

## CRYSTAL STRUCTURE

Any matter can exist in three states gaseous, liquid and solid. Nature of the state at usual air temperature determines the state of the matter.

① Solid state:- Atoms or molecule in solids are attached to one another with strong force of attraction. So solid maintain a definite volume and shape. A solid have two special properties - rigidity and elasticity.

② Solid state Physics:-

Solid state Physics is the branch of physics which deals with the physical properties of solids, particularly crystals including the behaviours of electrons in the solid. It is also known as the physics of condensed matter in a broader sense.

③ Classification of solids:-

Depending on the arrangement of atoms or molecules solids are classified into two category -

1. Crystalline Solids.
2. Non-crystalline or Amorphous solid.

1. Crystalline Solids:-

The crystalline state of solids is characterized by regular or periodic arrangement of atoms or molecules.

Most of the solid in nature are crystalline.

This is due to the reason that energy released

during the formation of an ordered structure is more than disordered structure. So crystalline state is low energy state in the nature and lower energy state is preferred by most of the solids.

example - Cu (Copper), Sodium chloride (NaCl),  
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Gypsum).

## 2. Amorphous solid :-

The non-crystalline or amorphous solids are characterized by the completely random arrangement of atoms or molecules.

The periodicity of atoms or molecules, if at all present, extends upto a few distance in the solids. This short distance is the order of several atomic diameter only.

Amorphous solids are formed when the atoms do not get sufficient time to undergo a periodic arrangement.

example - Plastics, Rubber, Glass,

## ① Types of Crystalline solid :-

### A. Single Crystal :-

If the periodicity of atom extends through out the material of solid.

example - Diamond, Quartz, Mica.

## B. Poly-crystalline solids:-

It is an aggregate of a number of small crystallites with random orientations separated by well defined boundaries. These small crystallites are called grains and the well defined boundary is called grain boundary.

Polycrystalline materials are more stable than single crystals.

example - Metals and ceramics.

## ■ Crystallography:-

The study of geometrical form and other physical properties of crystalline solids by using X-ray, electron beam etc. is called crystallography.

## ■ Some Crystallographic Terms:-

### 1. Lattice or Space Lattice:-

In a crystalline solid, there is a regular periodic arrangement of atoms. Now it is very convenient to imagine points in the space about which these atoms are located. These points in space are called lattice points.

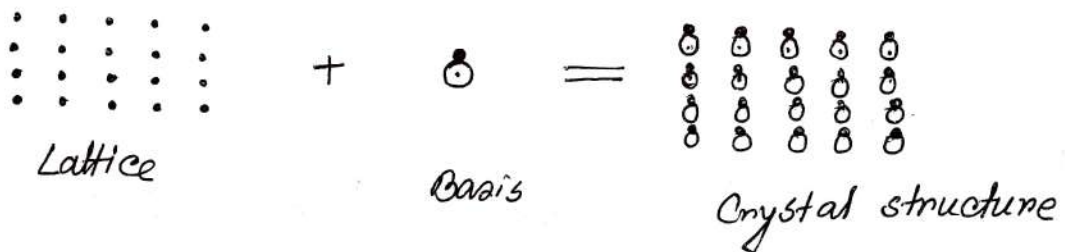
An arrangement of infinite numbers of points which are imaginary in 3-Dimension with each point having identical surroundings is known as point or space lattice.

## 2. Basis:-

To represent a crystal structure from a space lattice, an atom or molecule identical in composition must be placed on each lattice point. Such an atom or molecules is called Basis.

Thus crystal structure is real but lattice is imaginary.

$$\boxed{\text{Space Lattice} + \text{Basis} = \text{Crystal Structure}}$$

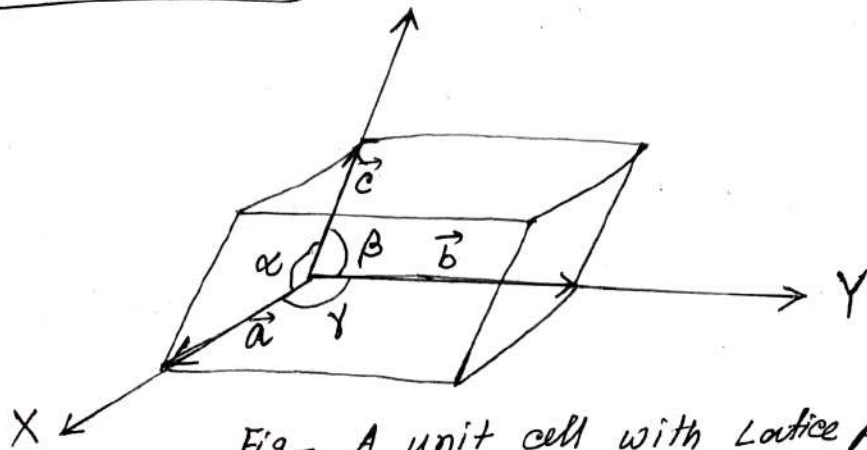


## 3. Unit cell:-

A unit cell may be defined as the smallest unit of the lattice whose continuous repetition generates the complete lattice. Thus unit cell is basic building block of crystal structure.

Unit cells for most of the crystals are parallelepiped or cubes having three sets of parallel planes or faces.

## 4. Lattice Parameters:-



A unit cell can be completely described by the three vectors  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  when the length of the vectors and the angles between them ( $\alpha, \beta, \gamma$ ) are specified.

Now, by taking any lattice point at origin, all other points on the lattice can be obtained by a repeated operation of the lattice vectors  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ .

These lattice vectors and interfacial angles ( $\alpha, \beta, \gamma$ ) constitute the lattice parameter. By using these parameter we can easily determine the form and actual size, volume of the unit cell.

### 5. Primitive Unit cell:-

Primitive unit cell is the smallest volume cell. All the lattice points belonging to a primitive cell lie at its corners. The effective number of lattice points in a primitive unit cell is one.

### 6. Non-Primitive Unit cell:-

A non primitive cell may have the lattice points at the corners as well as at the others locations both inside and on the surface of the cell.

The effective numbers of lattice points in a non-primitive cell is greater than one.

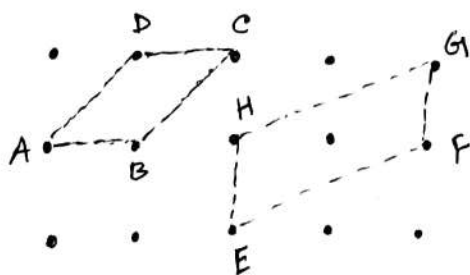


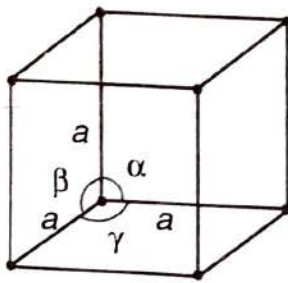
Fig - Primitive unit cell (ABCD) and Non Primitive (EFGH) unit cell.

## 7. Crystal Systems:-

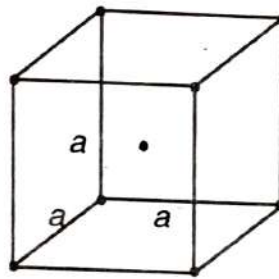
Based on the lattice parameters ( $\vec{a}, \vec{b}, \vec{c}$  and interfacial angles  $\alpha, \beta, \gamma$ ) there are seven different crystal systems. If atoms are existing only at the corners of the unit cells the seven crystal systems will yields seven type of lattices. More space lattices can be constructed by placing atoms or molecules at the body centres or at the centres of faces of the unit cells.

Scientist Bravais showed that the total numbers of different space lattice types is only fourteen (14). Hence the term is 'Bravais Lattice'.

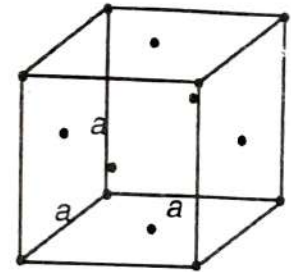
- Basic seven (7) types of crystal systems are-
- 1) Cubic ,
  - 2) Tetragonal ,
  - 3) Orthorhombic ,
  - 4) Trigonal or Rhombohedral ,
  - 5) Hexagonal ,
  - 6) Monoclinic ,
  - 7) Triclinic .



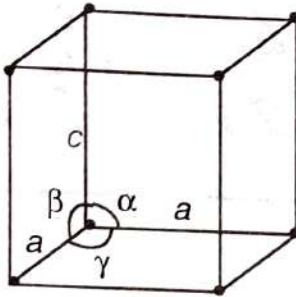
Simple cubic ( P )



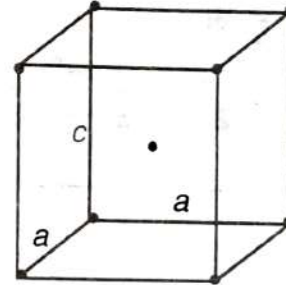
Body - centred cubic ( I )



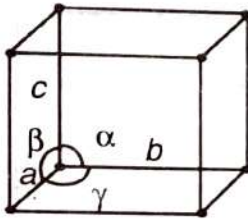
Face - centred cubic ( F )



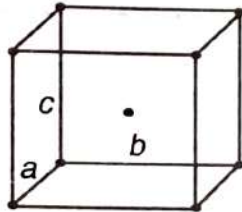
Simple tetragonal ( P )



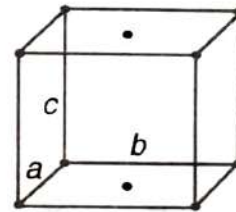
Body - centred tetragonal ( I )



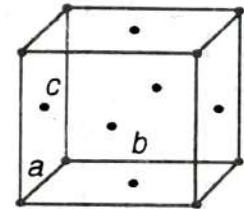
Simple orthorhombic ( P )



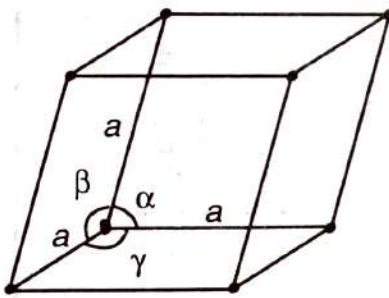
Body - centred orthorhombic ( I )



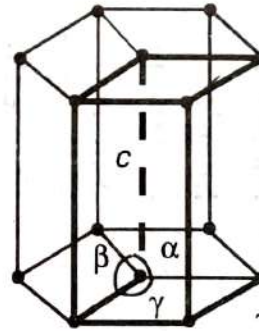
End - centred orthorhombic ( C )



