or packing fraction = 68% = 0.68

**Examples:**

K, Na, Fe

## (3) Face Centered Cubic (FCC):

The diagram for face centered cubic structure is given below.



$$a=b=c$$

$$\alpha=\beta=\gamma=90^\circ$$

In the above diagram atoms are at the corners and also atoms are at corners.

Position of atoms:  $(0,0,0)$ ,  $(1/2,1/2,0)$ ,  $(0,1/2,1/2)$ .

The Number of atoms per unit cell =  $(8 \times 1/8) + (6 \times 1/2) = 4$

Co-ordination Number = 12

$$\text{Atomic radius} = (4r)^2 = a^2 + a^2$$

Packing density (or) packing fraction = 74% = 0.74.

**Examples:**

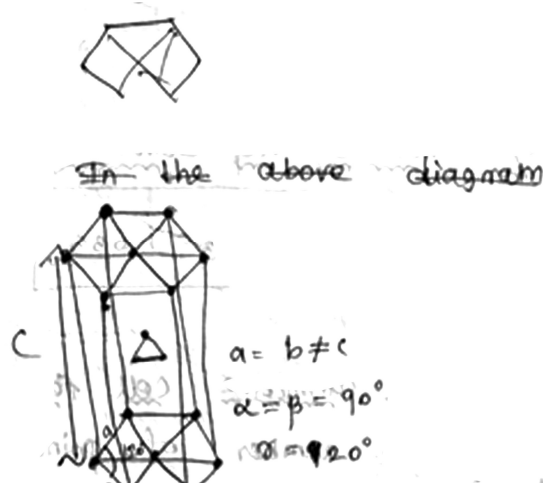


Gold, silver, copper.

**(4) Hexagonal Close packed (hcp) Structure:**

The diagram for Hexagonal Close packed Structure is given below.

**Diagram:**



In the above diagram the atoms are at the corners, 2 atoms at the centre of the unit cell.

The Number of atoms per unit cell =  $2(6 \times 1/6) + 3 + (2 \times 1/2) = 6$

Co-ordination Number = 12

Atomic radius =  $a = 2r$

(or)

$r = a/2.$

Packing density (or) packing fraction = 74% = 0.74.

**Examples:**

Mg, Zn, Ca.

**C/a ratio for Hcp Structure:**

$$C/a = \sqrt{\frac{8}{3}} = 1.633$$

**Wigner – Seitz primitive cell features:**

- (1) The number of points per unit cell is one.
- (2) There are no lattice points at the corners.
- (3) The lattice point is at the centre of the unit cell.

**Perpendicular distance between two parallel planes (Interplaner distance)**

For cubic crystal, the interplanar distance is  $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

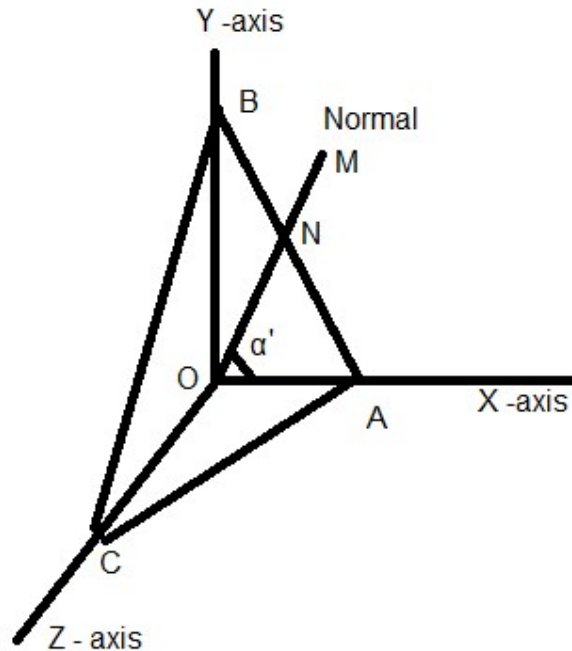
Where 'a' is the lattice constant,  
h,k,l are the miller indices.

**Proof:**





Consider a crystal plane (hkl) as shown in the diagram.



In the above diagram, the intercept of the plane are OA, OB and OC.

$$OA = a/h$$

$$OB = b/k$$

$$OC = c/l.$$

Draw a normal 'ON' to the plane from the origin 'O'

Imagine another parallel plane is at M.

Here,

$$ON = d$$

$$OM = 2d$$

Interplaner distance is  $OM - ON = 2d - d = d$

From the diagram,

$$\cos \alpha' = \frac{OA}{ON} = \frac{a/h}{d}$$

$$\cos \alpha' = a/hd$$

Similarly,

$$\cos \beta' = \frac{b}{kd}$$

$$\cos \gamma' = \frac{c}{ld}$$

From the cosine law, we have

$$\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$$

$$\text{(or)} \quad \left(\frac{a}{hd}\right)^2 + \left(\frac{b}{hd}\right)^2 + \left(\frac{c}{hd}\right)^2 = 1$$

For Cubic Crystal,

$$a = b = c$$

$$\frac{a^2}{h^2d^2} + \frac{a^2}{k^2d^2} + \frac{a^2}{l^2d^2} = 1$$

$$\frac{a^2}{d^2} = \frac{1}{h^2+k^2+l^2} = 1$$



$$d^2 = \frac{a^2}{h^2+k^2+l^2} = 1$$

$$ON = d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Similarly,

$$OM = 2d = \frac{2a}{\sqrt{h^2+k^2+l^2}}$$

Interplanar distance  $d = OM - ON$

$$= \frac{2a-a}{\sqrt{h^2+k^2+l^2}}$$

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

**Bragg's law: (x-ray diffraction):'**

The Bragg's law is  $2d \sin \theta = n\lambda$

Where 'd' is the interplanar distance

' $\theta$ ' is the angle of diffraction

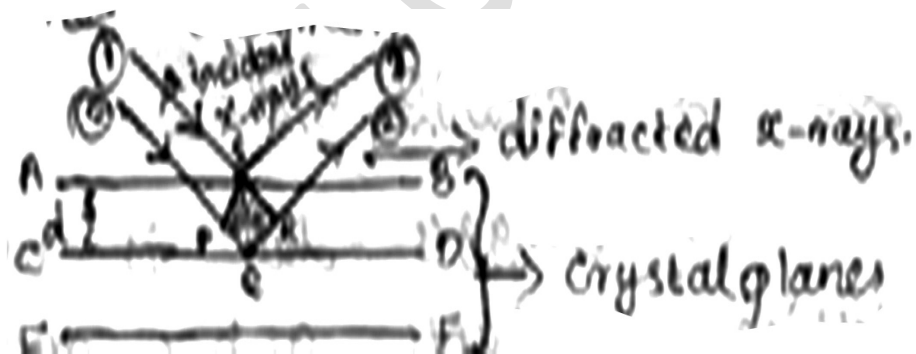
'n' is the order of diffraction

'n' = 0,1,2,3.

' $\lambda$ ' is the wavelength of x-rays.

**Proof:**

Consider Crystal planes AB, CD, EF as shown in the diagram.



In the above diagram 1 and 2 are x-rays

' $\theta$ ' is the angle of diffraction

When x-rays fall on a crystal, x-rays are diffracted. This is known as x-ray diffraction (XRD)

From the diagram,

$$\sin \theta = \frac{PQ}{SQ}$$

$$= \frac{PQ}{d}$$

Also,  $\sin \theta = \frac{QR}{d}$

Path difference =  $QR + PQ$

$$= d \sin \theta + d \sin \theta$$

$$= 2d \sin \theta$$

For Constructive interference,

Path difference =  $n\lambda$



When,  $n = 0, 1, 2, \dots$

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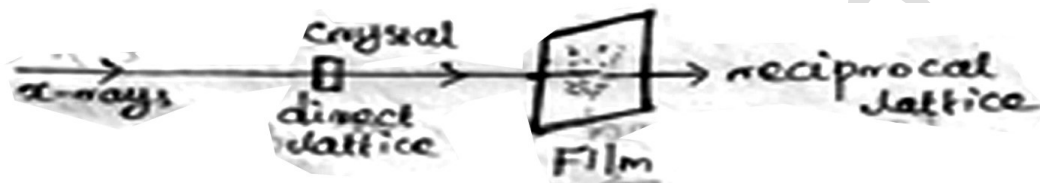
$$2d \sin\theta = n\lambda$$

This is known as Bragg's law.  
 This is the basic law for x-ray diffraction.

**Uses of Bragg's law:**

- (1) Bragg's law is used to find lattice constants a,b,c and  $\alpha,\beta,\gamma$ .
- (2) It is also used to find interplanar distance.
- (3) Bragg's law is used to solve crystal structure.

**Reciprocal lattice:**



The crystal lattice is called the direct lattice. The x-ray diffraction pattern in the film is called the reciprocal lattice.

**Reciprocal lattice vector:**

The reciprocal lattice vector ( $\vec{\sigma}_{hkl}$ ) is the reciprocal of the inter planar distance ( $d_{hkl}$ ) of direct lattice.

That is

$$\vec{\sigma}_{hkl} = 1/d_{hkl} \hat{n}$$

Where ' $\hat{n}$ ' is the unit vector.

**Expression for  $\vec{\sigma}_{100}$ ,  $\vec{\sigma}_{010}$ , and  $\vec{\sigma}_{001}$  :**

Consider a cubic lattice as shown in the diagram.

**Diagram**

In the above diagram  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  are the primitive translation vectors.

$d_{100}$  is the interplanar distance between two parallel (100) planes.

Volume of the unit cell =  $\vec{a} \cdot \vec{b} \times \vec{c}$  ----- (1)

Also,

Volume of the unit cell = area of the base  $\times$  height  
 $= (\vec{b} \times \vec{c}) \cdot d_{hk}$  ----- (2)

From (1) and (2) we get,

$$d_{100} = \frac{\vec{a} \cdot (\vec{b} \times \vec{c})}{(\vec{b} \times \vec{c})}$$

(or)

$$\vec{\sigma}_{100} = \frac{1}{d_{100}} = \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{\sigma}_{100} = \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})} = \vec{a}^*$$

Similarly,

$$\vec{\sigma}_{100} = \vec{b}^* = \frac{(\vec{c} \times \vec{a})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$



$$\vec{\sigma}_{100} = \vec{c}^* = \frac{(\vec{a} \times \vec{b})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Here  $\vec{a}^*$ ,  $\vec{b}^*$  and  $\vec{c}^*$  are primitive reciprocal vectors.

**Properties of Reciprocal Vectors:**

(1)  $\vec{\sigma}_{hkl} = 1/d_{hkl} \hat{n}$

Where ' $\vec{\sigma}_{hkl}$ ' is the reciprocal vector.

' $d_{hk}$ ' is the interplanar distance.

' $\hat{n}$ ' is the unit vector.

(2)  $\vec{a}^* = 1/\vec{a}$

(or)

$$a^* = 1/a$$

Similarly,

$$\vec{b}^* = 1/\vec{b}$$

(or)

$$b^* = 1/b$$

$$\vec{c}^* = 1/\vec{c}$$

(or)

$$c^* = 1/c$$

(3)  $\vec{a}^* \cdot \vec{a} = 1$

Similarly,

$$\vec{b}^* \cdot \vec{b} = 1$$

$$\vec{c}^* \cdot \vec{c} = 1$$

(4)  $\vec{a}^* \cdot \vec{b} = 0$

$$\vec{a}^* \cdot \vec{c} = 0$$

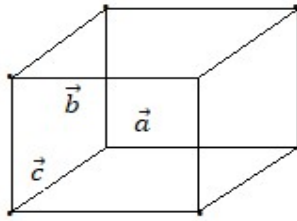
(5)  $(a^*)^* = a$

$$(b^*)^* = b$$

$$(c^*)^* = c$$

**Reciprocal lattice to the Simple Cubic (Sc) lattice:**

Consider a Simple cubic lattice shown in the diagram.



In the above diagram  $\vec{a}, \vec{b}, \vec{c}$  are primitive translation vector.

In vector notation,  $\vec{a} = a\hat{x}, \vec{b} = b\hat{y}, \vec{c} = c\hat{z}$

For Cubic lattice

$$\begin{aligned} a &= b = c \\ \vec{a} &= a\hat{x} \\ \vec{b} &= b\hat{y} \\ \vec{c} &= c\hat{z} \end{aligned}$$

Volume of the unit cell

$$\begin{aligned} V &= \vec{a} \cdot (\vec{b} \times \vec{c}) \\ &= a\hat{x} \cdot (b\hat{y} \times c\hat{z}) \end{aligned}$$

Where  $\hat{x}, \hat{y}, \hat{z}$  are unit vectors.

$$\begin{aligned} &= a\hat{x} \cdot (a^2 \hat{x}) \\ V &= a^3 \end{aligned}$$

We know that,

$$\begin{aligned} \vec{a}^* &= \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})} & \vec{b} &= b\hat{y} \\ & & \vec{c} &= c\hat{z} \\ &= \frac{(a\hat{y} \times a\hat{z})}{a^3} \\ &= \frac{a^2 \hat{x}}{a^3} \\ &= \frac{\hat{x}}{a} \\ \vec{a}^* &= \frac{1}{a} \hat{x} \quad \text{----- (3)} \end{aligned}$$

Similarly,

$$\vec{b}^* = \frac{1}{a} \hat{y} \quad \text{----- (4)}$$

$$\vec{c}^* = \frac{1}{a} \hat{z} \quad \text{----- (5)}$$

The above equations are corresponding the reciprocal simple cubic lattice.

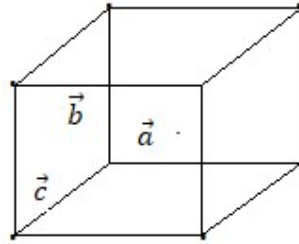
The reciprocal lattice to the simple cubic is simple cubic lattice.

$$\vec{a} \times \vec{b} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ ax & ay & az \\ bx & by & bz \end{vmatrix}$$

$$\begin{aligned} \hat{y} \times \hat{z} &= \hat{x} \\ \hat{i} \times \hat{j} &= \hat{k} \\ \hat{j} \times \hat{k} &= \hat{i} \end{aligned}$$

**Reciprocal lattice to the Body Centered Cubic Lattice (BCC):**

Consider a Body Centered Cubic lattice (BCC) as shown in the diagram.



$$a=b=c$$

In the above diagram  $\vec{a}, \vec{b}, \vec{c}$  are primitive translation vector.