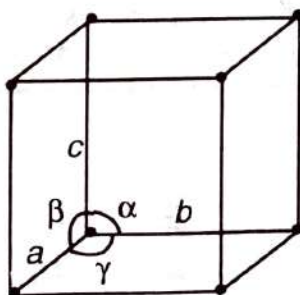
Face - centred orthorhombic ( F )



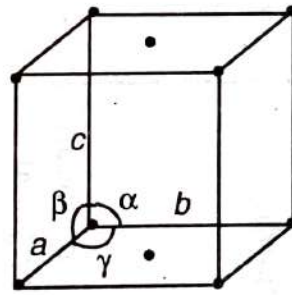
Simple rhombohedral ( R )



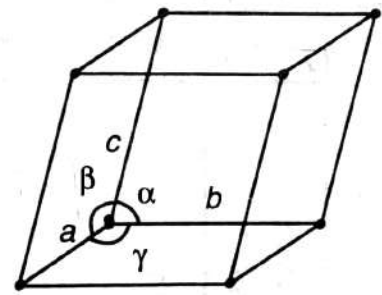
Simple hexagonal ( P )



Simple monoclinic ( P )



End - centred monoclinic ( P )



Simple triclinic ( P )

Fig.1.11. The Bravais lattices in three dimensions

**TABLE 1.2. Crystal systems and Bravais lattices in three dimensions**

S. No.	Crystal system	Lattice parameters	Bravais lattice	Common abbreviation	Lattice symbol	Examples
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred Face-centred	sc bcc fcc	P I F	Cu, Ag, Fe, Na, NaCl, CsCl
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred	st bct	P I	$\beta$ -Sn, TiO <sub>2</sub>
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred End-centred Face-centred	so bco eco fco	P I C F	Ga, Fe <sub>3</sub> C (cementite)
4	Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Simple	-	P (or R)	As, Sb, Bi
5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ,$ $\gamma = 120^\circ$	Simple	-	P	Mg, Zn, Cd, NiAs
6	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	Simple End-centred	- -	P C	CaSO <sub>4</sub> · 2H <sub>2</sub> O (gypsum)
7	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	-	P	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>



### Effective Numbers of Lattice point:-

A lattice point lying at the corner of the cell is shared by eight such cells and the one lying at the face centre position is shared by two cells.

So the following equation is used to calculate the effective number of lattice points,  $N$ , belonging to a particular unit cell;

$$N = N_i + (N_f/2) + (N_c/8)$$

where,  $N_i$  = the number of lattice points inside the cell completely.

$N_f$  = the number of lattice points on the face centre.

$N_c$  = the number of lattice points in the corner.

### Coordination Numbers:-

The coordination number of a given crystal structure is defined as the numbers of equidistant nearest neighbours that an atom has in the given structure.

Greater is the coordination number, the structure will be more closely packed up.

### Atomic Packing factor (f):-

The atomic packing factor or simply packing fraction is defined as the ratio of the volume occupied by the atoms present in a unit cell to the total volume of the unit cell.

## Crystal structures :-

Three relatively simple crystal structures are found for most of the common materials in solids:

- (i) Simple cubic structure (sc).
- (ii) Body centered cubic structure (Bcc).
- (iii) Face centered cubic structure (Fcc).

### Simple cubic (sc) structure :-

The conventional unit cell of sc structure is the same as its primitive cell. The atoms are located at the corners only and touch one another along the cube edges.

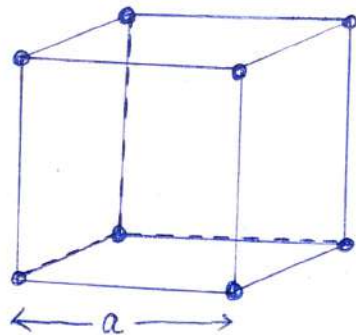


Fig. 1. unit cell of a sc structure.

(a) Coordination Number: 06

(b) Lattice constant:  $a = 2r$

(c) No of atoms per unit cell :  $N = \frac{1}{8} \times 8 = 1$

(d) No of Lattice point: 1

(e) Volume of Unit cell

$$V = a^3 = (2r)^3$$

(f) Volume of atoms in a unit cell =  $v = 1 \times \frac{4}{3} \pi r^3$

(g) Packing fraction:

$$f = \frac{v}{V} = \frac{4\pi r^3}{3 a^3}$$

$$= \frac{4}{3} \frac{\pi r^3}{8 r^3} = \frac{\pi}{6} = 0.52$$

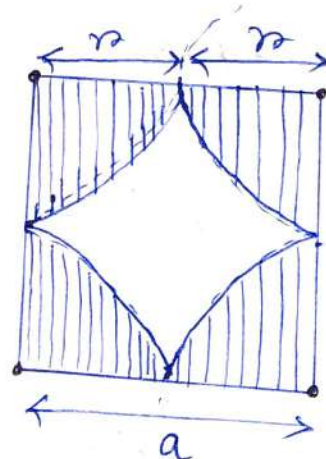


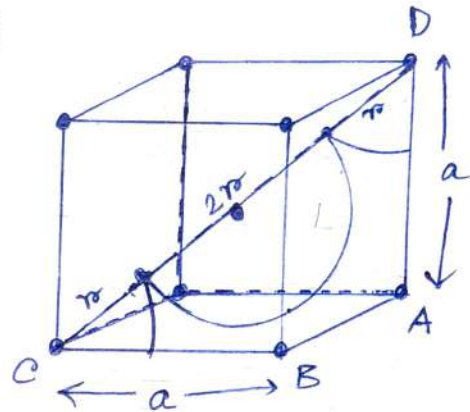
Fig. 2. Unit cell with a portion of atom.

example:- Only one element polonium exhibits this structure in certain temperature region. (Room Temperature).

### ① Body Centered cubic (BCC) structure:-

The conventional unit cell of BCC structure is non-primitive.

The atoms are located at the corners and another atom is at the body centre.



(a) Coordination Numbers: 08

(b) Lattice constant:

With the help of the Fig.-

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

$$\begin{aligned} CD^2 &= (AC)^2 + (AD)^2 \\ &= (2a^2) + (a)^2 \\ &= 3a^2 \end{aligned}$$

$$\therefore (4r)^2 = 3a^2$$

$$\text{or, } \boxed{a = \frac{4r}{\sqrt{3}}}$$

Fig: Body Centered Cubic structure (BCC).  
 $AB = BC = AD = a, CD = 4r$

(c) No. of atoms per unit cell:-  $N = \left(\frac{1}{8} \times 8\right) + 1 = 02$

(d) Volume of Unit cell:  $V = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$

(e) Volume of all atoms in a unit cell:  $v = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$

(f) Packing Fraction:  $f = \frac{v}{V} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = \frac{\pi \sqrt{3}}{8} = 0.68$

example:- The elements exhibits this structure are  
 Li, Na, K, Cr, Mo etc.

## ① Face centered Cubic structure (Fcc) :-

The Fcc unit cell is a non-primitive cell having eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces.

(a) Coordination Number: 12

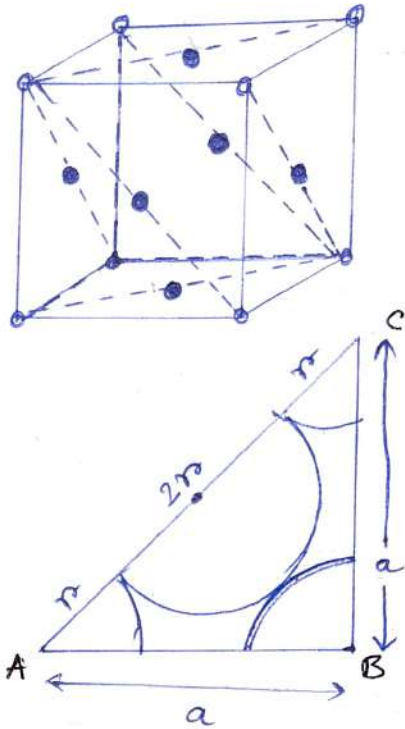
(b) Lattice Constant:

From Figure,

$$AB^2 + BC^2 = AC^2$$

$$\Rightarrow 2a^2 = (4r)^2$$

$$\Rightarrow \boxed{a = \frac{4r}{\sqrt{2}}}$$



(c) No of atoms per unit cell:  $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 04$

(d) Volume of unit cell:  $V = a^3 = \frac{64r^3}{2\sqrt{2}}$

(e) Volume of all the atoms in unit cell:  $V = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$

(f) Packing fraction:  $f = \frac{V}{V} = \left(\frac{16}{3}\right) \frac{\pi r^3}{64 r^3} \cdot \frac{2\sqrt{2}}{2\sqrt{2}}$   
 $= \frac{\sqrt{2}\pi}{6} = 0.74$

example:- The materials having this type of structure are Cu, Ag, Au, Al, Pb etc.

## Relation Between the Density of Crystal Material and Lattice Constant in a Cubic Lattice :-

Consider a cubic crystal of lattice constant  $a$ .

Let, the number of atoms per unit cell be  $n$  and  $\rho$  is the density of the crystal material. The atomic weight of the material is  $M$  and  $N_A$  be the Avogadro's number.

$$\therefore \text{weight of } N_A \text{ atoms} = M$$

$$\text{So weight of } n \text{ atoms} = \frac{Mn}{N_A}$$

$$\therefore \boxed{m = \frac{Mn}{N_A}} \quad \text{--- ①}$$

Again, density =  $\frac{\text{mass}}{\text{Volume}}$

$$\Rightarrow \rho = \frac{m}{a^3}$$

$$\Rightarrow \boxed{m = \rho a^3} \quad \text{--- ②}$$

From equation ① and ②

$$\rho a^3 = \frac{Mn}{N_A}$$

$$\text{or, } \boxed{a = \left( \frac{Mn}{N_A \rho} \right)^{1/3}}$$

## Lattice Directions and Planes :-

In a crystal there exists directions and planes which contain a large concentration of atoms. So it is necessary to locate these directions and planes for crystal analysis.

In this figure, two directions are shown by arrows in 2-D. The directions pass through the origin  $O$  and end at  $A$  and  $B$  respectively.

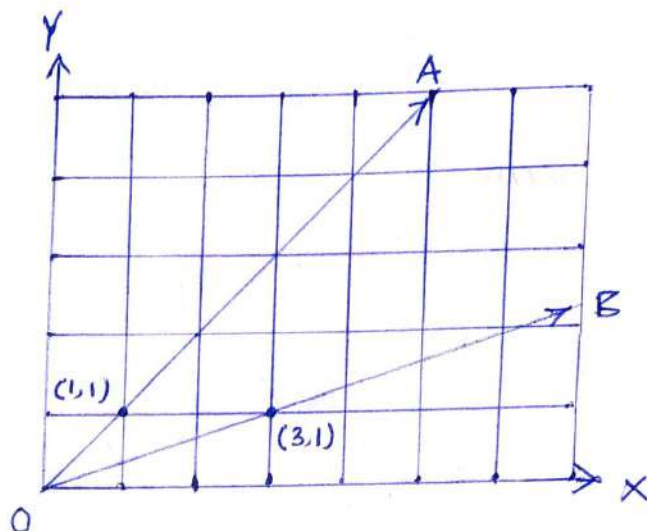


Fig:- Crystal Directions.

The directions can be described by giving the coordinates of the first whole numbered point  $(x, y)$  through which each of the direction passes. In 3-D, the directions are described by the coordinate of first whole number point  $(x, y, z)$ .

Generally square brackets are used to indicate a direction. A few directions are:

$$\begin{aligned} & \text{OA} [110], \text{OB} [310], \\ & \text{OC} [111], \text{OD} [102] \end{aligned}$$

## ● Miller Indices :-

The crystal lattice may be regarded as made up of a collection of a set of parallel equidistant planes, passing through the lattice points. These planes are known as lattice planes.

The lattice planes can be chosen in different ways as shown in the figure. But the problem is that how we can designate these planes in a crystal.

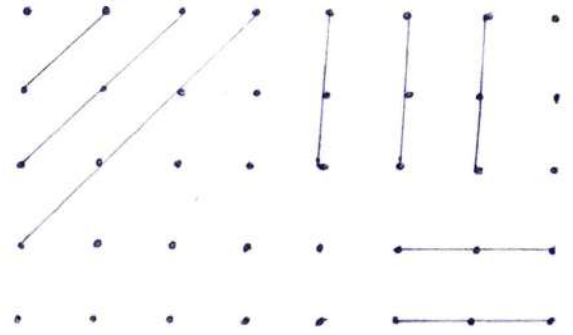


Fig:- Different Crystal planes.

A British crystallographer first introduced to designate these planes in a crystal. He designated a set of parallel planes in a crystal by three numbers  $(hkl)$  known as Miller indices.

### Steps to determine the Miller indices of a Plane:-

- (i) At first, choose any atom of the crystal as the origin and draw three crystallographic axis.
- (ii) Find the intercepts of the plane on the crystallographic axes.
- (iii) Take reciprocals of these intercepts.
- (iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets.

Thus, Miller indices may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

### Example:-

(i) Intercepts:  $\frac{2a}{a}, \frac{3b}{b}, \frac{c}{c}$   
 $2, 3, 1$

(ii) Reciprocals:  $\frac{1}{2}, \frac{1}{3}, 1$

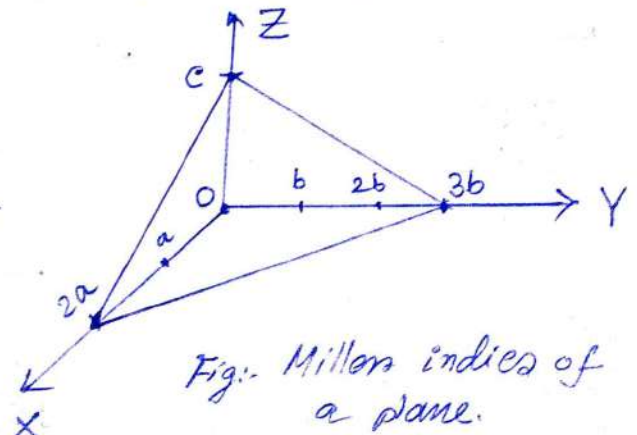


Fig: Miller indices of a plane.

(iii) Simplification:  $6 \times \frac{1}{2}$ ,  $6 \times \frac{1}{3}$ ,  $6 \times 1$   
 $3$ ,  $2$ ,  $6$

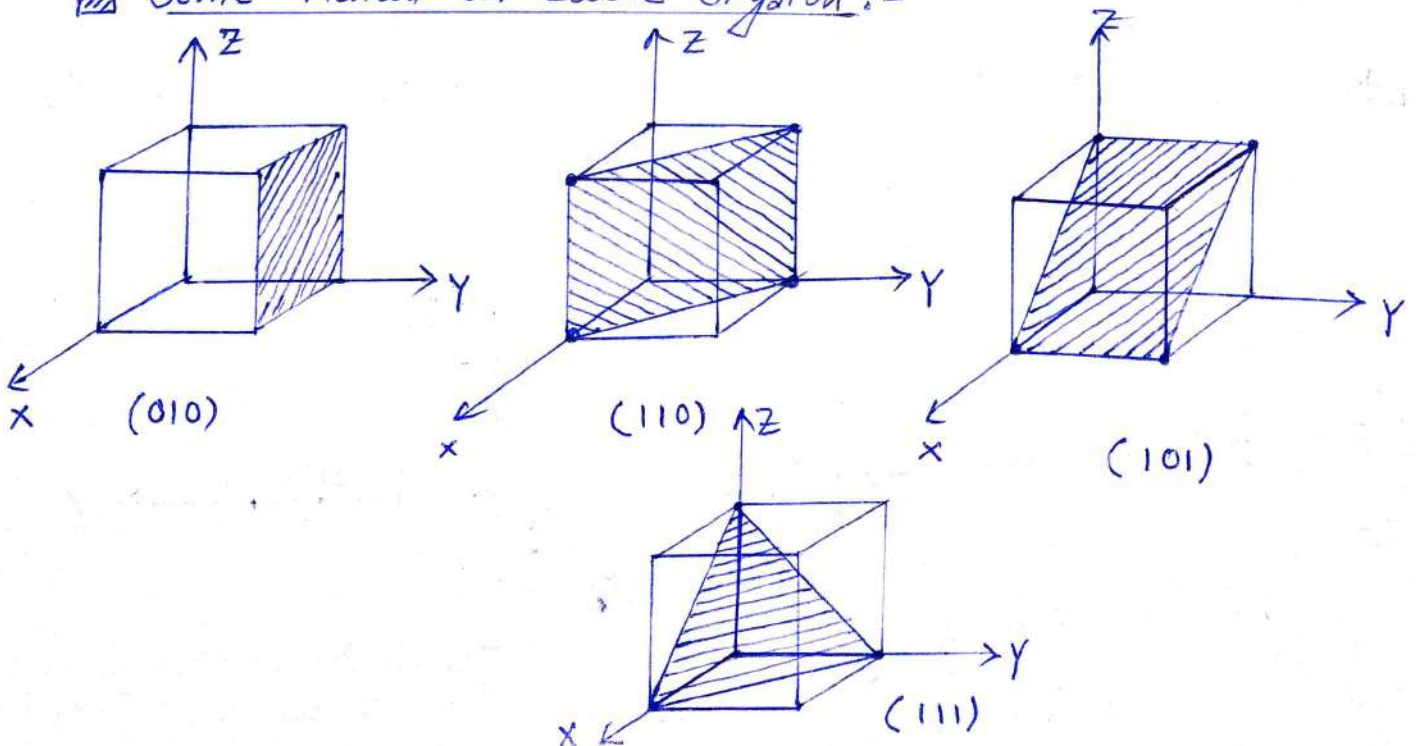
∴ Miller indices of the plane are  $(3\ 2\ 6)$ .

[\* The numbers within the bracket must be written without commas]

### ⊙ Some Important Features of Miller Indices:-

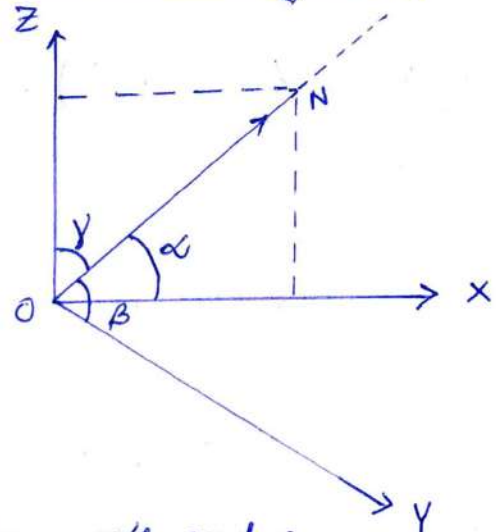
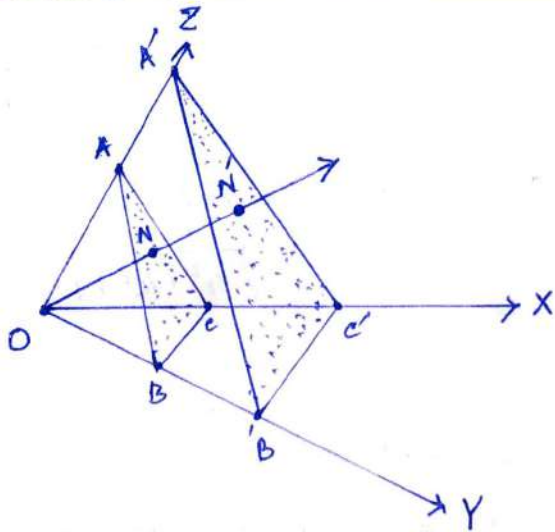
- (i) All the parallel equidistant planes have same Miller indices.
- (ii) A plane parallel to one of the coordinate axes has an intercept of infinity.
- (iii) If the Miller indices of two planes have the same ratio, then the planes are parallel to each other. i.e.,  $(844)$  and  $(422)$  or  $(211)$  are parallel.
- (iv) If a plane intercepts an axis on the negative side, a bar is put above the corresponding numbers of the Miller indices. i.e.,  $(0\bar{1}0)$ .

### ▣ Some Planes in Cubic Crystal:-





## Separation Between Lattice Planes in a Cubic Crystal:-



Let, two successive parallel planes  $n$ th and  $(n+1)$ th are respectively  $ABC$  and  $A'B'C'$  in a crystal of cubic shape. The edge of the cube is  $a$  and Miller indices of the planes are  $(hkl)$ . The direction cosines are  $\cos\alpha$ ,  $\cos\beta$  and  $\cos\gamma$ .