In vector notation  $\vec{a} = a\hat{x}, \vec{b} = b\hat{y}, \vec{c} = c\hat{z}$

For BCC Lattice,

$$\vec{a} = a/2 \hat{x} + a/2 \hat{y} - a/2 \hat{z} \text{ ----- (1)}$$

$$\vec{b} = a/2 (-\hat{x} + \hat{y} + \hat{z}) \text{ ----- (2)}$$

$$\vec{c} = a/2 (\hat{x} - \hat{y} + \hat{z}) \text{ ----- (3)}$$

Where,

$\hat{x}, \hat{y}, \hat{z}$  are the unit vectors

Volume of the unit cell

$$V = \vec{a} \cdot (\vec{b} \times \vec{c})$$

$$= a/2 (\hat{x} + \hat{y} - \hat{z}) \cdot \{a/2 (-\hat{x} + \hat{y} + \hat{z})\} \times \{a/2 (\hat{x} - \hat{y} + \hat{z})\}$$

$$= a/2 (\hat{x} + \hat{y} - \hat{z}) \cdot a^2/2 (\hat{x} + \hat{y})$$

$$= a^3/4 \text{ (2)}$$

$$V = a^3/2$$

$$\hat{i} \cdot \hat{i} = 1$$

$$\hat{i} \cdot \hat{j} = 0$$

We know that,

$$\vec{a}^* = \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{b}^* = \frac{(\vec{c} \times \vec{a})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{c}^* = \frac{(\vec{a} \times \vec{b})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Where  $\vec{a}^*, \vec{b}^*$  and  $\vec{c}^*$  are the primitive reciprocal lattice vectors.

$$\vec{a}^* = \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})} = \frac{a^2/2 (\hat{x} + \hat{y})}{a^3/2}$$

$$\vec{a}^* = 1/a (\hat{x} + \hat{y}) \text{ ----- (4)}$$

Similarly,

$$\vec{b}^* = 1/a (\hat{y} + \hat{z}) \text{ ----- (5)}$$

$$\vec{c}^* = 1/a (\hat{z} + \hat{x}) \text{ ----- (6)}$$

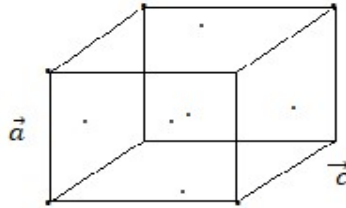
The equations (4), (5) and (6) belong to the Face Centered Cubic.



The reciprocal lattice to the body centered cubic lattice is FCC lattice.

**Reciprocal Lattice to the Face Centered Cubic Lattice (FCC):**

Consider a Face Centered Cubic lattice as shown in the diagram.



In the above diagram  $\vec{a}, \vec{b}, \vec{c}$  are primitive translation vectors.

In Vector notation  $\vec{a} = \frac{a}{2} \hat{x} + \frac{a}{2} \hat{y}$

$$\vec{a} = \frac{a}{2} (\hat{x} + \hat{y}) \text{----- (1)}$$

$$\vec{b} = \frac{a}{2} (\hat{y} + \hat{z}) \text{----- (2)}$$

$$\vec{c} = \frac{a}{2} (\hat{z} + \hat{x}) \text{----- (3)}$$

Where,

$\hat{x}, \hat{y}, \hat{z}$  are the unit vectors

Volume of the unit cell

$$\begin{aligned} V &= \vec{a} \cdot (\vec{b} \times \vec{c}) \\ &= \frac{a}{2} (\hat{x} + \hat{y}) \cdot (\hat{y} + \hat{z}) \cdot (\hat{z} + \hat{x}) \\ &= \frac{a}{2} (\hat{x} + \hat{y}) \cdot \frac{a^2}{4} (\hat{x} + \hat{y} - \hat{z}) \end{aligned}$$

$$V = \frac{a^3}{4}$$

We know that,

$$\vec{a}^* = \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{b}^* = \frac{(\vec{c} \times \vec{a})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{c}^* = \frac{(\vec{a} \times \vec{b})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Where  $\vec{a}^*, \vec{b}^*$  and  $\vec{c}^*$  are the primitive reciprocal lattice vectors.

$$\vec{a}^* = \frac{a^2/4 (\hat{x} + \hat{y} - \hat{z})}{a^3/4}$$

$$\vec{a}^* = \frac{1}{a} (\hat{x} + \hat{y} - \hat{z}) \text{----- (4)}$$

Similarly,

$$\vec{b}^* = \frac{1}{a} (-\hat{x} + \hat{y} + \hat{z}) \text{----- (5)}$$

$$\vec{c}^* = \frac{1}{a} (\hat{x} - \hat{y} + \hat{z}) \text{----- (6)}$$

The equations (4), (5) and (6) belongs to the body centered cubic (BCC).

The reciprocal lattice to the 'FCC' lattice is BCC lattice.





**Brillouin Zones:**

A Brillouin Zone is a wigner - seitz cell in a reciprocal lattice. They are used to understand the energy bands of crystals.

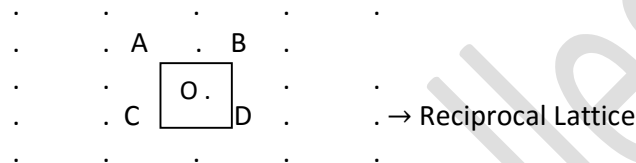
**Construction:**

**Steps**

1. Select a reciprocal lattice point.
2. Join the selected points to the nearest reciprocal lattice point.
3. Draw the perpendicular bisectors.
4. The volume enclosed is called the brillouin Zone.

**First Brillouin Zone:**

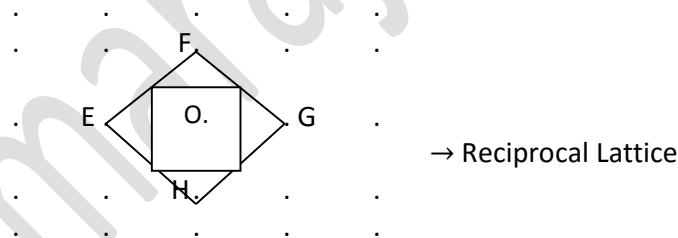
The diagram for the First Brillouin Zone is given below.



In the above diagram the points are reciprocal lattice points. 'O' is the orijin. A reciprocal lattice point is selected at 'O' ABCD is called the First Brillouin Zone , It has only one reciprocal lattice cell and so it is primitive cell.

**Second Brillouin Zone :**

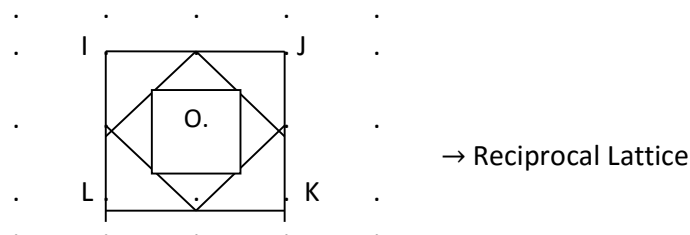
The diagram for the second Brillouin Zone is given below.



In the above diagram 'O' is the orijin. EFGH is called a second Brillouin Zone.

**Third Brillouin Zone:**

The diagram for the third Brillouin Zone is given below.



In the above diagram the points are reciprocal lattice points.

1. corresponds to First brillouin zone.



2. corresponds to Second Brillouin zone.
3. corresponds to Third Brillouin zone.

**Features:**

1. The boundaries of First Brillouin Zone are  
 $K_x = \pm \pi/a$  and  $K_y = \pm \pi/a$   
Where 'a' is the lattice constant.
2. The boundaries of Second Brillouin Zone are  
 $K_x = \pm 2\pi/a$  and  $K_y = \pm 2\pi/a$   
Where 'a' is the lattice constant.
3. The boundaries of Third Brillouin Zone are  
 $K_x = \pm 3\pi/a$  and  $K_y = \pm 3\pi/a$   
Where 'a' is the lattice constant.
4. First Brillouin Zone in Two dimensions is square
5. First Brillouin Zone in Three dimensions is cube.
6. The First Brillouin Zone in the Face centered cubic lattice is BCC lattice (or) octahedron.

**Uses:**

1. Brillouin Zones are used to find the crystals structure
2. They are used to understand energy bands.
3. They are used to understand x-ray diffraction patterns.

**Quasi crystals:**

If a crystal lacks translational symmetry, it is called a quasi crystal. It is ordered but not periodic.

**Example: For quasi crystals:**

1. Al – Mn alloy
2. Aluminium alloy
3. Al – Ni alloy. Etc.

**Types of Quasi crystals:**

1. Polygonal quasi crystals.
2. Icosahedral quasi crystals.
3. Stable quasi crystals.
4. Meta stable quasi crystals.

**1. Polygonal quasi crystals:**

It is non periodic in some directions.

**Examples:**

- a. Octagonal → 8-Fold-rotation axis
- b. Decagonal → 10-Fold-rotation axis
- c. Dodecagonal → 12- Fold-rotation axis

**2. Icosahedral quasi crystals**

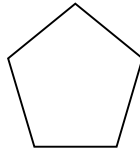
It is non-periodic in all directions.



**Examples:**

Pentagonal 5 – Fold-rotational axis.

**Diagram:**



**Pentagonal quasi crystal:**

In the above diagram in has 5 – Fold rotational axis. When it is repeated, there is a unfilled space.

Ref: Kittle book

It has no translational symmetry.

**3. Stable quasi crystals:**

It is stable and it is prepared by slow cooling and annealing

**4. Meta stable quasi crystals:**

It is more stable and it is prepared by melt spinning.

**Properties of QCS:**

1. Ordered and non – periodic
2. No translational symmetry
3. Quasi crystals have 5 – fold, 8 – fold, 10 – fold, 12- fold rotational axis
4. Quasi crystals do not have 1-fold, 2-fold, 3-fold, 4-fold, 6-fold rotational axis.
5. They are insulators.
6. High hardness
7. Less Corrosion.
8. Low Conductivity.
9. Low friction.
10. Will not stick.

**Applications:**

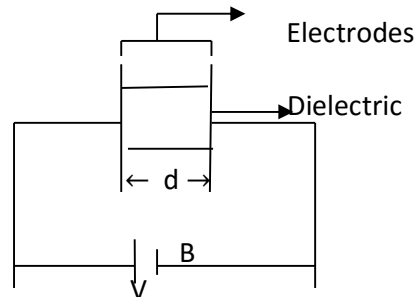
- (1) Quasi crystals are used as coating materials in non-stick cook wares.
- (2) They are used in thermal screens.
- (3) They are used as piston coating in cars.
- (4) Quasi crystals are used in hydrogen storage cylinders.
- (5) Quasi crystals are used as non-corrosive materials.



**UNIT – III**  
**BONDING IN SOLIDS**

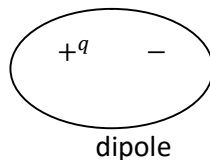
**Polarization:**

When an external electric field (voltage) is applied to a dielectric (insulator), the positive charge and negative charge in opposite directions. This is called as polarization.



In the above diagram the positive charge and negative charge in the materials or dielectric move in opposite direction.

when an electric field is applied to a dielectric, dipoles are created.



The dipole moment  $\mu = q \cdot x$

Where,

'q' is the charge,

'x' is the distance between +ve and -ve charges

**Unit : Coloumb . metre**

Polarization ( $\rho$ ) is defined as the dipole moment ( $\mu$ ) per unit volume (V)

$$\vec{P} = \vec{\mu} / V$$

Or

$$\vec{P} = N \cdot \vec{\mu}$$

'N' is the Number of atoms per unit volume.

Also,

$$\vec{P} \propto \text{Electric field.}$$

$$\vec{P} = \epsilon \times \vec{E}$$

Where,

$\epsilon_0$  is the permittivity of free space.

$\epsilon$  is the susceptibility of the material.

Also,

dipolement  $\propto$  electric field.

Or  $\mu \propto E$

Or  $\mu = \alpha E$

where,

' $\alpha$ ' is called polarizability.





$$(or) \quad E = \frac{Ze}{4\pi\epsilon_0 R^2} \text{----- (3)}$$

The induced dipolement

$$\mu_e = Ze \cdot R \text{----- (4)}$$

$$\mu_e = \alpha e \cdot E$$

$\mu$  = Charges distances

Also we have

$$\mu_e = \alpha e \cdot E \text{----- (5)}$$

Put (3) and (4) in (5)

$$Ze \cdot R = \alpha e \cdot \frac{Ze}{4\pi\epsilon_0 R^2}$$

(or)

$$\alpha e = 4\pi \epsilon_0 R^3$$

**Another Expression:**

We know that,

$$\vec{P}_e = \epsilon_0 \times \vec{E} \text{----- (6)}$$

And

$$\vec{P}_e = N \vec{\mu}_e \text{----- (7)}$$

Where,  $P_e \rightarrow$  Electronic Polarization.

'N' is the number of atoms perunit volume.

$\vec{E}$  is the electric field.

**Orientation polarization:**

It is also called dipolar polarization. When an external electric field is applied to molecules with permanent dipole moment like chloroform, the dipoles are aligned in the direction of the field. This is called as orientation polarization.

It is given by

$$\vec{P}_0 = \epsilon_0 \times \vec{E}$$

Where  $\epsilon_0$  is the permittivity of the free space

$\chi$  is the susceptibility

$\vec{E}$  is the electric field.

If the electric field is applied to permanent dipole moment Molecule. The induce dipolemomet.

$$\mu_o = \alpha_o \cdot E$$

Where ' $\alpha_o$ ' is the orientational polarizability

**Calculation of Orientational Polarizability:**

The diagram for orientation polarization is given below.

In the above diagram when the electric field is not applied, the dipoles are randomly oriented. When electric field is not applied the dipoles are randomly oriented. When electric field is applied, the dipoles are oriented (aligned) in the direction of the field.

When the temperature of the sample is increased, the dipoles are vibrating. The orientational polarization will be reduced. The orientational polarizability is inversely proportional to the temperature.

$$ie., \alpha_o \propto 1/T$$

$\alpha \rightarrow$  directly proportional

Also ' $\alpha_o$ ' is directly proportional to the square of dipole moment.

$$ie., \alpha_o \propto \mu_o^2$$

$$\alpha_o \propto \frac{\mu_o^2}{T}$$



(or)

$$\alpha_o = \frac{\mu_o^2}{3k}$$

Where 'k' is the Boltzman's constant.

$$\vec{P}_0 = \epsilon_0 \times \vec{E} \text{ ----- (1) and } \vec{P}_0 = N\vec{\mu}_0 \text{ ----- (2)}$$

Where ' $P_0$ ' is the orientational polarization.

' $\epsilon_0$ ' is the permittivity of the free space

' $\chi$ ' is the susceptibility

'N' is the Number of dipoles in per unit volume.