$\therefore$  The intercepts of the plane on the three <sub>(ABC)</sub> axis are:

$$OA = \frac{na}{h}, \quad OB = \frac{na}{k} \quad \text{and} \quad OC = \frac{na}{l}$$

similarly for  $A'B'C'$ :

$$OA' = \frac{(n+1)a}{h}, \quad OB' = \frac{(n+1)a}{k}, \quad OC' = \frac{(n+1)a}{l}$$

Now direction cosines are:

for  $ABC$  plane

$$\cos\alpha = \frac{ON}{OA} = \frac{ON}{na/h}$$

$$\cos\beta = \frac{ON}{OB} = \frac{ON}{na/k}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{ON}{na/l}$$

for  $A'B'C'$  plane

$$\cos\alpha = \frac{ON'}{OA'} = \frac{ON'}{(n+1)a/h}$$

$$\cos\beta = \frac{ON'}{(n+1)a/k}$$

$$\cos\gamma = \frac{ON'}{(n+1)a/l}$$

We know,  $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

So for ABC plane -

$$\frac{(ON)^2}{n^2} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) = 1$$

$$\text{or, } ON = \frac{na}{\sqrt{h^2 + k^2 + l^2}}$$

for A'B'C' plane -

$$\frac{(ON')^2}{(n+1)^2} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) = 1$$

$$\text{or, } ON' = \frac{(n+1)a}{\sqrt{h^2 + k^2 + l^2}}$$

∴ Separation for Lattice planes or  
interplanar spacing for cubical structure is

$$d_{hkl} = ON' - ON = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

\* If Lattice constants are different (other than cubical structure)

$$d_{hkl} = \frac{a}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

## X-Ray Diffraction by Crystals

X-rays are electromagnetic waves like ordinary light. So they should exhibit interference and diffraction. The wavelength of X-rays is of the order of  $0.1 \text{ nm}$ , so that ordinary devices such as ruled grating do not produce observable effect with X-rays. In the year 1912, German physicist Laue suggested that, a crystal which consists of a three dimensional array of regularly spaced atoms could serve the purpose of a grating. But the difference between a diffraction grating and a crystal grating is the crystal atoms are not in one plane, so acts like a space grating rather than a plane grating.

### ▣ The Bragg's Treatment: Bragg's Law:-

In 1912, W.H. Bragg and W.L. Bragg put forward a model for the conditions of diffraction in a very simple way.

A crystal may be divided into various sets of parallel planes. When a beam of monochromatic X-rays falls on a crystal, each atom becomes a source of scattering radiations. The combined scattering of X-rays from the planes can be looked upon as reflections from the planes.

Based on this consideration, Bragg's derived a simple mathematical relationship which serves as

a condition for the Bragg reflection to occur. This condition is known as the Bragg's Law.

Consider a set of parallel planes with interplanar spacing  $d$  and miller indices  $(hkl)$ .

Let, a parallel beam of X-rays of wavelength  $\lambda$  incident on these planes with glancing angle  $\theta$ .

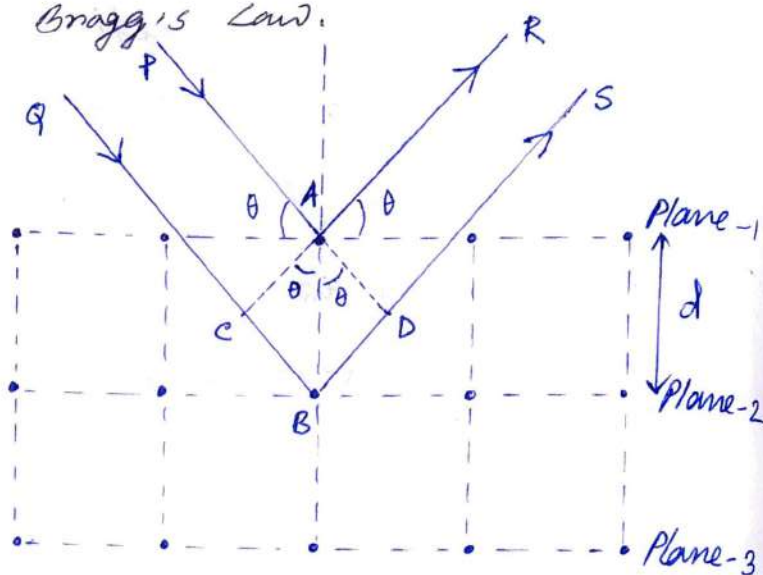


Fig: Reflection of X-rays from lattice planes in a crystal.

Now, from figure, a ray  $PA$  is reflected by atom at  $A$  and  $QB$  is reflected by atom  $B$  and directed towards  $AR$  and  $BS$  respectively. Two perpendiculars  $AE$  and  $AD$  are drawn. Now, these two reflected rays will be in phase or out of phase depending on the path difference  $(CB + BD)$ .

From Figure,  $CB = BD = d \sin \theta$

$\therefore$  path difference =  $CB + BD = 2d \sin \theta$ .

For constructive interference of the reflected ray, the path difference must be an integral multiple of  $\lambda$ . i.e.

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

$n = \text{an integer}$   
 $= 1, 2, 3, \dots$

This equation is Bragg's Law.

\*\* The highest possible order is determined by the condition that  $\sin \theta$  can not exceed unity.

Since,  $\sin\theta \leq 1$ , so  $\lambda$  must be  $\leq d$  for Bragg's reflection to occur. Let,  $d \leq 10^{-10}$  m.

$$\therefore \lambda \leq 10^{-10} \text{ m or } 1 \text{ \AA}.$$

X-rays having wavelength in this range, are preferred for analysis of crystal structure.

### ▣ Reciprocal Lattice:-

We have already read about X-ray diffraction occurs from various set of parallel planes having different orientations, and interplanar spacings. In practical situations, it's very difficult to visualize all the planes due to their 2-D structure.

- This above problem was first simplified by P.P. Ewald by introducing a new concept on lattice called reciprocal Lattice.

### ⊙ Concept of Reciprocal Lattice:-

A set of parallel plane could be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing ( $d_{hkl}$ ). Each normal represents the orientations of corresponding set of parallel planes and its length is reciprocal of the interplanar spacing. The points at the end of these normals form a lattice array. Since the distances in this array are reciprocal to distances in the crystal, the array is called 'reciprocal lattice' of the crystal.

### ① Defination of Reciprocal Lattice :-

The normals having length reciprocal to the interplaner spacing, are drawn with reference to an arbitrary origin and points are marked at the end. These points form a regular arrangement which is called reciprocal lattice.

### ② Direct to reciprocal Lattice conversion :-

The general rules for construction of the reciprocal lattice may be formulated by the following steps:

1. Fix up some points in the direct lattice as a common origin.
2. From this common origin draw normals to each and every set of parallel planes in the direct lattice.
3. Fix the length of each normal equal to the reciprocal of the interplaner spacing ( $1/d_{hkl}$ ) of the set of parallel planes  $(hkl)$ .
4. Put a point at the end of each normal.

The collection of all the points in space is the reciprocal lattice space.

## Example of Reciprocal Lattice:-

For a unit cell of monoclinic crystal:

$$a \neq b \neq c \text{ and}$$

$$\alpha = \gamma = 90^\circ \text{ and } \beta > 90^\circ.$$

For simplification, we orient the unit cell in such a way that  $\vec{b}$  is perpendicular to the plane of paper and  $\vec{a}, \vec{c}$  lie in the plane of paper.

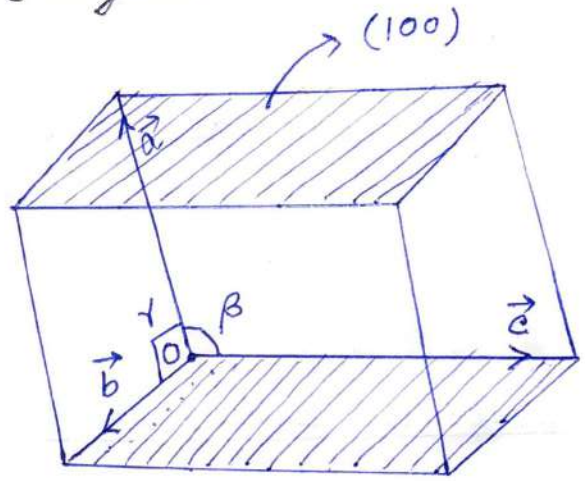


Fig- unit cell of monoclinic crystal.

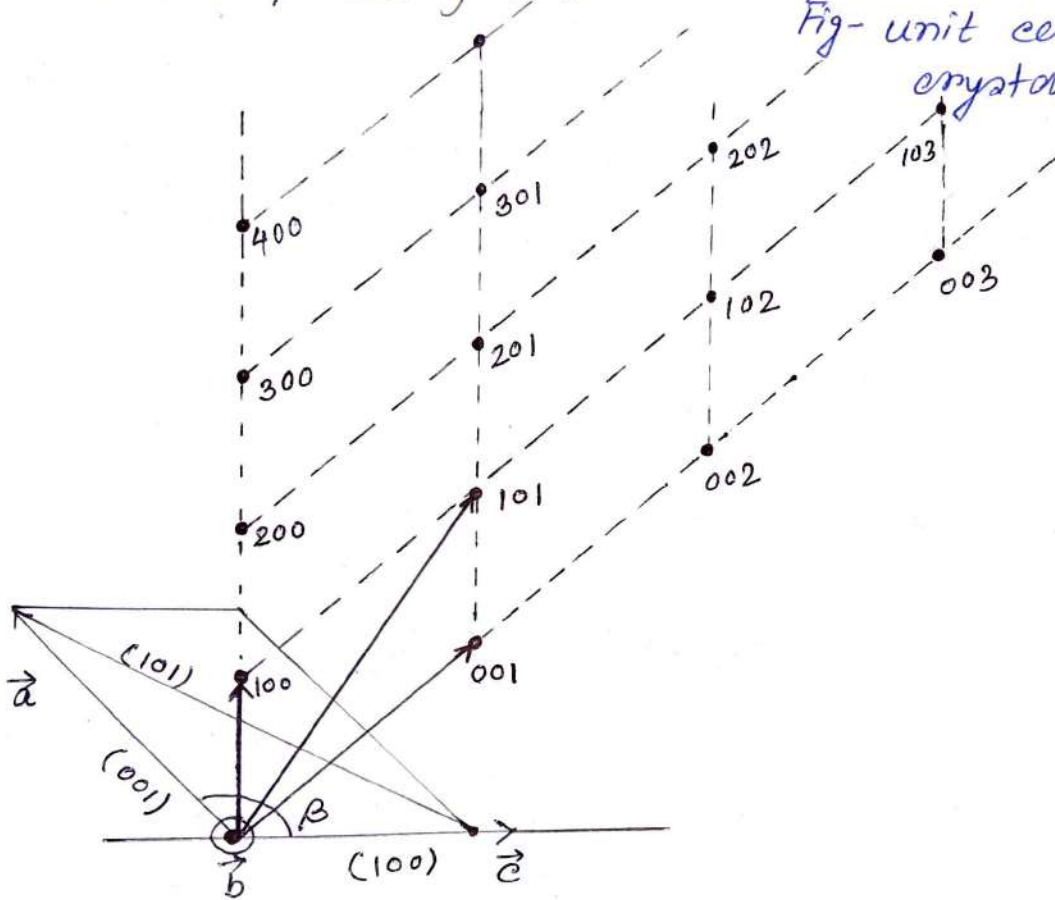


Fig- Two-dimensional reciprocal lattice to a monoclinic lattice. ( $\vec{b}$  is perpendicular to the plane of paper.)