Also we have,

$$\vec{\mu}_0 = \alpha_o \vec{E}$$

Put equation (1) and (2)

$$\vec{P}_0 = N\alpha_o \vec{E}$$

From

$$N\alpha_o \vec{E} = \epsilon_0 \times \vec{E}$$

Also,

$$\chi = \epsilon_r - 1$$

Where ' $\epsilon_r$ ' is the dielectric constant.

$$N\alpha_o \vec{E} = \epsilon_0 (\epsilon_r - 1) \vec{E}$$

(or)

$$\alpha_o = \frac{\epsilon_0 (\epsilon_r - 1)}{N}$$

## 2. Ionic Polarization:

When an external electric field is applied to an ionic crystal like sodium chloride, Positive ions and negative ions move in opposite directions. This is called ionic polarization.

It is given by

$$\vec{P}_i = \epsilon_0 \times \vec{E}$$

Where ' $\epsilon_0$ ' is the permittivity of the free space

' $\chi$ ' is the susceptibility and

' $\vec{E}$ ' is the Electric field.

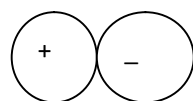
If the electric field is applied to an ionic crystal, the induced dipole moment is

$$\vec{\mu}_i = \alpha_i \vec{E}$$

Where ' $\alpha_i$ ' is the ionic polarizability.

### Calculation of ionic polarizability:

The diagram for ionic polarization is given below.



Without field

Cation



With field

anion



In the above diagram when electric field is not applied, the positive ion and negative ion are not separated. When the electric field is applied positive ion and negative ion are separated.



Let  $x_1$  be the distance moved by positive ion (cation). Let  $x_2$  be the distance moved by negative ion (anion).

The dipole moment for the +ve ion is  $ex_1$

The dipole moment for the -ve ion is  $ex_2$

The resultant dipole moment is  $\mu = ex_1 + ex_2$   
 $\mu = e(x_1 + x_2)$  ----- (1)

**Dipole moment =**  
**Charge x distance**

When the electric field is applied, the ions act like a spring system. Spring force on the ions are,

$$F = \beta_1 x_1 \text{ for the +ve ion and } F = \beta_2 x_2 \text{ for the -ve ion} \text{ ----- (2)}$$

Where,

' $\beta_1$ ' and ' $\beta_2$ ' are the force constants.

From Spectroscopy, we have

$$\beta_1 = M\omega^2 \text{ and } \beta_2 = m\omega^2 \text{ ----- (3)}$$

Where,

'M' and 'm' are the masses of +ive ion and –ve ion respectively.

' $\omega$ ' is the angular frequency.

The Electric force is

$$F = eE \text{ ----- (4)}$$

Where 'e' is the charge of the electron

'E' is the electric field.

From (2), (3) and (4), we have,

$$F = \beta_1 x_1$$

$$eE = M\omega^2 x_1$$

$$eE = m\omega^2 x_2$$

(or)

$$x_1 = \frac{eE}{M\omega^2} \text{ and } x_2 = \frac{eE}{m\omega^2} \text{ ----- (5)}$$

Substitute (5) in (1)

$$\mu = e \left( \frac{eE}{M\omega^2} + \frac{eE}{m\omega^2} \right)$$

$$\mu = \frac{e^2 E}{\omega^2} \left( \frac{1}{M} + \frac{1}{m} \right) \text{ ----- (6)}$$

We know that,

$$\mu_i = \alpha_i \cdot E \text{ ----- (7)}$$

Comparing (6) and (7)

$$\alpha_i \cdot E = \frac{e^2 E}{\omega^2} \left( \frac{1}{M} + \frac{1}{m} \right)$$

$$\alpha_i = \frac{e^2}{\omega^2} \left( \frac{1}{M} + \frac{1}{m} \right)$$

This is the expression for ionic polarizability.

**Space Charge Polarization:**

Accumulation of charges at electrodes or interfaces is called the space charge polarization.

The dipole moment for space charge polarization is

$$\mu_s = \alpha_s \cdot E$$

Where,

' $\alpha_s$ ' is space charge polarizability.

'E' → is the electric field.





The diagram for space charge polarization is given below.

In the above diagram when the electric field is applied the charges are accumulated at electrodes.

The total polarization is

$$P = P_e + P_o + P_i + P_s$$

The total polarizability is

$$\alpha = \alpha_e + \alpha_o + \alpha_i + \alpha_s$$

#### Frequency dependence of dielectric constant or polarization:

Dielectric constant is defined as the ratio, of the capacity with dielectrics to the capacity without dielectric.

$$\text{i.e., } \epsilon_r = \frac{C}{C_o}$$

It is also given by

$$\epsilon_r = \frac{\epsilon}{\epsilon_o}$$

Where,

' $\epsilon$ ' is the absolute permittivity.

' $\epsilon_o$ ' is permittivity of free space.

The time dependence of polarization is

$$P(t) = P [1 - \exp(-t/T)]$$

Where,

'P' is the maximum polarization.

't' is the time.

'T' is the relaxation time.

Similarly, the polarization depends on frequency.

The diagram for frequency depends on dielectric constant or polarization is given below.

#### Electronic Polarization:

When an external electric field is applied to an atom, positively charged Nucleus and negatively charged electrons. Move in opposite directions. This is called the electronic polarization.

It is a fast process. The frequency range is  $10^{14} - 10^{15}$  HZ.

#### Ionic polarization:

When an external electric field is applied to an ionic crystal, like sodium chloride positive ions and negative ions move in opposite directions. This is called ionic polarization.

It is a fast process. The frequency range is  $10^{12} - 10^{13}$  HZ.

#### Orientalional polarization:

It is also called dipolar polarization. When an external electric field is applied to molecules with permanent dipole moment like chloroform, the dipoles are aligned in the direction of the field. This is called is orientational polarization.

It is slow process. The frequency range is  $10^3 - 10^4$  HZ.

#### Space charge polarization:

Accumulation of charges at electrodes or interfaces is called the space charge polarization. It is slow process. The frequency range is  $50 - 10^2$  HZ. Polarization or dielectric constant decreases with frequency.



**Temperature dependence of dielectric constant:**

Dielectric constant is defined as the ratio of the capacity with dielectric to the capacity without dielectric ( $\epsilon_0$ )

$$\text{ie. } \epsilon_r = C/C_0$$

It is also given by

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

Where,

For electronic polarization and polarization, the dielectric constant is independent of temperature.

For orientational polarization, the dielectric constant is inversely proportional to temperature.

ie,

$$\alpha_0 = \frac{\mu^2}{3KT}$$

Where,

' $\alpha_0$ ' is the orientational polarizability.

'K' is the Boltzmann's constant.

'T' is the temperature.

For space charge polarization, the dielectric constant is directly proportional to temperature.

$$\text{ie. } \epsilon_r \propto T$$

When the temperature of a dielectric (insulator) increases, polarization increases and hence dielectric constant increases.

**Diagram:**

**Local field:**

Local field is also called as the Lorentz field or internal field ( $E_i$ )

The Local field is given by

$$E_i = E + P/3\epsilon_0$$

Where,

'E' is the applied field.

'P' is the polarization.

' $\epsilon_0$ ' is the permittivity of free space

**Derivation:**

Consider a diagram for calculating local field as given below.

In the above diagram a battery is connected to a capacitor. A dielectric is kept between the plates.

'C' is the spherical cavity around A.

According to Lorentz, the Local field the Atom 'A' is

$$E_i = E_1 + E_2 + E_3 + E_4 \text{ ----- (1)}$$

Where,

$E_1, E_2, E_3$  and  $E_4$  are components of  $E_i$

**To find  $E_i$  :**

$E_1$  is the field due to the charges on the plates.

We know that,

$$D = \epsilon_0 E_1$$

Where 'D' is the electric induction.

(or)



$$E_1 = D/\epsilon_0 \text{ ----- (2)}$$

Also we have,

$$D = \epsilon_0 E + P \text{ ----- (3)}$$

From (2) and (3)

$$E_1 = \frac{\epsilon_0 E + P}{\epsilon_0} = E + P/\epsilon_0 \text{ ----- (4)}$$

Where 'E' is applied field.

'P' is polarization.

**To find  $E_2$  :**

$E_2$  is the field due to the charges on the surface of the dielectric.

$$E = 0$$

$$E_2 = - P/\epsilon_0 \text{ ----- (5)}$$

**To find  $E_3$  :**

$E_3$  is the field other atoms to the spherical caving C.

The field

$$E_3 = 0 \text{ ----- (6)}$$

(For a spherical symmetry net field is zero.)

**To find  $E_4$  :**

$E_4$  is the due to polarization charges of the surface of the cavity C.

We know that,

$$D = \epsilon_0 E_4$$

$$E_4 = D/\epsilon_0$$

(or)

$$E_4 = \frac{\epsilon_0 E + P}{\epsilon_0}$$

$$\text{Here } E = 0$$

$$E_4 = P/\epsilon_0$$

The field is shared in all three dimension

For one dimension

$$E_4 = P/\epsilon_0$$

$$E_i = \left(E + P/\epsilon_0\right) + \left(-P/\epsilon_0\right) + 0 + P/3 \epsilon_0$$

(or)

$$E_i = \left(E + P/3 \epsilon_0\right)$$

This is the expression for Lorentz field or Local field.

**Clausius – Mossotti Equation:**

Consider an elemental dielectric like silicon or carbon.

$$\alpha_o = \alpha_i = \alpha_s = 0$$

$$\alpha = \alpha_e = \alpha_o = \alpha_i = \alpha_s$$

$$\alpha = \alpha_e$$

Polarization

$$P = N \alpha E_i \text{ ----- (1)}$$

Where 'N' is the Number of atoms per unit volume.

' $\alpha$ ' is the polarizability.

' $E_i$ ' is the local field.

We know that,

$$E_i = \left(E + P/3 \epsilon_0\right) \text{ ----- (2)}$$

$$\mu = \alpha E$$

$$p = N\mu$$



Where 'E' is the applied field.

$\epsilon_0$  is the permittivity of free space.

Put (2) in (1)

$$P = N \alpha \left( E + \frac{P}{3 \epsilon_0} \right)$$

(or)

$$P \left( 1 - \frac{N \alpha}{3 \epsilon_0} \right) = N \alpha E$$

(or)

$$P = \frac{N \alpha E}{\left( 1 - \frac{N \alpha}{3 \epsilon_0} \right)}$$

We know that,

$$D = \epsilon E = \epsilon_0 \epsilon_r E \text{ ----- (4)}$$

And

$$D = \epsilon_0 E + P \text{ ----- (5)}$$

Where  $\epsilon_r \rightarrow$  is the dielectric constant.

$D \rightarrow$  is the electric induction.

Put (5) in (4)

$$\epsilon_0 E + P = \epsilon_0 \epsilon_r E$$

(or)

$$\epsilon_0 E (\epsilon_r - 1) = P \text{ ----- (6)}$$

$$P = \frac{N \alpha E}{\left( 1 - \frac{N \alpha}{3 \epsilon_0} \right)}$$

From (3) and (6) we have

$$\frac{N \alpha E}{\left( 1 - \frac{N \alpha}{3 \epsilon_0} \right)} = \epsilon_0 E (\epsilon_r - 1)$$

$$\frac{N \alpha E}{\epsilon_0 E (\epsilon_r - 1)} = \left( 1 - \frac{N \alpha}{3 \epsilon_0} \right)$$

(or)

$$\frac{N \alpha}{\epsilon_0 (\epsilon_r - 1)} + \frac{N \alpha}{3 \epsilon_0} = 1$$

(or)

$$\frac{N \alpha [3 + (\epsilon_r - 1)]}{3 \epsilon_0 (\epsilon_r - 1)} = 1$$

(or)

$$\frac{\epsilon_r + 2}{\epsilon_r - 1} = \frac{3 \epsilon_0}{N \alpha}$$

(or)

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N \alpha}{3 \epsilon_0}$$

This is called as Clausius – Mossotti equation.

**Dielectric breakdown:**

When a very high electric field is applied on a dielectric (insulator), breakdown occurs.

- (i) Intrinsic breakdown
- (ii) Thermal breakdown
- (iii) Electrochemical breakdown
- (iv) Defect breakdown
- (v) Discharge breakdown

**Measurement of dielectric constant:**

**Definition:**



Dielectric constant is defined as the ratio of the capacity with dielectric to the capacity without dielectric ( $\epsilon_o$ )

**Circuit diagram:**

The bridge here is called as the scherring bridge and using this bridge the dielectric constant and dielectric loss are measured. The bridge consists of four arms (1), (2), (3) and (4). The capacitor  $C_1$  and the resistance  $r_1$  is connected in series in arm:1. The capacitor  $C_4$  and Resistance  $R_4$  are connected in parallel in arm 4. The capacitor  $C_3$  is connected in arm 3. The resistance ' $R_2$ ' is connected in arm 2.

A detector 'D' is connected as in the diagram. The transformer is connected to the bridge.

**Theory:**

The impedance in the arm1 is  $r_1 + 1/j\omega C_1$

Where  $i = \sqrt{-1}$

' $\omega$ ' is the angular frequency

The impedance in the arm 2 is  $R_2$

The impedance in the arm 3 is  $\frac{1}{j\omega C_3}$

The impedance in the arm 4 is  $\frac{R_4}{1+j\omega C_4 R_4}$

The condition for null deflection is  $\frac{r_1 + \frac{1}{j\omega C_1}}{R_2} = \frac{\frac{1}{j\omega C_3}}{\frac{R_4}{1+j\omega C_4 R_4}}$

(or)

$$(r_1 + \frac{1}{j\omega C_1})R_4 = R_2 (1 + \frac{R_4 j\omega C_4}{j\omega C_4})$$

$$r_1 R_4 + \frac{R_4}{j\omega C_1} = \frac{R_2}{j\omega C_3} + \frac{R_2 C_4 R_4}{C_3}$$

Equating real and imaginary parts.

$$r_1 R_4 = \frac{R_2 C_4 R_4}{C_3}$$

And

$$\frac{R_4}{C_1} = \frac{R_2}{C_3}$$

i.e.,  $C_1 = \frac{R_4 C_3}{R_2}$

using this formula the capacitance of the dielectric is found.

$$\begin{aligned} & r_1 + \frac{1}{j\omega C_1} \\ \text{Arm 4} \\ & \frac{1}{R} = \frac{1}{R_4} + \frac{1}{1/j\omega C_4} \\ & \frac{1}{R} = \frac{1}{R_4} = j\omega C_4 \\ & \frac{1}{R} = \frac{1+R_4 j\omega C_4}{R_4} \end{aligned}$$

**Experiment:**

$$\epsilon_r = C/C_o \quad \text{----- (1)}$$

The dielectric constant ( $\epsilon_r$ ) is determined using following formula in (1)

Where 'C' is the capacitance with dielectric.

' $C_o$ ' is the capacitance without dielectric.

The capacitance ' $C_o$ ' is measured, when the dielectric is not placed in the capacitance  $C_1$

The capacitance 'C' is measured when the dielectric is placed in the capacitance ( $C_1$ )



**Measurement of dielectric loss:**

The dielectric loss the energy loss in a dielectric when AC voltage is applied.  
The dielectric loss is measurement using the following formula.

$$\text{Dielectric loss (tan } \delta) = r_1 c_1 \omega$$

Kamaraj College



## UNIT – IV SUPER CONDUCTIVITY

### **Super Conductivity – Experimental Survey:**

The study of Super conductors is called the Super conductivity and it was discovered by kammerlingh ones in 1911. He got Nobel prize for Super conductivity.

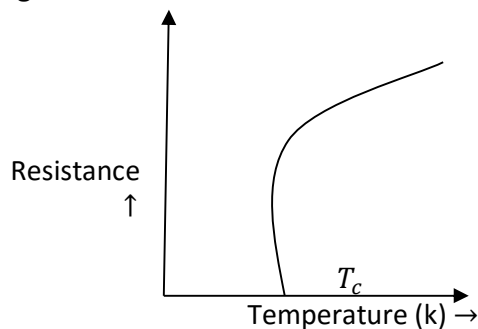
If a material or substance, has almost zero resistance, it called a super conductor.

### **Example:**

Mercury at  $T_c = 4.2$  k

Niobium at  $T_c = 9$ k

### **Diagram:**



In the above diagram ' $T_c$ ' is the critical or transition temperature.

At  $T = T_c$ , Resistance = 0

At  $T < T_c$ , Resistance = 0

At  $T > T_c$ , Resistance  $\neq 0$

At critical temperature ( $T_c$ ) and  $T < T_c$  the following is observed.

- (i) Resistance is equal to zero
- (ii) Energy loss is zero
- (iii) At  $T < T_c$ , the material is a super conductor.
- (iv) At  $T > T_c$ , the material is a Normal conductor.
- (v) There is a discontinuous change in specific heat at  $T = T_c$ .
- (vi) There is a change in thermal conductivity. The theory for Super conductivity is given by Bardeen, Cooper and Schriff in 1957.

According to BCS theory, there are cooper pairs in a supper conductor. Cooper pairs are responsible for super conductivity.

The magnetic lines of force are expelled from a Super conductor and they cannot penetrate into a super conductor. This is called meissner effect.

In a super conductor, entropy (disorder) is low. Above the critical temperature occurrence of super conductors are disordered.

### **3. Super Conductivity:**

The study of super conductor is called the super conductivity and its was discovered by kammerlingh onner in 1911 the nobal prize for super conductivity.

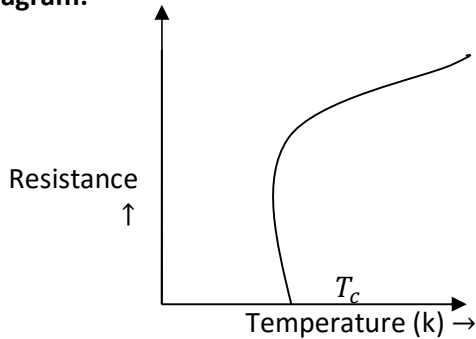
If a material or substance has almost zero resistance, it is called Super conductor.

### **Example:**

Mercury at  $T_c = 4.2$  k, Niobium at  $T_c = 1$ k



Diagram:



In the above diagram  $T_c$  is critical or transition a temperature.

At  $T = T_c$ , Resistance = 0

At  $T < T_c$ , Resistance = 0

At  $T > T_c$ , Resistance  $\neq 0$

At critical temperature ( $T_c$ ) and  $T < T_c$  the following is observed.

- (i) Resistance is equal to zero
- (ii) Energy loss is zero
- (iii) At  $T < T_c$ , the material is the super conductor.
- (iv) At  $T > T_c$ , the material is the Normal conductor.
- (v) There is a discontinues change in specific heat at  $T = T_c$ .
- (vi) There is change in thermal conductivity.

Super conductivity occurs in same metal alloys, ceramics etc.

#### Metalic Super conductors:

Super conductivity is noticed in metals like Hg,Nb etc.

#### Alloys:

Super conductivity is noticed in alloys like Nbsn, NbGe, NbAl, NbN, etc.

#### Ceramics:

Super conductivity is noticed in ceramics like  $YBa_2Cu_3O_7$  (Yttrium barium copper oxide)  
LaBaCuO (Lanthanide Barrium Copper Oxide)

#### Type – I Super Conductors:

A type I Super conductor has only one critical field ( $T_c$ ).

#### Examples:

Hg (Mercury), Al (Aluminium), Zn (Zinc). They are also called as Soft Conductor.

#### Type – II Super Conductor:

A type – II Super conductor has two critical fields. ( $H_c$ ,  $CHC_1$  and  $HC_2$ )

#### Examples:

Zr (Zirconium) Nb (Niobium). They are also called as Super conductor.

#### High $T_c$ Super Conductor:

Some Super conductors have high critical Temperature ( $T_c$ ).

#### Examples:

$YBa_2CO_3 O_7$ , LaBaCuO.





**List of Super Conductors with  $T_c$  Values:**

Super Conductor	$T_c$ (K)
(1) Mercury	4.2k
(2) Niobium	9.1 k
(3) $Nb_3Sn$	18.05k
(4) $Nb_3Ge$	23.2k
(5) YBacuo	83k

**(4) Properties of Super Conductor:**

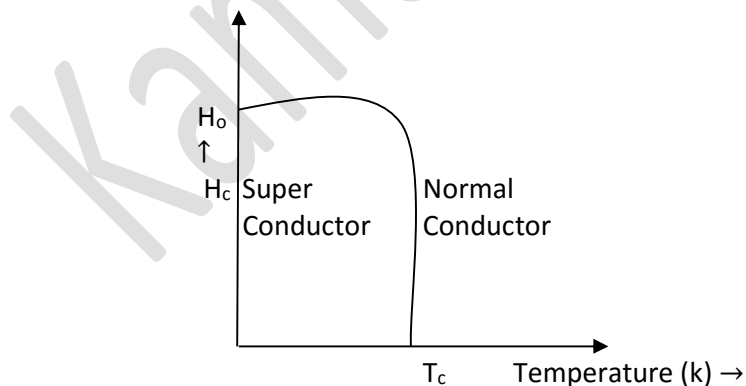
- (1) Resistance  $R=0$  at  $T \leq T_c$
- (2) A Super conductor is a perfect diamagnetic.
- (3) Susceptibility = - 1
- (4) Permeability = 0
- (5) The  $T_c$  is different for different substances.
- (6) Ferro and antiferro magnetic materials are not super conductor.
- (7) The current in a super conductor persists of a long time.
- (8) Energy loss is zero.
- (9) For pure super conductors,  $T_c$  is sharp.
- (10) The magnetic lines of force are expelled from a super conductor and they cannot penetrate into a super conductor. This is called meissner effect.
- (11) There is a small change in thermal conductivity.
- (12) There is a sudden change in specific heat.

**(5) Effect of magnetic field:**

The magnetic lines of force are expelled from a super conductor and they cannot penetrate into a super conductor. This is called meissner effect.

**Effect of magnetic field:**

The minimum field required to destroy super conductivity is called the critical field ( $H_c$ ).  $H_c$  depends upon the temperature. The variation of critical field with temperature is given below.



When  $T = T_c$ , Critical field =  $H_c = 0$

- (1) When  $T < T_c$  and  $H < H_c$ , the material is a super conductor.
- (2) When  $T > T_c$  and  $H > H_c$ , the material is a normal conductor.

The expression for critical field ( $H_c$ ) is

$$H_c = H_0 [1 - (T/T_c)^2]$$

Where,

$T \rightarrow$  Absolute temperature



$H_0 \rightarrow$  Critical field at ok  
 $T_c \rightarrow$  Critical temperature

**Meissner effect:**

The magnetic lines of force are expelled from a super conductor and they cannot penetrate into a super conductor. This is called meissner effect.

The diagram for meissner effect in given below.

In the above diagram, in a Super conductors magnetic lines of force do not penetrate.

In the normal conductors magnetic lines of force penetrate.

We know that,

$$B =$$

Where,  $\mu_0 (H+M)$

$B \rightarrow$  Magnetic induction

$\mu_0 \rightarrow$  Permeability of free space.

$H \rightarrow$  Applied field.

$M \rightarrow$  Magnetisation.

For a Super conductor,

$$B = 0$$

$$0 = \mu_0 (H+M)$$

(or)

$$H+M = 0$$

(or)

$$H = -M$$

(or)

$$\frac{M}{H} = -1$$

Here,

$\frac{M}{H} =$  Susceptibility ( $X$ )

$$\frac{M}{H} = X = -1$$

For a Super conductor

$$X = -1$$

Hence, a super conductor is a diamagnetic material

We also know that,

Where,

$\mu_r \rightarrow$  Relative permeability.

For a Super conductor,

$$\mu_r = 0$$

$$X = -1$$

**Features of Meissner effect:**

- (1)  $B = 0$
- (2)  $\mu_r = 0$
- (3) Susceptibility ( $X$ ) = -1
- (4) Magnetic flux will not penetrate into the super conductor.
- (5) When  $H > H_c$ , the material is a normal conductor.
- (6) When  $H < H_c$ , the material is a super conductor.
- (7) When  $T = T_c$ ,  $H_c = 0$



**Type – I Super Conductors:**

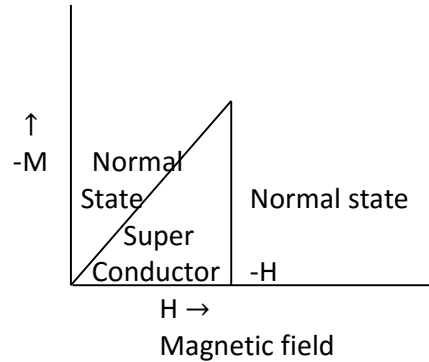
In a Type – I Super Conductor, there is complete meissner effect. They are called as soft super conductors.

A type – I Super Conductor has only one critical field ( $H_c$ ).

**Examples:**

Al,Zn,Hg, Ga.

The diagram for type – I Super Conductor given below.



In the above diagram when  $H < H_c$ , the material is a Super conductor.

When  $H > H_c$ , the material is a Normal conductors.

**Type – II Super Conductors:**

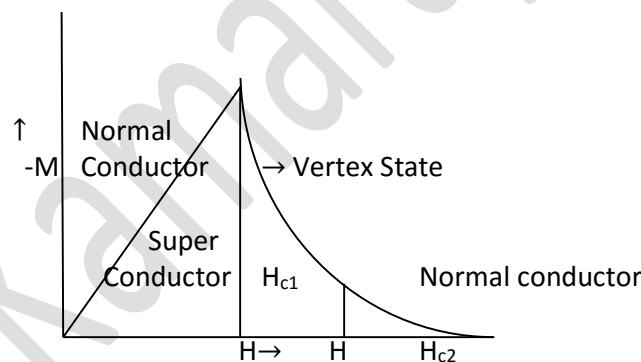
In a type – II Super conductors, there is a partial meissner effect. They are called as hard Super Conductors.

A type – II Super Conductors has two critical fields ( $H_{c1}$  and  $H_{c2}$ ).

**Examples:**

Nb, Zr, YBacuo

The diagram for type – II Super conductor given below.



In the above diagram when  $H < H_{c2}$  the material is partial super conductor.

When  $H > H_{c2}$ , the material is a normal super conductor.

When 'H' is between  $H_{c1}$  and  $H_{c2}$ , it is called vertex state.

Vertex state is also called a mixed state.

**Thermal Properties:**

- (1) Entropy
- (2) Specific heat
- (3) Thermal conductivity



**Entropy:**

Entropy means disorder. Entropy is a measure of disorder. It is given by

$$\text{Entropy } S = \frac{dQ}{dT}$$

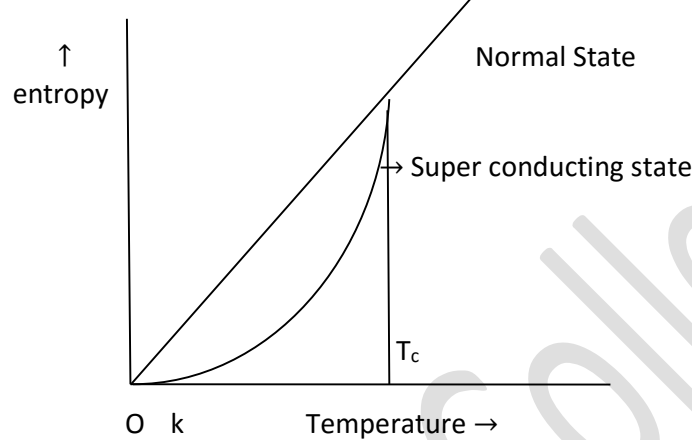
$dQ \rightarrow$  Change in energy,

$dT \rightarrow$  Change in Temperature.

For a normal conductor as the temperature decreases, the entropy decreases linearly.

For a super conductor, as the temperature ( $p=0$ ) decreases, the entropy decreases not linearly.

A graph of entropy with temperature is given below.



In the above diagram, when  $T < T_c$ , entropy is less in the super conducting state and entropy is more for normal state.

**Heat Capacity (or) Specific heat Capacity:**

Specific heat capacity is defined as the heat required to increase the temperature of a substance of 1kg through 1 Kelvin.

Specific heat for water is 4200 J/kg/k

The Specific heat is given by  $C = \gamma T + \beta T^2$  ----- (1)

Where ' $\gamma$ ' and ' $\beta$ ' are constants. ' $T$ ' is the temperature.

In the above equation, the first term is due to electrons and the second term is due to lattice.

$C = C_{\text{electron}} + C_{\text{lattice}}$  ----- (2)

Where,

$C_{\text{electron}} \rightarrow$  Electronic Specific heat.

$C_{\text{lattice}} \rightarrow$  Lattice Specific heat.

For the normal state, the specific ( $T > T_c$ )

Heat is

$C_N = (C_{\text{electron}})_N + (C_{\text{lattice}})_N$  ----- (3)

For the super conductivity state, the ( $T < T_c$ )

Specific heat is

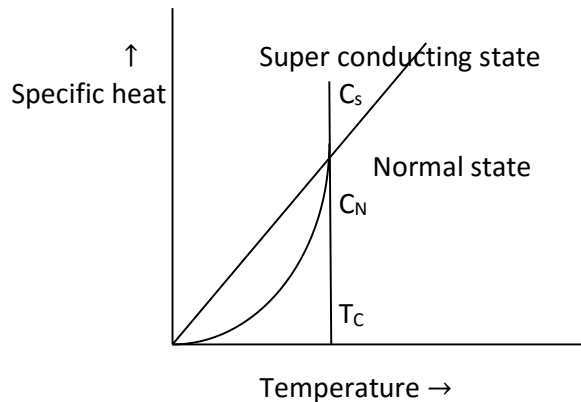
$C_S = (C_{\text{electron}})_S + (C_{\text{lattice}})_S$  ----- (4)

But

$(C_{\text{lattice}})_N = (C_{\text{lattice}})_S$

$C_N - C_S = (C_{\text{electron}})_N - (C_{\text{electron}})_S$  ----- (5)

A graph of specific heat with temperature is given below.