In the above figure, the planes of the type  $(h0l)$  are parallel to  $b$ -axis ( $\gamma$ ) i.e. perpendicular to the plane of paper. Hence normal to these planes lies on the paper. These planes are represented by lines for the ease of 2D. Now at the origin normals are drawn and their length is  $1/d_{h0l}$ .

Since the planes (200) have half the interplanar spacing as compared to the plane (100), the reciprocal lattice point (200) is twice from the origin. If the normals to all the lattice (hkl) planes are drawn, a three dimensional reciprocal lattice is obtained.

### ▣ Reciprocal Lattice Vectors:-

A reciprocal lattice vector ( $\sigma_{hkl}$ ) is defined as, a vector having magnitude equal to the reciprocal to the interplanar spacing ( $d_{hkl}$ ) and direction coinciding with normal to the (hkl) planes.

$$\sigma_{hkl} = \frac{1}{d_{hkl}} \hat{n}$$

where,  $\hat{n}$  = unit vector normal to the (hkl) planes.

### ● Fundamental Reciprocal Lattice Vectors:-

Like a direct lattice, a reciprocal lattice has a unit cell which is the form of parallelepiped. The unit cell is formed by the shortest normals along the three directions i.e., along the normals to the planes (100), (010) and (001).

These normals produce reciprocal lattice vectors designated as  $\sigma_{100}$ ,  $\sigma_{010}$  and  $\sigma_{001}$ . These vectors are fundamental reciprocal vectors.



## Relation between Fundamental lattice vectors of Direct and

### Reciprocal Lattice :-

Let,  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  be the primitive translational vectors of direct lattice.

$\therefore$  Volume of the unit cell,

$$V = (\text{area}) \times \text{height}$$

$$\text{or, } V = \text{area} \times d_{100}$$

$$\text{or, } \frac{1}{d_{100}} = \frac{(\text{area})}{V} = \frac{|\vec{b} \times \vec{c}|}{V}$$

In Vector form we can write -

$$\frac{1}{d_{100}} \hat{n} = \frac{\vec{b} \times \vec{c}}{V}$$

[where  $\hat{n}$  = unit vector normal to (100) planes]

$$\text{or, } \boxed{d_{100} = \frac{|\vec{b} \times \vec{c}|}{V}}$$

$$\text{[where, } d_{100} = \frac{1}{d_{100}} \hat{n}]$$

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

$$\text{[as } V = \vec{a} \cdot (\vec{b} \times \vec{c})]$$

Similarly, the fundamental reciprocal vectors are -

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

$$b^* = d_{010} = \frac{|\vec{c} \times \vec{a}|}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$c^* = d_{001} = \frac{|\vec{a} \times \vec{b}|}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\text{[as, } \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})]$$

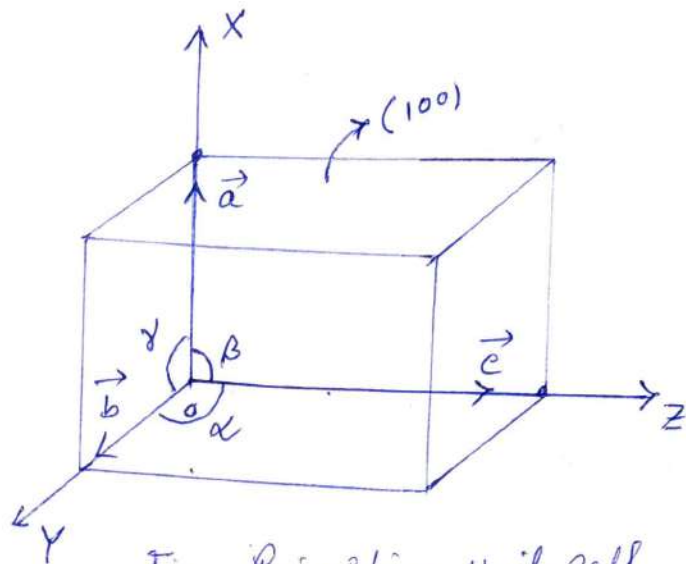


Fig:- Primitive Unit cell.

From the above equations, we have a simple relationship between reciprocal translation vectors to the crystal translation vectors —

- (i)  $a^*$  is normal to  $\vec{b}$  and  $\vec{c}$ .  
 (ii)  $b^*$  is normal to  $\vec{c}$  and  $\vec{a}$ .  
 (iii)  $c^*$  is normal to  $\vec{a}$  and  $\vec{b}$ .

In vector notation, it means,

$$\left. \begin{array}{l} a^* \cdot b = 0 \quad a^* \cdot c = 0 \\ b^* \cdot c = 0 \quad b^* \cdot a = 0 \\ c^* \cdot a = 0 \quad c^* \cdot b = 0 \end{array} \right\} \begin{array}{l} a^* \cdot a = 1 \\ b^* \cdot b = 1 \\ c^* \cdot c = 1 \end{array}$$

\*\* In some text book,  $a^* \cdot a = b^* \cdot b = c^* \cdot c = 2\pi$

### Lattice Translation Vectors:-

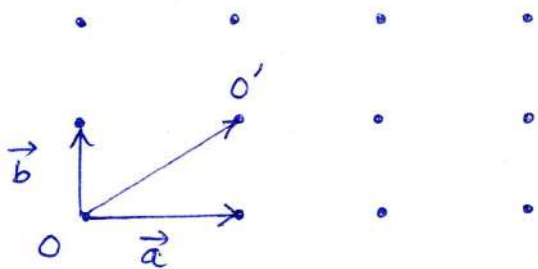


Fig:- Lattice Translation vector in 2D.

In two dimension direct lattice, there are 2 vectors  $\vec{a}$  and  $\vec{b}$  which are called fundamental translation vectors or crystal axes on basis vectors.

Now to move from 0 to  $0'$ , we use translation operation. The translation operation  $T$  is given

by - 
$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

where  $n_1$  and  $n_2$  are integers.

For 3-D, 
$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

But in case of reciprocal lattice,  $a^*$ ,  $b^*$  and  $c^*$  are the primitive reciprocal lattice vectors. So reciprocal lattice vector can be written as - 
$$G = h a^* + k b^* + l c^*$$

where,  $h, k, l$  are integers.

- The fundamental translation vectors of the crystal lattice and reciprocal lattice have dimensions of  $[L]$  and  $[L]^{-1}$ .
- A crystal lattice is a lattice in a real or ordinary space i.e., the space is defined by co-ordinates. But a reciprocal lattice is a lattice in the reciprocal space, associated  $k$ -space or Fourier space (momentum space).

### ▣ Reciprocal Lattice of Simple Cubic (sc) :-

The primitive translation vectors of a simple cubic lattice can be written as -

$$\vec{a} = a\hat{i}, \quad \vec{b} = a\hat{j}, \quad \vec{c} = a\hat{k}$$

∴ Volume of the simple cubic unit cell,

$$\begin{aligned} V &= \vec{a} \cdot (\vec{b} \times \vec{c}) \\ &= a^3 (\hat{i} \cdot \hat{j} \times \hat{k}) \\ &= a^3 \end{aligned}$$

Reciprocal lattice vectors to the sc lattice are obtained as -

$$a^* = 2\pi \frac{(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})} = 2\pi \frac{a\hat{j} \times a\hat{k}}{a^3} = \frac{2\pi}{a} \hat{i}$$

Similarly,

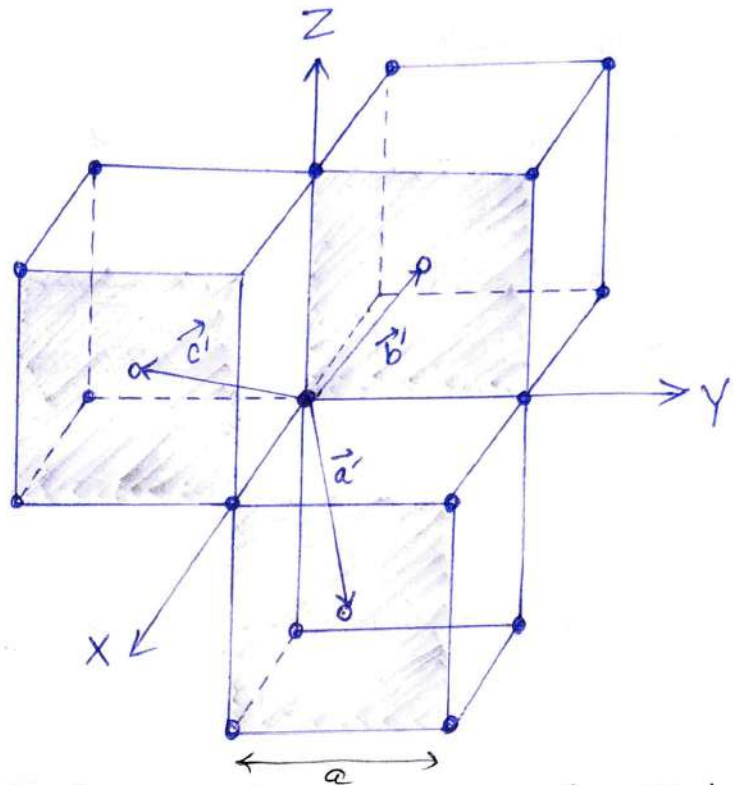
$$b^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})} = \frac{2\pi}{a} \hat{j}$$

$$c^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})} = \frac{2\pi}{a} \hat{k}$$

So, reciprocal of simple cubic is also simple cubic with cube side  $\frac{2\pi}{a}$  i.e., it is self reciprocal.

Volume of reciprocal simple cubic unit cell =  $\left(\frac{2\pi}{a}\right)^3$ .

## ▣ Reciprocal of Body centered cubic (bcc) Lattice:-



The primitive translation vectors of a body centered cubic Lattice (Figure) as shown in figure are -

$$\vec{a}' = \frac{a}{2} (\hat{i} + \hat{j} - \hat{k})$$

$$\vec{b}' = \frac{a}{2} (-\hat{i} + \hat{j} + \hat{k})$$

$$\vec{c}' = \frac{a}{2} (\hat{i} - \hat{j} + \hat{k})$$

where,  $a$  = length of the cube edge.

So, volume of the unit cell is given by -

$$V = \vec{a}' \cdot (\vec{b}' \times \vec{c}') = \frac{a^3}{8} \begin{vmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{vmatrix}$$

$$= \frac{a^3}{8} \times 4 = \frac{a^3}{2}$$

The Reciprocal lattice vectors are obtained as -

$$a^* = 2\pi \frac{\vec{b}' \times \vec{c}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = 2\pi \frac{(a^2/2)}{a^3/2} (\hat{i} + \hat{j}) = \frac{2\pi}{a} (\hat{i} + \hat{j})$$

Similarly,

$$b^* = 2\pi \frac{\vec{c}' \times \vec{a}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = \frac{2\pi}{a} (\hat{j} + \hat{k})$$

$$c^* = 2\pi \frac{\vec{a}' \times \vec{b}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = \frac{2\pi}{a} (\hat{k} + \hat{i})$$

### ▣ Reciprocal of Face centered cubic (FCC) lattice:-

Primitive translation vectors of FCC lattice as shown in figure —

$$\vec{a}' = \frac{a}{2} (\hat{i} + \hat{j})$$

$$\vec{b}' = \frac{a}{2} (\hat{j} + \hat{k})$$

$$\vec{c}' = \frac{a}{2} (\hat{k} + \hat{i})$$

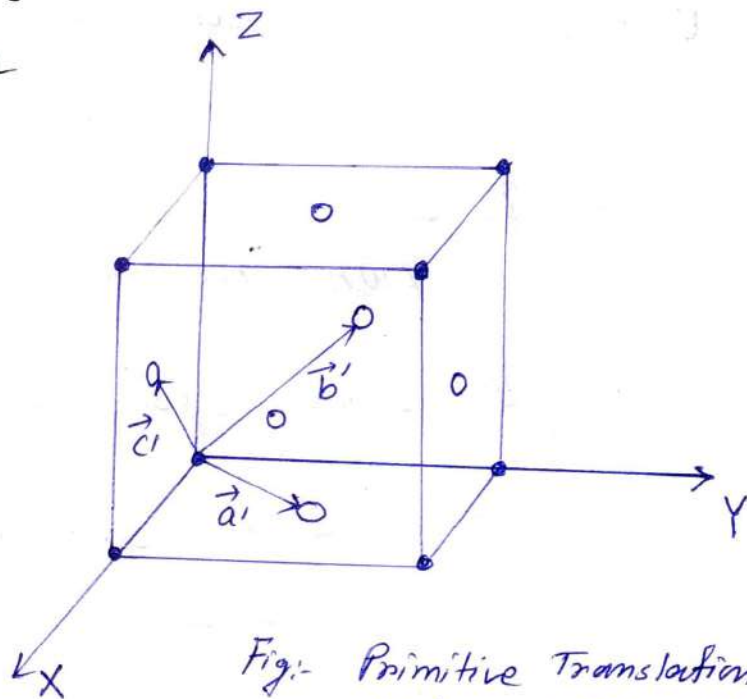


Fig:- Primitive Translation vectors of FCC lattice

Volume of the primitive cell,

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

$$= \frac{a}{2} (\hat{i} + \hat{j}) \cdot \frac{a^2}{4} [(\hat{j} + \hat{k}) \times (\hat{k} + \hat{i})]$$

$$= \frac{a}{2} (\hat{i} + \hat{j}) \cdot \frac{a^2}{4} (\hat{i} + \hat{j} - \hat{k})$$

$$= \frac{a^3}{8} \times 2 = \frac{a^3}{4}$$

Primitive translation vector for FCC reciprocal lattice are obtained as —

$$a^* = 2\pi \frac{\vec{b}' \times \vec{c}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = 2\pi \frac{(a^2/4) (\hat{i} + \hat{j} - \hat{k})}{a^3/4}$$

$$= \frac{2\pi}{a} (\hat{i} + \hat{j} - \hat{k})$$

similarly,

$$b^* = 2\pi \frac{\vec{c}' \times \vec{a}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = \frac{2\pi}{a} (-\hat{i} + \hat{j} + \hat{k})$$

$$c^* = 2\pi \frac{\vec{a}' \times \vec{b}'}{\vec{a}' \cdot (\vec{b}' \times \vec{c}')} = \frac{2\pi}{a} (\hat{i} - \hat{j} + \hat{k})$$

From the above discussions and relation we can conclude that —

- (i) Direct lattice is the reciprocal lattice to its own reciprocal lattice.
- (ii) Simple cubic (sc) lattice is self reciprocal.
- (iii) Bcc and fcc lattices are reciprocal to each other having length of the cube edge as  $\frac{2\pi}{a}$ .
- (iv) The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice.

## ▣ Bragg's Law in Reciprocal Lattice:-

The Bragg's diffraction condition obtained earlier by considering reflection from parallel lattice plane is used to express geometrical relationship between the vectors in the reciprocal lattice.

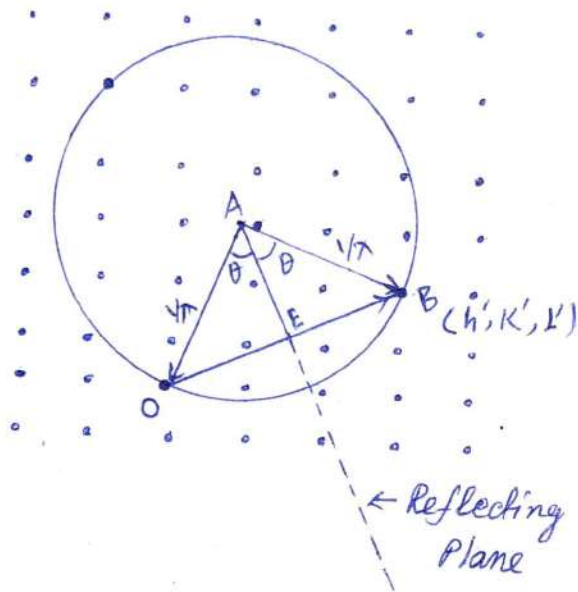


Fig:- Ewald construction in the reciprocal lattice.

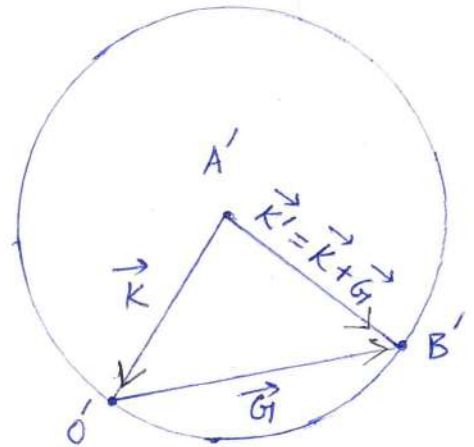


Fig- Magnified Ewald construction relating reciprocal lattice vectors to the wave vectors of the incident and reflected radiation.

A reciprocal lattice is shown in the above figure. A vector  $\vec{AO}$  of length  $1/\lambda$  in the direction of incident X-ray beam is drawn from a lattice of reciprocal which terminates at O. Taking A as centre a sphere of radius OA is drawn which intersect some point B of the reciprocal lattice.

Let, coordinate of B point is  $(h', k', l')$  which may have highest common factor n is, the coordinates are of the type  $(nh, nk, nl)$ .  $\vec{OB}$  is the reciprocal lattice vector.

Therefore normal to the plane  $(h' k' l')$  or  $(h k l)$  have length equal to  $1/d_{h'k'l'}$  or  $n/d_{hkl}$ .

$$\therefore |\vec{OB}| = n/d_{hkl} \quad \text{--- (1)}$$

If,  $\angle EAO = \theta$  is the angle between incident ray and the normal. Then for  $\triangle AOB$ , we have -

$$OB = 2OE = 2OA \sin \theta = \frac{2 \sin \theta}{\lambda} \quad \left[ \because OA = \frac{1}{\lambda} \right]$$

--- (2)

Now, from equation (1) and (2) -

$$\frac{2 \sin \theta}{\lambda} = \frac{n}{d_{hkl}}$$

$$\text{or, } \boxed{2 d_{hkl} \sin \theta = n \lambda}$$

This is Bragg's law and  $n$  is the order of reflection. Here, we can notice that, a common factor  $n$  of the the coordinate  $(nh, nk, nl)$  represents  $n$ th order reflection from the plane  $(hkl)$ .

### ① Ewald construction:-

The Bragg's condition is satisfied for a given wavelength  $\lambda$  provided the surface of radius  $1/\lambda$  drawn about the arbitrary point (A) and intersect a point of the reciprocal lattice. This type of geometrical construction is called Ewald construction.

### ② Modified form of Bragg's Law:-

To obtain the modified form of Bragg's law in reciprocal lattice, we redraw the vectors  $\vec{OA}$ ,  $\vec{OB}$  and  $\vec{AB}$  such that each is magnified by a constant factor of  $2\pi$ .



Let the new vectors are  $\vec{A'O'}$ ,  $\vec{O'B'}$  and  $\vec{A'B'}$ .

$$|\vec{A'O'}| = 2\pi (|\vec{A'O}|) = \frac{2\pi}{\lambda} = K$$

$\therefore \vec{A'O'} = \vec{K}$ , where  $\vec{K}$  = wave vector.

$\vec{O'B'} = \vec{G}$  = The reciprocal lattice vectors.