In the above diagram, for the normal state specific heat increases linearly with temperature. For the super conducting state specific heat increases exponentially with temperature.

i.e, For the super conducting state specific heat capacity is given by

$$C_s = A \exp\left(\frac{-\Delta}{kT}\right)$$

Where,

'A' is a constant

'Δ' is the energy gap

'k' is the Boltzmann's Constant

'T' is the absolute temperature.

At  $T = T_c$ ,  $C_s > C_n$

At  $T < T_c$ ,  $C_n > C_s$

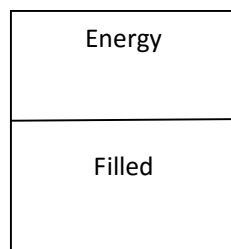
**Note:**

- (i) At  $T = T_c$ , there is a sudden change in specific heat.
- (ii) At  $T = T_c$ , there is a discontinuity in the specific heat.
- (iii) At  $T < T_c$ , entropy is less.
- (iv) At  $T < T_c$ ,  $R = 0$

**Energy gap:**

Energy gap is energy difference between valence band and conduction band. For a normal conductor energy gap is zero. For a super conductor there is a little energy gap.

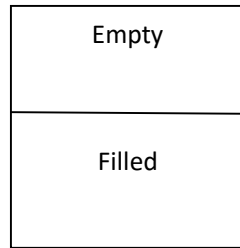
The energy level diagram for a normal conductor and super conductor are given below.



For a normal conductor



In the above diagram 'Ep' is the sermi energy



For Super Conductor at Ok.

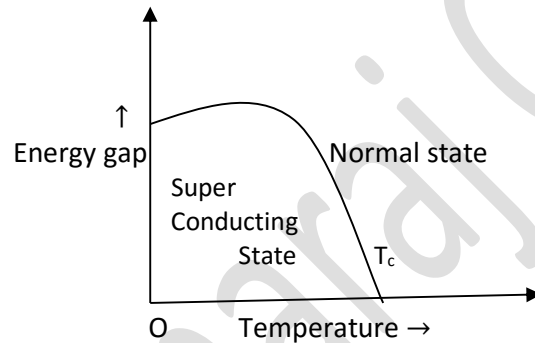
In the above diagram 'Eg' is the energy gap. From the theory of specific heat, the specific heat in the super conducting state is

$$C_s = A \exp\left(\frac{-\Delta}{kT}\right)$$

Where, 'A' is a constant  
 'Δ' is the energy gap  
 'k' is the Boltzmann's Constant  
 'T' → Change in Temperature.

Here  $E_g = \Delta$

The variation of energy gap with temperature is given below.



In the above diagram, when the temperature increases, energy gap decreases.  
 At  $T = T_c$ , Energy gap is the zero.

In the super conducting state,

$$T < T_c$$

Energy gap  $\neq 0$

In the Normal State,

$$T > T_c$$

Energy gap = 0

**Existence of energy gap in a superconductor:**

**Proof:**

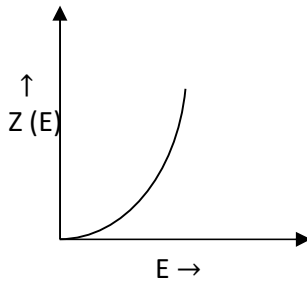
The existence of energy gap in a Super conductor can be proved by optical and electrical methods.

Density of states can be used to check the energy gap in super conductor. The number of energy volume states (energy levels) per unit is called density of states.

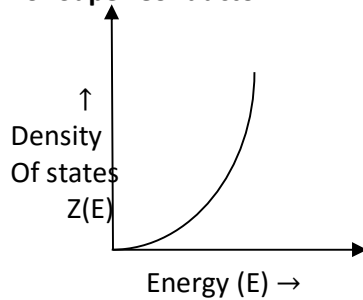
The variation of density of states [ Z(E) ] with energy is given below.



For normal conductor



For Super Conductor:



In the above diagram there is no energy gap in a normal conductor. But there is a energy gap in the super conductor.

**Isotope Effect:**

Isotopes have same atomic number and different mass number. According to isotope effect, the critical temperature ( $T_c$ ) is inversely proportional to isotopic mass ( $m$ ).

i.e,

$$T_c \propto 1/M^\alpha$$

(or)

$$T_c \propto M^{-\alpha}$$

$$(or) T_c = \frac{\text{a constant}}{M^\alpha}$$

$$(or) T_c M^\alpha = \text{a constant}$$

This is called as isotopic effect. Here ' $\alpha$ ' is a constant. It is prove that  $\alpha \approx 1/2 = 0.5$ .

**Examples:**

The mass of isotopes of mercury varies from 199.5 to 203.4. The  $T_c$  varies from 4.192 to 4.185.

$$T_c \propto 1/M^\alpha$$

**To find the value of  $\alpha$ :**

By isotope effect,

$$T_c M^\alpha = \text{a constant.}$$

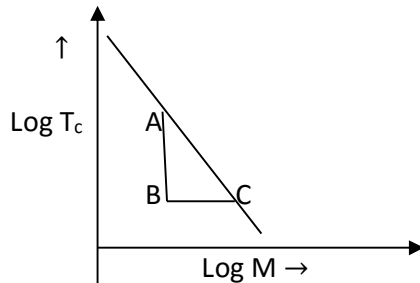
Taking log on both sides.

$$\log T_c + \alpha \log M = \text{a constant.}$$

This is equal to

$$(or) \log T_c = -\alpha \log M + \text{a constant.}$$

Draw a graph between  $\log T_c$  and  $\log M$ .



The Slope =  $\frac{AB}{BC} = \alpha$ , This ' $\alpha$ ' is found.

**Thermodynamics in Super conductors:**

In thermodynamics, a liquid is converted into a vapour and vice versa.

i.e, liquid  $\leftrightarrow$  vapour

In a Similar manner,

In a Super conductivity, the super conducting state is converted into the normal state and vice versa.

i.e, Super Conducting state  $\leftrightarrow$  Normal State

In the Super Conducting State,

$$T < T_c$$

$$X = -1$$

$$H < H_c$$

$$B = 0$$

In the Normal State,

$$T > T_c$$

$$X \neq -1$$

$$H > H_c$$

$$B \neq 0$$

From thermodynamics, the Gibbs free energy is,

$$G ( T,P ) = U - T_s + P_v \text{ ----- (1)}$$

Where,

U  $\rightarrow$  Internal energy

T  $\rightarrow$  Absolute temperature

S  $\rightarrow$  Entropy

P  $\rightarrow$  Pressure

V  $\rightarrow$  Volume

When a Super Conductor is placed in a magnetic field, the susceptibility  $X = -1$ .

In the equation (1),  $P_v$  is equal to workdone or potential energy.

When the material is placed in a magnetic field

$$\text{The magnetic potential energy} = \frac{1}{2} \mu_0 X H_a^2$$

Where,

' $\mu_0$ ' is the permittivity of free space.

' $H_a$ ' is the applied magnetic field.

i.e,

$$P_v = \frac{1}{2} \mu_0 X H_a^2$$

But for a Super conductor,

$$X = -1$$

$$P_v = \frac{1}{2} \mu_0 H_a^2 \text{ ----- (2)}$$





From (1) and (2) we have

$$P \rightarrow H_a$$

$$G(T, H_a) = U - T_s + \frac{1}{2} \mu_0 H_a^2$$

$$\text{Let } U - T_s = G(T, 0) + \frac{1}{2} \mu_0 H_a^2$$

For Super conducting state,

Gibbs energy is

$$G_s(T, H_a) = G_s(T, 0) + \frac{1}{2} \mu_0 H_a^2$$

For Normal State,

Gibbs energy is

$$G_n(T, H_a) = G_n(T, 0) + \frac{1}{2} \mu_0 H_a^2$$

At  $H = H_c$

For Super conducting state,

Gibbs energy is

$$G_s(T, H_c) = G_s(T, 0) + \frac{1}{2} \mu_0 H_c^2 \text{ ----- (3)}$$

At  $H_a = H_c$

For a Normal State,

Gibbs energy is,

$$G_n(T, H_c) = G_n(T, 0) + \frac{1}{2} \mu_0 H_c^2 \text{ ----- (4)}$$

But at,

$$G_s(T, 0) = G_n(T, 0)$$

From equations (3) and (4) we have

$$G_s(T, H_c) = G_n(T, H_c)$$

Therefore, at the Super conducting transition ( $H_a = H_c, T = T_c$ )

The Gibbs energy at Normal state is equal to the Gibbs energy at Super Conducting State.

At the Super conducting transition the Normal State and the Super conducting state are reversible.

**Entropy: at  $T = T_c$  and  $H_a = H_c$ :**

Entropy means disorder, The entropy is given by

$$S = \left[ \frac{\partial G}{\partial T} \right]_{H_a} \text{ ----- (5)}$$

Where,

'G' → is the Gibbs energy

'T' → is the Temperature

'H<sub>a</sub>' → Applied magnetic field.

For the Super Conducting state,

$$G_s(T, H_a) = U - T_s + \frac{1}{2} \mu_0 H_a^2 \text{ ----- (6)}$$

Where,

'S<sub>s</sub>' is the entropy in the Super conducting State.

Differentiate with respect to T

$$\begin{aligned} \frac{\partial G_s}{\partial T} &= -S_s + \frac{1}{2} \mu_0 2H_a \frac{\partial H_a}{\partial T} \\ &= -S_s + \mu_0 H_a \frac{\partial H_a}{\partial T} \text{ ----- (7)} \end{aligned}$$

Similarly,

For the Normal State

$$\frac{\partial G_n}{\partial T} = -S_n + \mu_0 H_a \frac{\partial H_a}{\partial T} \text{ ----- (8)}$$

From equation (7) and (8) we have,

At  $H_a = H_c$



$$S_s = S_n$$

i.e, Entropy in the super conducting state is equal to entropy in the normal state at  $H_a = H_c$

In the graph,

- (i) When  $H_a = H_c$ ,  $G_s ( T, H_c ) = G_n ( T, H_c )$
- (ii) When  $H_a < H_c$ ,  $G_s ( T, H_c ) < G_n ( T, H_c )$
- (iii) When  $H_a > H_c$ ,  $G_s > G_n$

Kamaraj College



**UNIT – V**  
**NANOTECHNOLOGY**

**1) London Equations:**

F. London and H. London proposes a two fluid model for super conductors.

According to the London theory, a super conductor has two types of electrons:

1. Super electron.
2. Normal electron.

In the super conducting state, the super electrons are more. In the normal state, the normal electrons are more. The total electron density is given by

$$n = n_s + n_n$$

where,

$n_s \rightarrow$  super electron density.

$n_n \rightarrow$  normal electron density

When an electric field (t) is applied to a super conductor, the electric force  $F = -eE$  ----- (1)

where,

'E' is the electric field.

'e' is the charge of electron.

According to newton's law, we have

$$F = ma$$

$$F = \frac{M \partial r_s}{\partial t} \text{-----}(2)$$

Where,

'M' is mass electron.

'v<sub>o</sub>' is velocity of super electron.

't' is the time.

From (1) and (2)

$$-eE = m \frac{\partial r_s}{\partial t}$$

$$\frac{\partial r_s}{\partial t} = \frac{-eE}{m} \text{-----}(3)$$

The current density

$$J_s = n_s e v_s$$

$J = nev$

Differentiate w.r.t. 't'

$$\frac{\partial \sqrt{s}}{\partial t} = -n_s e \frac{\partial \sqrt{s}}{\partial t} \text{-----}(4)$$

Substitute (3) in (4)

$$\frac{\partial \sqrt{s}}{\partial t} = \frac{tn_s e^2 E}{M} \text{-----}(5)$$

This is the first London equation. Consider the first London equation

$$\frac{\partial \sqrt{s}}{\partial t} = \frac{+n_s e^2 E}{M}$$

Taking '∇' on the both sides.

$$\nabla \times \frac{\partial \sqrt{s}}{\partial t} = \frac{-n_s e^2 E}{M} (\nabla \times E)$$

$$\frac{\partial}{\partial t} (\nabla \times \sqrt{s}) = \frac{-n_s e^2 E}{M} (\nabla \times E) \text{-----}(6)$$

From Maxwell's equations

We have

$$\nabla \times E = \frac{-\partial B}{\partial t} \text{-----}(7)$$

Put (7) in (6)



$$\frac{\partial}{\partial t} (\nabla \times \sqrt{s}) = \frac{-n_s e^2 E}{M} \left( \frac{-\partial}{\partial t} \right)$$

From

$$\frac{\partial}{\partial t} (\nabla \times \sqrt{s}) = \frac{-n_s e^2 E}{M} \left( \frac{-\partial B}{\partial t} \right)$$

Integrating

$$(\nabla \times \sqrt{s}) = \frac{-n_s e^2 E}{M}$$

This is the second London equation. Here is the magnetic

**London Penetration Depth:**

When a super conductor is placed in a magnetic field his magnetic fluid penetrates slightly through, the surface of the super conductor, the depth at which the magnetic flux penetration depth.

From Marwell’s equation,

$$\nabla \times \vec{B} = \mu_0 J_s$$

Where,

B → flux density.

J<sub>s</sub> → Current density for super electron.

μ<sub>0</sub> → Permeability of free space.

Taking

$$\nabla \times (\nabla \times B) = \mu_0 (\nabla \times J_s) \text{ ----- (2)}$$

But

$$\nabla \times (\nabla \times B) = \nabla (\nabla \cdot B) - \nabla^2 B$$

For a Super Conductor

$$\nabla \cdot B = 0$$

$$\nabla \times (\nabla \times B) = -\nabla^2 B \text{ ----- (3)}$$

Put (3) in (2)

$$-\nabla^2 B = \mu_0 (\nabla \times J_s) \text{ ----- (4)}$$

From Second London equation

$$\nabla \times J_s = \frac{-n_s e^2 B}{M} \text{ ----- (5)}$$

Put (5) in (4)

$$-\nabla^2 B = \frac{-\mu_0 n_s e^2 B}{M}$$

$$\nabla^2 B = \frac{\mu_0 n_s e^2 B}{M}$$

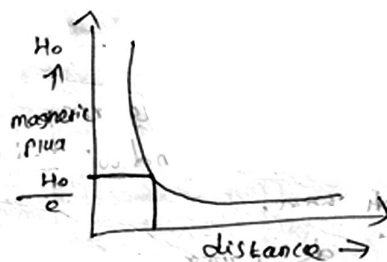
$$\nabla^2 B = \frac{B}{\lambda^2}$$

Where,

$$\lambda = \sqrt{\frac{M}{\mu_0 n_s e^2}}$$

This is for penetration depth.