From vector algebra,  $\vec{A'B'} = \vec{K} + \vec{G}$

Now, for diffraction the point  $B'$  must be on the sphere, i.e.,

$$|\vec{A'B'}| = |\vec{A'O'}|$$

or,  $(\vec{K} + \vec{G})^2 = K^2$

or,  $K^2 + 2\vec{K} \cdot \vec{G} + G^2 = K^2$

or,  $2\vec{K} \cdot \vec{G} + G^2 = 0$

— This is the vector form of Bragg's Law in the reciprocal lattice.

⊙ Note:-

The vector  $\vec{A'B'} = \vec{K}'$  = The direction of reflected or scattered beam of X-ray.

$$\therefore \vec{K}' = \vec{K} + \vec{G}$$

which gives  $K'^2 = K^2$

and  $\vec{K}' - \vec{K} = \Delta\vec{K} = \vec{G}$

- (i) The above equations indicates that, scattering does not change the magnitude of wave vector  $\vec{K}$ , but only direction changes.
- (ii) The scattered wave differs from the incident wave by  $\vec{G}$ .

## ▣ Bragg's Law in Reciprocal Lattice:-

The Bragg's diffraction condition obtained earlier by considering reflection from parallel lattice plane is used to express geometrical relationship between the vectors in the reciprocal lattice.

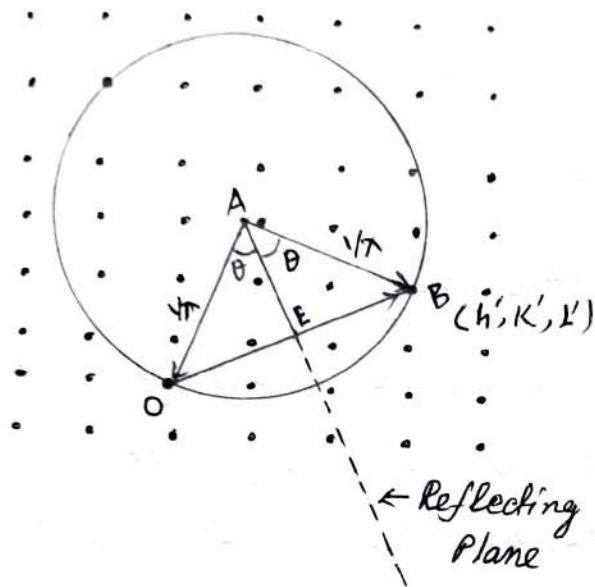


Fig:- Ewald construction in the reciprocal lattice.

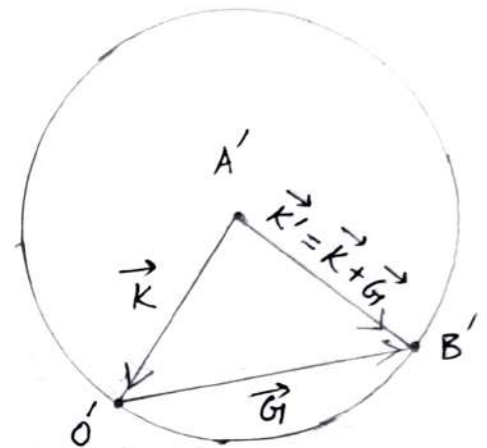


Fig- Magnified Ewald construction relating reciprocal lattice vector to the wave vectors of the incident and reflected radiation.

A reciprocal lattice is shown in the above figure. A vector  $\vec{AO}$  of length  $1/\lambda$  in the direction of incident X-ray beam is drawn from a lattice of reciprocal which terminates at O. Taking A as centre a sphere of radius OA is drawn which intersect some point B of the reciprocal lattice.

Let, coordinate of B point is  $(h', k', l')$  which may have highest common factor  $n$  i.e., the coordinates are of the type  $(nh, nk, nl)$ .  $\vec{OB}$  is the reciprocal lattice vector.

Therefore normal to the plane  $(h' k' l')$  or  $(h k l)$  have length equal to  $1/d_{h'k'l'}$  or  $n/d_{hkl}$ .

$$\therefore |\vec{OB}| = n/d_{hkl} \quad \text{--- ①}$$

If,  $\angle EAO = \theta$  is the angle between incident ray and the normal. Then for  $\triangle AOB$ , we have -

$$OB = 2OE = 2OA \sin \theta = \frac{2 \sin \theta}{\lambda} \quad \left[ \because OA = \frac{\lambda}{n} \right] \quad \text{--- ②}$$

Now, from equation ① and ② -

$$\frac{2 \sin \theta}{\lambda} = \frac{n}{d_{hkl}}$$

$$\text{or, } \boxed{2 d_{hkl} \sin \theta = n \lambda}$$

This is Bragg's law and  $n$  is the order of reflection. Here, we can notice that, a common factor  $n$  of the the coordinate  $(nh, nk, nl)$  represents  $n$ th order reflection from the plane  $(hkl)$ .

### ① Ewald construction:-

The Bragg's condition is satisfied for a given wavelength  $\lambda$  provided the surface of radius  $1/\lambda$  drawn about the arbitrary point (A) and intersect a point of the reciprocal lattice. This type of geometrical construction is called Ewald construction.

### ② Modified form of Bragg's Law:-

To obtain the modified form of Bragg's law in reciprocal lattice, we redraw the vectors  $\vec{OA}$ ,  $\vec{OB}$  and  $\vec{AB}$  such that each is magnified by a constant factor of  $2\pi$ .

Let the new vectors are  $\vec{A'O'}$ ,  $\vec{O'B'}$  and  $\vec{A'B'}$ .

$$|\vec{A'O'}| = 2\pi (|\vec{AO}|) = \frac{2\pi}{\lambda} = k$$

$\therefore \vec{A'O'} = \vec{k}$  , where  $\vec{k}$  = wave vector.

$\vec{O'B'} = \vec{G}$  = The reciprocal lattice vector.

From vector algebra,  $\vec{A'B'} = \vec{k} + \vec{G}$

Now, for diffraction the point B' must be on the sphere, i.e.,

$$|\vec{A'B'}| = |\vec{A'O'}|$$

or,  $(k + G)^2 = k^2$

or,  $k^2 + 2k \cdot G + G^2 = k^2$

or,  $2k \cdot G + G^2 = 0$

— This is the vector form of Bragg's Law in the reciprocal lattice.

⊙ Note:-

The vector  $\vec{A'B'} = \vec{k}'$  = The direction of reflected or scattered beam of X-ray.

$$\therefore \vec{k}' = \vec{k} + \vec{G}$$

which gives  $k'^2 = k^2$

and  $\vec{k}' - \vec{k} = \Delta\vec{k} = \vec{G}$

(i) The above equations indicates that, scattering does not change the magnitude of wave vector  $\vec{k}$ , but only direction changes.

(ii) The scattered wave differs from the incident wave by  $\vec{G}$ .

## ▣ Brillouin Zones:-

From the Ewald construction, we have learnt that all the  $k$  values for which the reciprocal lattice points intersect the Ewald sphere are Bragg reflected.

● Definition:- A Brillouin zone is the locus of all the  $k$ -values in the reciprocal lattice which are Bragg reflected.

### ● Brillouin zone for a simple square lattice:-

Lets consider a simple square lattice of side  $a$ . The primitive translational vectors of this lattice are

$$\vec{a} = a\hat{i} \quad \text{and} \quad \vec{b} = b\hat{j}$$

The corresponding translational vectors of the reciprocal lattice are -

$$a^* = \frac{2\pi}{a}\hat{i} \quad \text{and} \quad b^* = \frac{2\pi}{a}\hat{j}$$

∴ Reciprocal lattice vector,  $\vec{G} = \frac{2\pi}{a}(h\hat{i} + k\hat{j})$

where,  $h, k$  are integers and  $\vec{r} = k_x\hat{i} + k_y\hat{j}$ .

Now from the Bragg's Law of reciprocal lattice -

$$2\vec{k} \cdot \vec{G} + G^2 = 0$$

$$\text{or, } \frac{4\pi}{a} [(k_x\hat{i} + k_y\hat{j}) \cdot (h\hat{i} + k\hat{j})] + \frac{4\pi^2}{a^2} (h^2 + k^2) = 0$$

$$\text{or, } \boxed{h k_x + k k_y = -\frac{\pi}{a} (h^2 + k^2)}$$

The  $k$ -values which are Bragg reflected are obtained by considering all possible combinations of  $h$  and  $k$ .

● i) For  $h = \pm 1$  and  $k = 0$ ,  $k_x = \pm \frac{\pi}{a}$  and  $k_y = \text{arbitrary}$

● ii) For  $h = 0$  and  $k = \pm 1$ ,  $k_y = \pm \frac{\pi}{a}$  and  $k_x = \text{arbitrary}$ .