Variation of magnetic flux with the distance is given below.

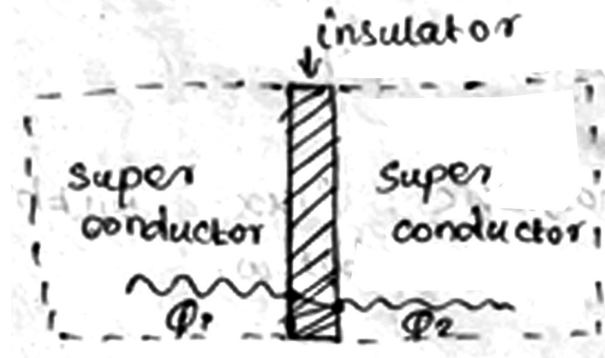




The above graph ' $\lambda$ ' is the penetration depth.

**Josephson Effect:**

If an insulating layer is sandwiched between two super conductors, the electrons (Cooper pairs) will tunnel through from one super conductor to another super conductor even at zero potential difference across the junction. This is known as Josephson Effect.



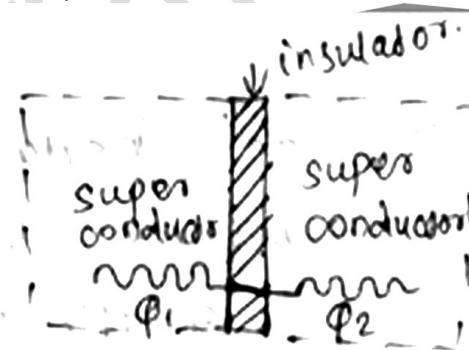
**Statement:**

In the above diagram, an insulating layer is sandwiched between two super conductors.

A dc current flows from one super conductors to another super conductors. ' $\phi_1$ ' is the phase of current in the first super conductor (Left side). ' $\phi_2$ ' is the phase of current in the second super conductor (Right side).

**Josephson Effect:**

If an insulating layer is sandwiched between two super conductors, a DC current flows from one super conductors to another super conductor even at zero potential difference across the junction. This is known as DC Josephson effect.



In the above diagram ' $\phi_1$ ' is the phase of current in the first super conductor (left side). ' $\phi_2$ ' is the phase of current in the second super conductor (Right side).

The phase difference is

$$\phi_0 = \phi_1 - \phi_2$$

The tunneling current is

$$I = I_0 \sin(\phi_0)$$

Where,

' $I_0$ ' is the maximum current.

In the DC Josephson effect, a DC current flows from one super conductor to another super conductor phase change.



When an external DC voltage is not applied across, the junction, A dc current flows from one super conductor current is given by.

$$I = I_0 \sin(\phi_0)$$

**AC Josephson Effect:**

If an insulating layer is sandwiched between two super conductors and a static potential (dc Voltage) is applied across the junction, an additional phase difference is produced and it generates electro magnetic waves (Micro waves). This is known as AC Josephson effect.

The additional phase difference is

$$\Delta\phi = \frac{Et}{\hbar}$$

Where, 'E' is the energy

't' is the time

$$h = \frac{h}{2\pi}$$

where,

'h' is the planck's constant.

$$E = h\nu$$

$$\omega = \frac{\text{angle}}{\text{time}}$$

$$E = \hbar\omega$$

$$E = \hbar \frac{\Delta\phi}{t}$$

A Super conductor consists of cooper pairs. Each cooper pair, consists of two electrons. Therefore the energy of a copper pair.

$$E = 2 eV_0$$

Where 'V<sub>0</sub>' is the applied DC voltage.

'e' is the charge of electron.

Put (2) in (1)

$$\Delta\phi = \frac{2 eV_0 t}{\hbar} \text{----- (3)}$$

For AC Josephson effect, the tunneling current is

$$I = I_0 \sin(\phi_0 + \Delta\phi) \text{----- (4)}$$

Substitute (3) in (4)

$$I = I_0 \sin(\phi_0 + \frac{2 eV_0 t}{\hbar}) \text{----- (5)}$$

(or)

$$I = I_0 \sin(\phi_0 + \omega t) \text{----- (6)}$$

Comparing equation (5) and (6)

$$\omega = \frac{2 eV_0}{\hbar}$$

This is equal to the angular frequency of electromagnetic waves (microwaves).

**The current – voltage characteristics:**

For the Josephson effect are given below:

In the above graph 'V<sub>0</sub>' is the applied voltage, 'I' is the tunneling current. V<sub>c</sub> is the critical voltage and 'I<sub>c</sub>' is the critical current.

**Special cases:**

- (1) When V<sub>0</sub> = 0, DC current (I<sub>c</sub>) flows across the junction. This is DC josephson effect.
- (2) When V<sub>0</sub> < V<sub>c</sub>, DC Josephson effect is present.
- (3) When V<sub>0</sub> > V<sub>c</sub>, Ac Josephson effect is present.

**Application of Josephson effect:**

- (1) Josephson effect is used to generate microwaves.
- (2) It is used to define the standard volt.
- (3) Josephson effect is used to measure the low temperature.
- (4) This effect is used in switching circuits.



**Bcs theory:**

This theory proposed by Bardeen cooper and schritter in 1957. They got Nobel prize for physics. Bcs theory explains about zero resistance. Isotopic effect messiner effect etc,

There are two aspects

- (i) Electron – electron interaction
- (ii) Cooper pair

**(i) Electron – electron interaction via lattice deformation: (Phonon)**

A Super conductor consists of positive ions and super electrons.

A Super electron is surrounded by a group of positive ions as shown in the figure.

In the above diagram, the electron is inside core of positive ions.

When another electron comes neat to positive core, there is an interaction between the two electrons. When electron is inside the positive core, there is a deformation in the lattice. The lattice deformation is called as the phonon. The electron interaction takes place via lattice deformation or phonon. The wave vector diagram for interaction of two electrons is given below.

Wave vectors equations are

$$K_1 - q = k_1^1 \text{ ----- (1)}$$

$$K_2 + q = k_2^1 \text{ ----- (2)}$$

Where 'K<sub>1</sub>' is the wave vector first electron.

'K<sub>2</sub>' is the wave vector for second electron.

'q' is the interaction energy.

'K<sub>1</sub>' and 'K<sub>2</sub>' wave vector for first and second outgoing electron.

**Applications of Superconductors:**

- (i) Super conductors are used in low loss transformers.
- (ii) They are used in transmission lines.
- (iii) Super conductors are used in generates and motors.
- (iv) They are used in magnetic levitates
- (v) Super conductors are used in SQUIDS (Superconducting quantum interference device)
- (vi) They are used in generation of high magnetic fields.
- (vii) Super conductors are used in switching circuit.
- (viii) They are used in super computers
- (ix) They are used in laborasory research institutions.

**Nano-materials:**

Nano is a Greek word for 'dwarf' and it means one billionth of a meter. i.e. one nanometer (nm)- $1 \times 10^{-9}$  meter.

A normal human hair is roughly 75,000 nm In thickness, We may need 10 hydrogen atoms, lined up end to-end, to make 1nm.

One nm is smaller than one micron which is  $1 \times 10^6$ m, and it is bigger than one Angstrom unit which is  $1 \times 10^{-10}$ m. Albert Einstein, as a part of his doctoral research work, calculated the size of a sugar molecule as 1nm.

When a material is prepared to come down in size to the nanoscale, its properties are fantastically different and novel from those at bulk scale. For example gold in bulk form is inert, whereas in nano size it is a good catalist to speed up chemical reactions. Some other examples of materials in nanofom exhibiting different behavior are as follows:



1. Samples of gold nano particles again, can appear is different colours such as orange, purple red and or greenish depending upon the size of the particles making up the sample.
2. Nano scale aluminium can combust spontaneously and can be used in rocket fuel.
3. At room temperature nano scale copper becomes highly elastic material that can be stretched upto 50 times its original length.
4. Nanoscale zinc oxide is transparent. However at large scale it becomes white and opaque.
5. Graphite, a form of carbon is soft and malleable. But carbon nanotubes exhibit tensile strength of about 100 times that of steel.

Natural nanoscale materials like proteins and other bio – molecules do many functions and processes of living systems. For example, haemoglobin is about 5nm in diameter and it carries oxygen through the blood stream.

For the wonderful properties of nanoparticles and nanostructures, scientists were striving hard to invent many devices that can be put to use to the comfort of mankind right from the fourth century (fused glass containing nano metal of silver and gold. A cup made of such glass is kept even today at the British Museum at London).

Chemical catalysis is an example of old nanotechnology. Today, catalysis can speed up many chemical transformations such as converting of crude oil into gasoline, small organic materials into drugs and polymers (long-chain molecules) and graphite into synthetic diamond.

The idea of manipulation of matter with high precision in the atomic scale was first given by Richard P. Feynman in his speech in annual meeting of American physical society in 1959 entitled “There is plenty of Room at the Bottom – An Invitation to Enter New Field of Physics”. His argument goes as follows a biological system can be exceedingly small. Many of the cells are exceedingly small but they are very active they manufacture substances; they walk around; they wiggle and they do all kinds of marvelous things all as a very small scale. Also they store information. consider the possibility that we too can make a thing very small, which does what we want – then we can manufacture an object that manoeuvres at that level. Nano electronics 1957.

Molecular Beam Epitaxy in 1968 (for controlled deposition of single atomic layers)

- Smiley’s buckyballs (C-60 molecule made up of 60 carbon atoms)
- Carbon nanotubes in 1991 and many other structures that Feynman forecasted in his talk in 1959. Feynman is rightly called the Father of Nano technology.

Nanotechnology is the design, production, application and characterization of nanostructures and systems by controlling shape and size at nanometer scale. It is highly an interdisciplinary area where the basic principles of nanotechnology will help us to have easy passage in reaching nanomaterials that are useful in Engineering and I.T. Physics, Chemistry, biology, etc.

#### **Top-down and bottom-up approaches in synthesis and Fabrication of nano-materials:**

There are two physical approaches to the fabrication and synthesis of nano-materials:

Top - down approach and Bottom-up approach.

1. Top-down fabrication is a construction process in which we first work at the large scale and then cut away until we have a smaller product. This is similar to a sculptor cutting away a block of marble, producing the final product: a statue. Thus, “Top down” is carving down to make nanoscale structure in precise patterns. i.e. it involves milling (grinding) and attrition. The final product may contain some amount of impurities from milling medium. It





is difficult to design and control nanostructures of desired shape and size by this method. This approach is also limited to materials of poor thermal conductivity but large volume changes. Moreover there would be imperfection of the surface structure. This imperfection may lead to reduced material strength and conductivity due to inelastic surface scattering.

2. Bottom-up approach is a construction process where we work with the smallest units of a material first (in this context, atoms) and build them up into the form of the final product. To see the position and move atoms from one point to another in the nanomaterial, we have high power instruments such as Atomic Force Microscope. Building the final product atom by atom (one atom at a time) will be time-consuming. So, a so called 'self' assembly process is employed. Under specific conditions the atoms and molecules spontaneously arrange themselves to the final product.

#### **Nano-materials:**

Nanomaterials are objects that have at least one external dimension in the order of nanometer (roughly one to hundred nm).

They are metals, metal oxides, ceramics, polymeric materials or composite materials with very small dimension in the range 1-100 nanometre. Nano materials exhibit unique physical and chemical properties such as mechanical, thermal, electronic and catalytic properties. These novel properties make them suitable for applications in electronic, environmental, scientific, medical, military and commercial sectors. Nanotechnology has been developed due to the invention of tools like atomic force microscope, (AFM) and Scanning tunneling microscope (STM) to see the nano world.

Some examples of nanomaterials are – carbon based nanomaterials such as buckyballs (hollow spheres) or fullerenes (C-60 molecules), carbon nanotubes etc. Also we have Nanobuds, Inorganic Nano tubes, Nanoshells, Quantum wires, Quantum dots, Organic diamondoids with cage-like poly cyclic adamantane structure (encapsulation of drugs especially with cage-like smart nano materials)

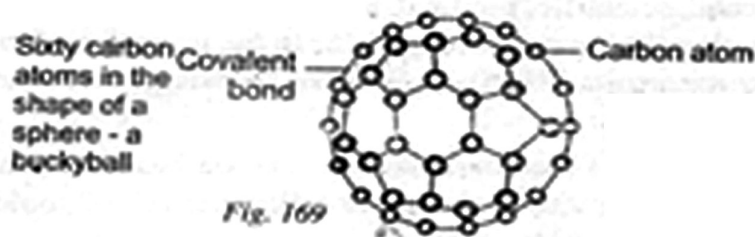
There are various types of man-made nanomaterials such as metals, metal oxides, semiconducting materials, nanofilms, nanosheets, nanowalls carbon based materials inorganic nanotubes, nanowires and quantum dot (clusters). The nanomaterials are composed of nanoparticles whose surface area to volume ratio is large and it makes them exhibit useful properties and makes them ideal for variety of applications.

#### **Carbon – based materials:**

These consist of carbon and are generally in the form of hollow spheres, ellipsoids and tubes. Carbon nanomaterials with spherical or ellipsoidal structures are called fullerenes and those with cylindrical structures are nanotubes.

Fullerenes consist of hexagonal and pentagonal ring of carbon atoms with spherical shapes. A new allotropic form of carbon was invented by Kroto and Smalley around 1985. It is C-60 molecule and is called 'buckminster fullerene' in respect of the renowned architect Buckminster Fuller of that period. Any closed carbon cage is then named as fullerene.

The fullerene C-60 has spherical molecular shape with diameter of about 1nm. It consists of 60 carbon atoms which are arranged in 20 hexagons and 12 pentagons similar to the soccer ball configuration.



Spherical fullerenes are called 'bucky balls'. The smallest bucky ball is C-20 and it consists of 12 pentagons only. The bigger bucky balls are denoted as C-n where  $n = 12, 13, 14$ .

Fullerenes generally have properties such as heat resistance, chemically inactive, soluble in many solvents and super conductivity.

### Classification of Nanomaterials:

#### Basis:

There is reduction in spacial dimension or confinement of particles in a particular crystallographic direction within the nanostructure. This leads to changes in physical properties of the system in that direction. Hence classification of nanostructured materials and systems depends on the number of dimensions, which lie within the nanometer range.

- (i) Systems confined in 3 dimensions [otherwise called zero dimension structures]  
Example: Nanoparticles, nanograins, Nanoshells, Nanorings, buckyballs, colloidal particles.
- (ii) Systems confined in 2 dimensions [One dimension structure]  
Example: Nanorods, nanofilaments, nanowires, quantum wires.
- (iii) Systems confined in 1 dimension [Two dimension structures].

Example: discs, platelets, ultrathin films, quantum coils. As we go down from bulk size materials, we can visualize materials of lower dimensions as follows:

When the reduction from bulk material three dimensions originally is in one direction, it results in a structure with two dimensions ( $3-1=2$ ) and it is called a film. A thin film or atomic layer of materials has only one nano dimension. The remaining two directions are macroscopic.

If the reduction is in two directions, clearly, the resultant structure will be in one dimension, which is called quantum wire (1D) Example: Spider silk, which is about 1000nm in diameter.

If the reduction is in all three dimensions, the material reduces to a point, which is well known as quantum dot as we discussed first as 0D particle.  
Again, nanomaterials are broadly classified into two as

- (i) Nanostructured materials and
- (ii) Nanophase materials (or nanoparticles)

Nanostructured materials are condensed bulk materials, which are made of nanoscale grains.

Nanophase materials are usually nano particles distributed uniformly in a medium.

There are other terms, used to describe different nano particles. Nanocrystals are specifically denoted to single crystal nanoparticles.



Very small nanoparticles are called quantum dots. They have nano-dimensions in all the three directions. These are referred to as OD particles. Their size (thickness) varies from a few nm to a few hundred nm. A OD material in common experience is the particle in the mist or fog. Since no dimension is microscopic, individual OD particle cannot be easily handled. They are used in powder form or they are scattered on the surface of microscopic object. The charge carriers can move along the three directions. The thickness of the OD material is less than the mean free path of the charge carriers.

#### **Carbon Nanotubes (CNT):**

CNT's were discovered in 1991 by Zigima. These are cylindrical fullerenes. There was two types of CNT's. Single walled nanotube (SWNT) and multiwalled nanotube (MWNT). SWNT consists of one cylindrical tube with diameter of about 1-2nm. MWNT consist of several concentric tubes having a diameter of about 2-2-5nm. The interlayer distance of MWNT is about  $3.34\text{\AA}$ . CNTs have length ranging from several micrometers to centimeters.

#### **CNTs have special physical and chemical properties as follows:**

Young's modulus  $E=1$  terra pascal. Tensile strength = 120 GPa. (before breaking)

CNTs are flexible along their axes and are very good electrical conductors. These properties make them highly useful as in micro-electro-mechanical devices, atomic force microscope tips and display devices.

#### **Carbon Nanobuds:**

These are fabricated by combining carbon nanotubes and fullerenes. The fullerene buds are covalently bonded to the outer side walls of the CNT. Carbon nanobuds have amazing properties of, both fullerenes and CNTs. They have huge capacity for hydrogen and helium storage and catalytic reactivity. In composite nano-materials, the bonded fullerene molecules may be used as molecular anchors and prevent slipping of nano tubes, which may improve the composite's mechanical properties.

#### **Inorganic nanotubes:**

These are like carbon nanotubes. Example:  $T_2O_{20}$ . The nanotubes can be used in catalysis and energy storage.

#### **Nano Shells:**

These are new type of nanoparticles and are ball-shaped. They are made up of a core of nano-semiconducting substance like silica glass, which is coated with extremely thin metallic layer (shell) such as gold or silver. Nanoshells are of the size of a virus (about 100nm wide). Gold nanoshells have properties similar to gold colloids. Gold nanoshells can absorb light and create red colour that can be used in medical products. The optical properties change as the relative size of the core and the shell changes. So by varying the dimensions of core and shell, we can tune across a wide range of wavelength spectrum.

#### **Synthesis of Nanomaterials:**

The basic principle for the synthesis of nanoparticles is to introduce a large number of nuclei and to inhibit the growth and aggregation of grains.

The purpose is to have materials synthesised with suitable size, morphology (external texture) and chemical composition. In other words any synthetic method should have control of size of the material in the nanoscale range so that one or other size dependent property may be attained.



### 1. Chemical vapour deposition (CVD) method:

CVD is one of the earliest methods used to produce carbon nanotubes in bulk quantities and at lower cost. In this method, a hydrocarbon (say-methane gas ( $CH_4$ ) having one carbon atom and four hydrogen atoms) flows with in a heated chamber (furnace) containing a substrate, coated with a catalyst such as iron (cobalt, nickel or zidite) particles. The temperature in the chamber is high enough to break the bonds between the carbon atoms in the  $CH_4$  molecule-resulting in carbon atoms with no hydrogen atoms attached. Those carbon atoms attach to the catalyst particles, where they bond to other carbon atoms forming a single layer of carbon atoms or nanotube, which can be collected from the cooler substrate. Single walled nanotubes (**SWNT**) in bulk quantities are thus synthesised. Multi walled nanotubes (**MWNT**) need a mixture of hydrogen and ethylene as source gases. A typical nanotube is 1000times longer than the width. The length-to-width ratio is known as aspect ratio of the nanotube. The large aspect ratio adds to the reinforcement as it resists the movement of a long molecule.

A schematic diagram of reaction chamber where the reaction process takes place in CVD is shown below:

The various of processes taking place in the CVD reaction chamber are briefly given below:

1. Transport of precursor agents
2. Gas phase reactions of precursor
3. Mass transport of reactants to the substrate surface
4. Adsorption of reactants on the substrate surface
5. Surface diffusion, nucleation and surface chemical reactions, leading to film formation.
6. Desorption of precursor and volatile byproducts.

The growth rate is determined by several parameters such as

(i)pressure of the reactor and (ii)temperature of the substrate(iii)nature of the gas – phase.

As regards pressure, the gas-phase reactions becomes important for growth rate in the pressure region between atmospheric pressure (760 torr) to intermediate pressure like 10 torr) As the pressure falls below 1 torr, the growth rate is found to be controlled by temperatures of the gas and the substracte and also by desorption of precursor fragments and matrix elements from the growth surface.

When the temperature increases (beyond  $700^{\circ}c$ ) the growth rate is found to be almost independent of the temperature.

The CVD offers an advantage to grow on a desired substrate. Also the process can yield MWNT (fewer) in excess of 20gm/hour.

A variety of CVD methods have been developed. They differ in the way by which chemical reactions are initiated, the types of precursors used (metal organic, for example) and on the process conditions.

Accordingly, we have plasma enhanced CVD, Laser induced CVD, Hot wire CVD, Metal organic (CVD) etc.

### 2.Sol – gel technique of synthesis of nanomaterials

The sol is a name of a colloidal solution, made of solid particles with a few hundred nm in diameter, suspended in a liquid phase. The gel can be considered to be a solid macromolecule, immersed in a solvent.

The sol-gel process consists of the chemical transformation of a liquid (the sol) into a gel state when it is given post-treatment for transition into solid oxide material.

Colloidal particles are much larger than normal molecules or nanoparticles. However, upon mixing with a liquid, colloidies appear bulky, whereas the nanosized molecules always look clear.



We expect to obtain a net work in continuous liquid phase (gel) through the formation colloidal suspension and gelation. The precursor agent for synthesis in these colloids consists of ions of metal alkoxides and alkoxsilanes. The most widely used are tetra methoxysilanes. (**TMOS**) and ethoxysilanes (**TEOS**), which form silica gels. The sol – gel process initially needs preparation of a homogeneous solution of one or more alkali oxides. These are organic precursors for silver, alumina, zirconium and many others. A catalyst is used to start reaction and control pH value.

The sol-gel formation takes place in four stages:

- (i) Hydrolysis
- (ii) Condensation reaction
- (iii) Growth of particles
- (iv) Agglomeration of particles.

i. Hydrolysis:

During hydrolysis, addition of water causes replacement of alkoxy group (hydroxyl). Hydrolysis occurs by the attack of oxygen, contained in the water on the silicon atoms in silica gel. It can be accelerated by adding a catalyst such as HCl or  $\text{NH}_3$ .

ii. Condensation:

Reaction leads to polymerization (formation of siloxane bond). Thus the end result of condensation is the formation of monomer, dimer, and high order rings. It is possible to vary the structure and properties of sol-gel derived inorganic networks by control of pH value and  $\text{H}_2\text{O}/\text{Si}$  molar ratio.

iii. Growth and agglomeration:

As the number of siloxane bonds (during polymerization) increases, the molecules aggregate in the solution, where they form a network. A gel is formed upon drying. Water is driven off and the network shrinks and densification takes place.

**Advantage:**

The unique advantage of the sol-gel technique is that it ensures densification even at a low temperature.

It is also possible to use the sol to synthesize powder (micro spheres and nano spheres). Extremely low density aerogel can also be obtained. If the viscosity of the sol is adjusted into a suitable range, ceramic fibres can be drawn by this method.

It is possible to synthesize ceramic materials of high purity and homogeneity by this technique. Totally different from the traditional process of fusion of oxides.

**Applications:**

The sol-gel derived materials have many applications in various fields like biosensors, optics, electronics, energy, space and medicine (example: controlled drug delivery)

**2. Synthesis of nano-materials by Electro deposition:**

The arrangement for electro deposition consists of an electro chemical cell (or voltameter) in which controlled current can be sent through the electrolyte (Electro chemical cell with  $\text{CuSO}_4$  solution, for example) at a certain voltage. The cell contains a specially designed cathode, a reference electrode and an anode. The cathode substrate on which electro – deposition of the nanostructure takes place can be made of either metallic or non metallic materials. Using the surface of the cathode as a reactive or active template, various designed nanostructures with controlled size and shape or morphologies. Can be synthesised.





The nucleation of nanostructure on the substrate is influenced by

- (i) The crystal structure of the substrate,
- (ii) Specific free surface energy,
- (iii) Adhesion energy and
- (iv) Lattice orientation of the electrode surface.

The final size deposition on the cathode depends on the kinetics of nucleation and growth. The growth may be instantaneous or progressive nucleation.

In the case of instantaneous nucleation all the nuclei form simultaneously on the substrate surface and subsequently grow with the time of electro deposition. On the other hand in the progressive nucleation, the number of nuclei that are formed is a function of time of deposition. These nuclei that gradually grow and overlap and exhibit zones of reduced nucleation rate around the growing stable nuclei.

Electrodeposition can yield finished products that are porosity free i.e; they need no subsequent consolidation process. Moreover, initial capital investment is low and also production rates are high with this technique.

#### **4. Ball milling method of synthesis of nano materials (Balls impact upon the powder)**

The objective milling is to reduce the particle size and blending of particles in nanophases. Among the techniques of solid phase synthesizing aluminium nano particles, the ball milling is easier and quicker.

The ball milling system consists of one turn disc (or turn table) and two or four bowls. Graphite powder (experimental substance) is placed into a stainless steel container (the bowl) which contains four hardened heavy steel balls. The container bowl is purged and argon is introduced. The turn disc rotates in one direction while the bowls rotate in the opposite direction.

#### **Working:**

The centrifugal forces, created by the rotation of the bowl about its own axis together with the rotation of the turn disc are applied to the powder mixture and the milling balls in the bowl. The powder mixture is fractured and cold-welded under high energy impact.

Since the rotating bowl and the disc are opposite in direction, the centrifugal forces are alternately synchronized (same direction for one half rotation and opposite for the other half). The hardened milling balls and the powder (being ground) are alternately rolling on the inner wall of the bowl and then striking on the opposite wall. The impact energy of the milling ball is high enough to crush the powder, its acceleration being 40 times greater than the gravitational acceleration.

The milling is carried out at room temperature for about 150 hours. Following milling, the powder is annealed under an inert gas flow at temperatures of 14,000C for six hours.

#### **Applications**

- a. The ball milling process forms nanotube nuclei in the graphite powder material and the annealing process activates nanotube growth. Similarly brown nitride nanotubes are produced by this method. It is reported that this method produces more multiwalled nanotubes and few single walled nanotubes.
- b. Amorphous alloys and metallic compounds can be made by milling method.
- c. It is possible to synthesise quasi – crystalline phases in MgZrO – Al and Mg-Cu-Al alloys [Ivanov and Eekert, 1989]

#### **Demerits**

- a. Contamination from the grinding media (bowl etc)



- b. Stickiness of material during grinding
- c. Combustible liquids with boiling less than  $120^{\circ}\text{C}$  cannot be used.

**Merits**

- 1. This technique can be used to fine-tune the grain sized in nanoscale within short duration.
- 2. It is possible to synthesise quasi-crystalline phases in Mg-Zn-Al and Mg-Cu-Al alloys [Ivanov and Eckert, 1989]

**Characterization of nano-materials:**

Along with synthesis and fabrication processes, nanomaterials need to be characterized to assess their morphology, size, shape and defects. Nanoscale objects absorb, emit, make and break bond, vibrate and travel. They are always active. It is very difficult to watch them and also nanosize-objects are too small to be observed with naked eye. Studying these thin structures requires special and clever instruments, known as characterization tools such as spectroscopic and microscopic techniques. There is no single method which can be used for every type of nano materials.

- 1. (a) Infrared spectroscopy is extremely handy for the study of single walled nanotubes (SWNT), understanding of the bonds between SWNTs and materials like polymers. It is the key to build super strong materials.
- 1. (b) To find how a nanomaterial handles strain, Raman spectroscopy is useful-particularly to Measure how the strain changes the vibration of the materials. If we are trying to develop composites, in which nanotubes are bonded to another material such as a polymer, Raman spectroscopy can tell us how the strains on the nanotubes are distributed.
- 1. (c) Ultraviolet (UV) and visible (Vis) spectroscopy is employed in the creation of nanosensors that can detect a material and identify its composition by bonding with it. This is known as capturing, which changes the nanosensor's properties. In other words, the U.V is spectroscopy enables us to verify the type of molecule that our particular nanosensor will capture.
- 2. In the microscope series for evaluating nanomaterials apart from Electron microscope we have Atomic Force Microscope (AFM), Scanning Electron Microscope, (SEM) Scanning Tunneling Microscope (STM) and Transmission Electron Microscope (TEM).

An AFM is used to view the surface features (known as topography) of atoms. AFM resembles a phono graphic record (gramophone record) over which a crystal tipped needle (stylus) would move along the grooves, cut in a spinning vinyl plate. When the motion of the plate vibrated the needle, the machine translated the vibration into sound.'

In a similar way AFM consists of a tiny tip of a ceramic material and is positioned at the end of a cantilever ( a solid beam). The tip of the cantilever travels over the surface of the sample material. As the tip travels, it is attracted to or pushed away from the sample's surface. It deflects the cantilever beam. A laser beam focused on the mirror at the tip deflects accordingly and indicates the deflection. The AFM thus produces a visible profile of the little hills and valleys that make up the sample's surface.

A summary of the various parameters of characterization and analytical Tools useful for each parameter is given below.



- |   |  |
|---|--|
| 1. Size, Shape of primary Particles, aspect ratio | Atomic Force Microscope, Transmission, Electron Microscope, X-ray diffraction, UV Vs spectroscopy, Raman spectroscopy. |
| 2. Aggregation and agglomeration                  | Transmission Electron Microscopy, Small Angle neutron scattering, Dynamic light Scattering.                            |
| 3. Size distribution                              | XRD, ultra centrifugation.   |
| 4. Surface activity                               | Fourier Transform I.R., ultra violet, photo Electron spectroscopy.   |
| 5. Surface charge                                 | Dynamic Light scattering, Electro phoresis   |
| 6. Crystal structure                              | XRD  |

The results obtained experimentally are compared with the desired results and presented in the specific dossier form for documentation purposes to REACH a world wide organization. (REACH is a European Union regulation concerning the Registration, Evaluation, Authorisation and restriction of chemicals).

**Properties of nano-materials:**

It is well known that property of a material is related to its structure. For nanomaterials, the properties are dependent on size of the material in the nanoscale and on the surface effects. Consider a spherical particle of radius r.

Its surface area =  $4 r^2$ ; Its volume =  $\frac{4}{3} \pi r^3$

The ratio (surface area/volume) =  $\frac{4 \pi r^2}{\frac{4}{3} \pi r^3} = 3/r$

As r increases, the (S/V) ratio decreases. However, in the nanometer range ( $1 \times 10^{-9}$ ) as r decreases, the surface to volume ration increases. Thus when nanomaterials are divided into smaller parts, the percentage of surface atoms would be larger, when compared to interior atoms. As surface atoms posses more surface energy than bulk atoms, the surface atoms are more chemically reactive. More over, the surface area is increased, when compared to the bulk cluster. Thus as the size of nanomaterial is reduced, it leads to great changes in the physical and chemical properties of materials.

**1. Mechanical Properties:**

Nanomaterials are formed of nano-size particles. Reduction in particle size is followed by increase in perfection. The structural perfection of the materials enhances their mechanical properties such as hardness, and strength, combined with ductility (Capable of being drawn into a wire) elastic modulus, 4 times higher than young's modulus) fracture toughness, scratch resistance etc. This situation favours mechanical coupling and energy dissipation within arrays of components at the nanometer scale and leads to ways to integrate different classes of materials at the nano-size into useful devices such as microscope probe tips, nano-resonators and mass sensors and other quality materials at low cost. Again at these grain sizes, mobile dislocations in the material have poor chance to occur in general, smaller, structures have less surface defects.





## 2. Thermodynamic properties:

The thermodynamic properties of nanocrystals depend on surface-to-volume ratio. The reduced coordination number of surface atoms increases the surface energy. Hence atom diffusion occurs at relatively lower temperature. The normal melting of gold is  $1063^{\circ}\text{C}$ . The melting point is lowered to  $300^{\circ}\text{C}$  for the particles reduced to diameter less than 5nm. Nano crystal palladium (6nm) shows higher specific heat from 30 to 50 percent, when temperature increases from 150K to 300K. For the same range of temperature, copper shows increase of specific heat from 9 to 11 percent.

## 3. Catalytic activity (Chemical properties)

It is known that when particle size is reduced to nanoscale, it results in higher surface area and higher number of surface atoms. The increase in surface area is associated with increase in catalytic activity (to speed up chemical reaction) in many cases. Larger surface area increases adsorption of reactant molecules in its surface and it results in higher catalytic activity. Gold is inert in bulk form. But as a nanoparticle, it catalyses CO into  $\text{CO}_2$ .

## 4. Magnetic properties

Bulk gold and platinum are non magnetic; but at the nanosize they act as magnetic particles. All nanoparticles become ferromagnetic when they are capped with appropriate molecules such as thiol. Giant Magnetic Resistance (GMR) is a phenomenon observed in nanoscale multilayers, consisting of magnetic buffer (Cr, Cu) GMR is useful in data storage and sensing.

## 5. Optical properties

Semiconductors and metals show large changes in optical properties such as colour, as a function of particle size.

Colloidal suspension of gold nanoparticles of diameter 2-5 nm exhibit yellow colour. That of 10-20 nm exhibit red colour and that of greater than 20nm exhibit purple colour. Photocatalysis, photo conductivity, photo emission and electroluminescence are some examples of optical properties of nanomaterials that are size dependent.

## 6. Electronic Properties

In semiconductor nanoparticles, the band gap (energy difference between the upper edge of valence band and the lower edge of conduction band) increases as the particle size is reduced to nanoscale i.e the interband transition frequency shifts to higher frequencies. The changing of band gap of the material by altering the nanosize of the material is known as band gap tuning. This enables to have desired optical absorption properties of the material. The material transmits or absorbs incident radiation, depending on the band gap value of the material.

A conductor (no energy gap) of normal size would become or semiconductor (of small energy gap) or even insulator (Large band gap) as the material is reduced to nanoscale, where the electrical conductivity is altered.

When a semiconductor absorbs a photon( $h\nu$ ), bound electron-hole pairs are formed. These are known as excitons. When the size of the nanomaterial is less than the Bohr radius of the exciton, smaller than the de Broglie wavelength of electron or hole, the nanomaterial is said to be in quantum – confinement state or regime. In such a state quantum-size defects such as discrete energy levels of electron, quantum tunneling and linear optical phenomenon like harmonic frequency generation follow.



#### Applications of Nanomaterials:

1. Nanomaterials are stronger but lighter, and better electrical conductors. Light weighting of cars, trucks and aeroplanes, boats and space craft could lead to fuel savings in large amount. Cutting tools made of nanomaterials such as tungsten carbide, tantalum carbide and titanium carbide are much harder, wear-resistant and last longer.
2. Clear nano scale films on eyeglasses, computer and camera displays, windows and other surfaces can make them water and residue repellent, antireflective, self-cleaning, resistant to U.V and IR light and are scratch resistant.
3. Nano-engineered materials in automobiles include higher power rechargeable battery system thermo electric-materials for temperature control, tyres with lower rolling resistance, low-cost sensors thin film smart solar panels and fuel additives for cleaner exhaust.

#### 4. Optical applications:

There are various optical and opto electronic nanomaterial devices such as switches, wave guides, amplifiers, Bragg gratings, splitters, isolators, circulators and detectors. Transparent plastics like polymethy methacryolate are widely used for optical components.

#### 5. Electronics and IT applications:

Transistors, the basic switches in modern computing have gone smaller and smaller through nanotech. In 2014, INTEL created a 14nm, transistor, One by one, In 2015, IBM a 7nm, in 2016 Berkelay National Lab created a 1nm transistor. Smaller, faster and better transistors may mean that our computer's entire memory may be stored on a single tiny chip. Computers will be able to 'boot' almost instantly.

Ultra high definition displays and televisions are being made that use quantum dots to produce more vibrant colours. They are also more energy efficient. Nanocubes are good electron emitters.

#### Other computing and electronic products include:

Flash memory chips for smart phones and ultra responsive hearing aids, anti microbial coatings anti on key boards and cell phone casings.

#### 6. Medical and health-care applications:

Graphine nanoribbons are found to help repair spinal cord injuries. Neurons grow well on the conductive graphine surface. Nanoscale molecules with diamond structure have been isolated from petroleum. These are called diamondoids and are useful in drug delivery and genetherapy.

They are useful for vaccine delivery without the use of needles. Carbon nanotubes and nanowires are used to detect DNA sequences and protein. Dendrimer is an artificial organic molecule (2-20nm across). Dendimers are magnetically tagged with iron oxide and injected into human body. Dendimers, being water soluble molecules, have strong chemical bonds and can take a drug (say, for AIDS) right into the affected cells without hitting the healthy cells in the body.

#### Physics of nanoscale materials:

Nano-scale materials, or nanomaterials, are materials where the particle or crystal size is in the scale of a few nm. The nanomaterial properties change as a function of size. The nanomaterials obtain vastly different properties while the chemical composition is the same. There is no universal size below which all nanomaterials show interesting trends in properties. In some cases the properties may become interesting below a few tens of nm, and in some other cases the properties



may become interesting only where the size drops even further to below a few nm. So if the material simply has a particular size or crystal size of a few nm, its properties are exactly the same as that of a bulk matter. Then there is no interest in this nanomaterial.

Let us see the impact of nanoscale materials on their electrical and optical properties.

In a semiconducting material, the valence band and conduction band are separated by a band gap energy  $E_g$ . At zero Kelvin the valence band is filled with electrons and the conduction band is empty (no free electrons in it). We have noted that in intrinsic semiconducting materials, optical absorption occurs by transition of an electron from the valence band to conduction band. This transfer of an electron to the conduction band creates a hole in the valence band, as shown in the figure.

Intrinsic semiconductor conduction band Electron-hole pair: An Exciton electron in conduction band.

Figure shows the transfer of an electron to the conduction band, due to the absorption of a photon of appropriate energy.

Since the electron and hole have opposite charge, they exert an attractive force on each other and maintain a connectivity with each other. This electron hole pair, operates as an associated pair of particles called an 'Exciton'. The attractive force between them makes them more stable than they would be as independent particles.

The exciton is similar to a hydrogen atom in the sense that it contains two entities of opposite charge, just like the hydrogen atom. Hence the exciton can be treated similar to a hydrogen atom. It is possible to define an exciton Bohr radius, similar to the Bohr radius of the hydrogen atoms. The Bohr radius is of the order of several nanometers. Thus the exciton differs from the hydrogen atoms. The exact value of exciton Bohr radius varies from material to material and is dependent on the dielectric constant of the material which impacts the interaction to some degree.

For nanomaterials selected for their optical and electronic properties, the size scale is of the order of exciton Bohr radius for that specific material. This value could be specific such as 3 nm or 8nm etc. If the nanomaterial is synthesized in this size scale, we begin to see nano scale effects in the electrical and optical properties of the material.

One can 'confine' (limit to within certain bounds) the exciton by making the particle size smaller. The confinement of the exciton influences the band gap displayed by the material. By making the size of the particle smaller, and making the confinement more severe, the band gap increases. By synthesizing particles with a narrow size (Small thickness) distribution, but with size in nanometer range, it is possible to get several samples of the same material such that the band gap is different in each sample. This is particularly useful for creating devices without having to use dissimilar materials, thereby eliminating diffusion, corrosion and sealing issues, associated with dissimilar material contacts.

With regard to synthesizing materials in different size scales, we have a few possibilities as shown in figure.

The possibilities with respect to synthesizing materials in different size scales are

**(1) Bulk material:**

No confinement effects observed.



### (2) Quantum Well:

In this case a very thin layer of material is synthesized, with the thickness of the layer in the range of the exciton Bohr radius. This implies that the exciton is confined in one dimension and free in two other dimensions.

### (3) Quantum wire:

A very narrow wire of the material qualifies as quantum wire. Here the confinement effects are observed in two dimensions. The exciton is free in one dimension in quantum wire.

### (4) Quantum dot:

The material has a very small size in all three dimensions: Hence the exciton is confined in all three dimensions in quantum dot.

Materials synthesized in the nanoscale have very high surface area. Hence they are very reactive with their environments. Hence it is a challenge to stabilize these particles. Such stability is usually brought about by trapping the material in host materials such as polymers. The particles can be made to grow within the structure of the polymer and by selecting the polymers and processing conditions, specific narrow size range, nano particles can be synthesized.

### Example:

These nanoscale effect has been effectively demonstrated in the CdS system, and in the PbS system. The bulk band gap of CdS system is in the visible region of the electromagnetic spectrum. By confinements, the band gap can be tailored or turned to increase into the UV range of the spectrum, and by introducing confinement effects, the band gap can increase into the U.V region of the spectrum.

The above ability to manipulate the band gap implies that with the same chemical composition it is possible to obtain samples with a wide range of colours, across the entire visible spectrum.

Solar radiation has a significant amount of energy in the IR region of the spectrum. Therefore having materials that absorb significantly in this wavelength region of the electromagnetic spectrum, makes them excellent for use in developing solar cells. By utilizing band gap tuning, it becomes possible to have a larger variety of materials capable of being used for solar cell application, than is possible by merely looking at the bulk band gap of the materials.

### Effect of dimensions on properties of solids:

Most properties of solids are altered when their dimensions approach the nanoscale. As an example, consider a particle of  $1 \times 1 \times 1 \text{ nm}^3$ . This contains roughly  $4^3 = 64$  atoms. Only 8 atoms of them are in the interior, while 87% of the atoms are at the surface. The electronic, magnetic, chemical and mechanical properties of nanoparticles are dominated by surface atoms. Simply by finely dispersing ordinary bulk materials new properties can be created: inert materials become catalysts, insulators become conductors or stable materials become combustible. A rather inert material like Au may, for example, become an efficient and selective catalyst when of the size of a few nm.

Graphene is a one-atom-thick layer of carbon atoms arranged in the hexagonal lattice (sheet) as shown in figure. Each carbon atom is covalently bonded to their other carbon atoms. Graphene has the same structure of carbon atoms linked in hexagonal shapes to form carbon nanotubes, but graphene is flat (2D structure) rather than cylindrical.

A sheet of graphene is very strong because of the interlocking carbon-to-carbon covalent bonds. The carbon atoms are bonded to only three other atoms, although they have the capacity



to bond to forth atom. One of the three covalent bonds is double covalent bond with another carbon atom. This capability gives great tensile strength to graphene. Though each graphene sheet is strong, it is one carbon atom thick, (ie) less than one nm). Since all the electrons are put to use within the molecular sheet, the bonding between sheets of graphene is done with van der waals forces, which are very weak. So the graphene sheets can slide along each other easily. Graphene is the strongest material known to exist, 200 times stronger than steel, lighter than paper, and has extraordinary mechanical and electrical properties.

**Properties:**

1. Graphene's electron mobility is faster than any known material. Transistors built on graphene are much faster than the transistors built on silicon wafers.
2. Because of the strength of covalent bonds, graphene has a very high tensile strength, ie, Graphene is both incredibly strong as well as light and thin.
3. It is a good conductor of heat and electricity and is impermeable.

**Uses and applications:**

1. Graphene sheets are used as electrodes in ultra-capacitors, which will have as much storage capacity as batteries; but recharging within a minute.
2. Strands of DNA can be attached to graphene to form sensors for rapid disease diagnosis.
3. High strength composite materials can be made for flat screen TVs replacing indium.

**Questions:**

1. What are nanomaterials? Give five examples.
2. Describe Top-Down and Bottom-up approaches in the synthesis and fabrication of nanomaterials.
3. Explain, with examples, classification of nanomaterials.
4. Describe, giving neat sketch of equipment, the synthesis of nanomaterials by
  - (i) Chemical vapour deposition technique;
  - (ii) Sol-gel technique.
  - (iii) Electro-deposition method. And
  - (iv) Ball-milling method.
5. What is meant by characterisation of nanomaterials? Describe, giving principle of each, the various tools employed in characterization of nanomaterials and their specific uses.