ii) For  $h = \pm 1$  and  $k = \pm 1$ ,  $\pm k_x \pm k_y = \frac{2\pi}{a}$

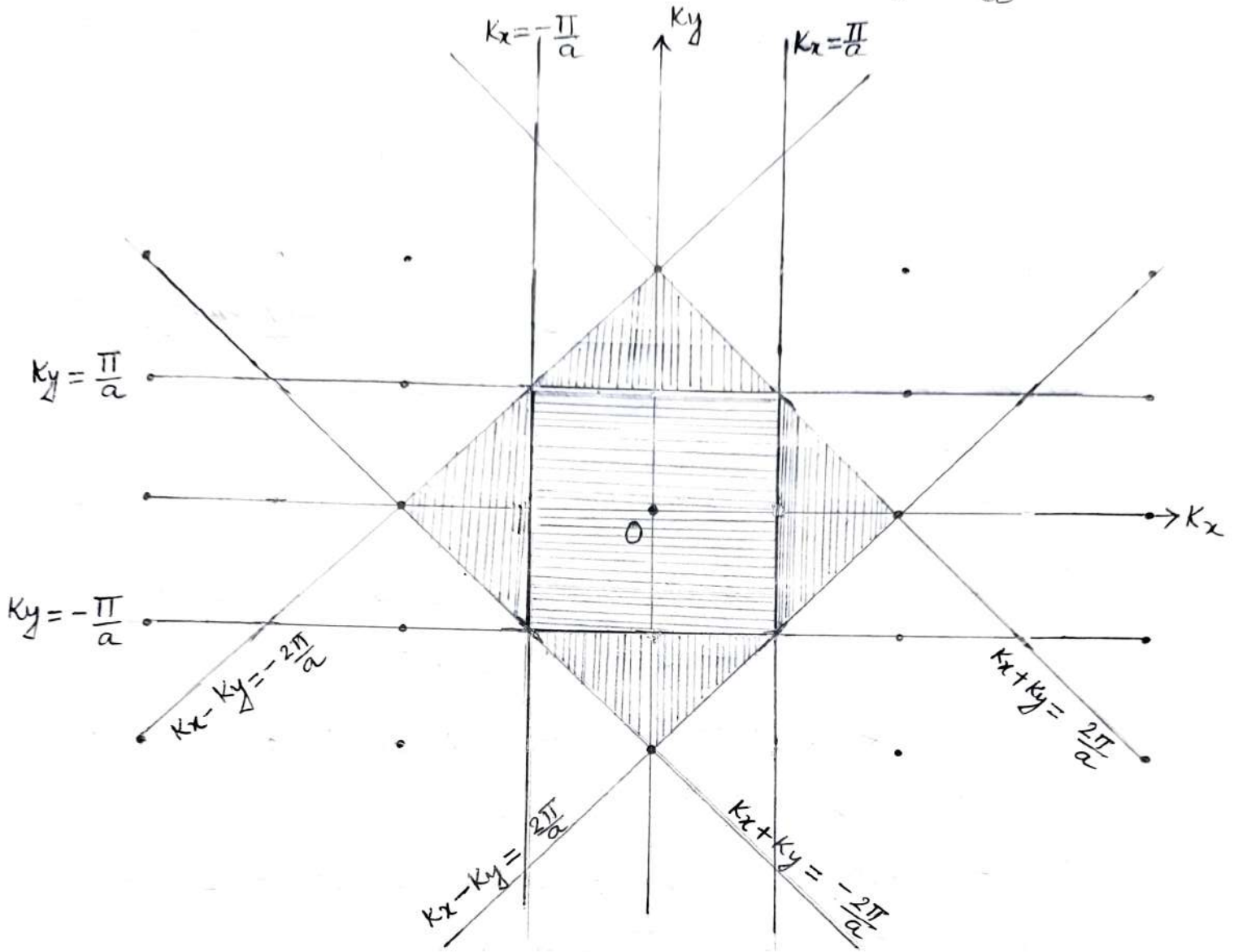
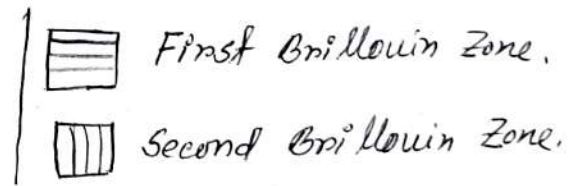


Fig:- Brillouin zone of a square lattice in its reciprocal lattice.



⊙ First Brillouin Zone:-

From the equations,  $k_x = \pm \frac{\pi}{a}$  and  $k_y = \pm \frac{\pi}{a}$ , Four lines are plotted in the figure taking origin at 0. All the  $k$  vectors from 0 to the lines will produce Bragg reflection.

The square bounded by these four lines is called first Brillouin zone.

So first Brillouin zone of a square lattice is also a square of side  $\frac{2\pi}{a}$ .

### ⊙ Second Brillouin Zone:-

From the equation,  $\pm k_x \pm k_y = \frac{2\pi}{a}$ , we get a set of four lines. These lines are also plotted on the figure. The additional area bounded by these four lines is the second Brillouin Zone.

### ⊙ Importance of Brillouin Zone of 1st and 2nd Order:-

- (i) The boundaries of the Brillouin zones represent the locus of  $k$ -values that are Bragg reflected and hence may be considered as the reflecting planes.
- (ii) The boundaries of the first zone represent the reflecting planes for the first order reflection.
- (iii) Similarly, for the the second zone represent the reflecting planes for 2nd order reflection.
- (iv) A  $k$ -vector does not terminate at a zone boundary can not produce Bragg reflection.

### ▣ Brillouin Zones of a Simple Cubic Lattice :-

From the above square lattice discussion, the Brillouin zones of a simple cubic lattice can be constructed by the generalized equation -

$$h k_x + k k_y + l k_z = - \left( \frac{\pi}{a} \right) (h^2 + k^2 + l^2)$$

- (i) First zone is a cube having side equal to  $\frac{2\pi}{a}$ .
- (ii) Second zone is formed by adding pyramids to each face of the cube (first zone) as in the figure triangles are attached to the square in 2-D.

## ■ The Von Laue Treatment of X-ray Diffraction :-

Von Laue treated the phenomenon of diffraction in a more general way by considering the scattering of x-rays from individual atoms in the crystal. The diffraction maxima appear in some specific directions only by the recombination of scattered x-rays from the atoms in the crystal.

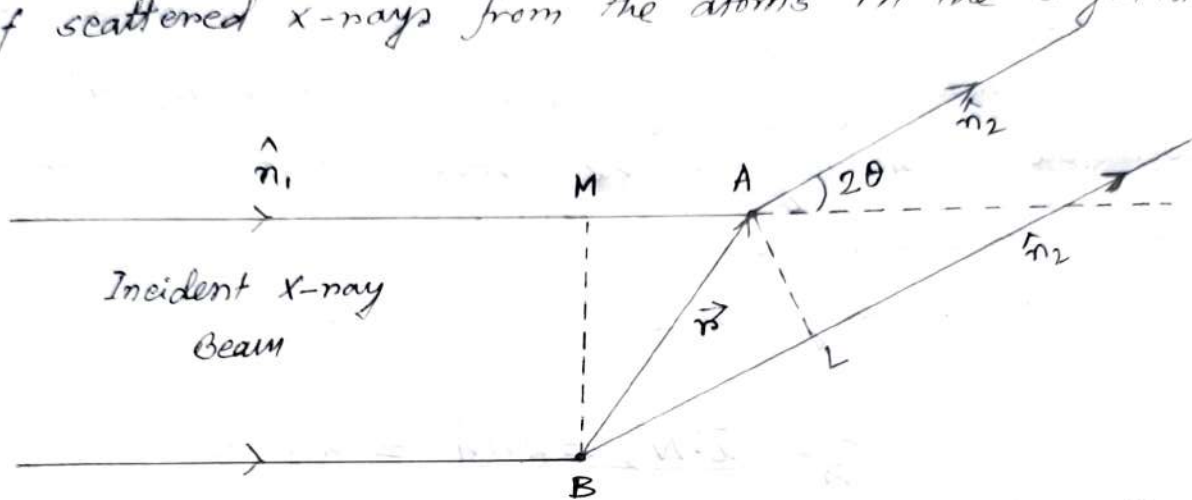
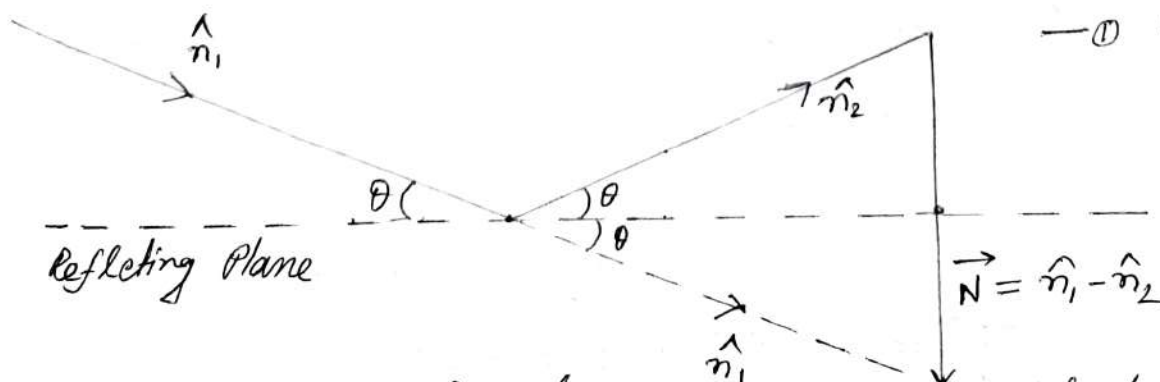


Fig:- Scattering of X-ray from two identical scattering centres separated by  $r$ .

Let, the scattering of an identical incident beam by two identical scattering centres A and B placed at a distance  $r$ .  $\hat{n}_1$  and  $\hat{n}_2$  are the unit vectors in the direction of incident and scattered beams respectively. The angle between  $\hat{n}_1$  and  $\hat{n}_2$  is  $2\theta$ . BM and AL are perpendiculars drawn to the direction of incident and scattered beams.

$$\begin{aligned} \therefore \text{Path difference} &= AM - BL = \vec{r} \cdot \hat{n}_1 - \vec{r} \cdot \hat{n}_2 \\ &= \vec{r} \cdot (\hat{n}_1 - \hat{n}_2) \\ &= \vec{r} \cdot \vec{N} \quad \left[ \text{Let, } \vec{N} = \hat{n}_1 - \hat{n}_2 \right] \end{aligned}$$



$$\begin{aligned} \frac{|\vec{N}|}{2} &= \sin\theta \\ \Rightarrow N &= 2\sin\theta \end{aligned}$$

Fig:- Geometrical relationship between the incident, scattered beam, reflecting plane with normal.



∴ Phase difference between the rays scattered from A and B —

$$\phi = \frac{2\pi}{\lambda} (\vec{n} \cdot \vec{N}) \quad \text{--- (2)}$$

The scattered X-ray beam radiations from A and B will interfere constructively if  $\phi$  is integral multiple of  $2\pi$ . Due to periodicity of crystal in 3-dimension,  $\vec{n}$  may coincide with any of the three crystallographic axes  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ . So for the diffraction maxima we get the following three conditions —

$$\left. \begin{aligned} \frac{2\pi}{\lambda} (\vec{a} \cdot \vec{N}) &= 2\pi h' = 2\pi n h \\ \frac{2\pi}{\lambda} (\vec{b} \cdot \vec{N}) &= 2\pi k' = 2\pi n k \\ \frac{2\pi}{\lambda} (\vec{c} \cdot \vec{N}) &= 2\pi l' = 2\pi n l \end{aligned} \right\} \text{--- (3)}$$

where,  $h'$ ,  $k'$  and  $l'$  are integers and Miller indices of the plane  $(hkl)$  have a common factor  $n$ .

Let,  $\alpha$ ,  $\beta$  and  $\gamma$  be the angles between the scattering normal  $N$  and crystallographic axes  $a$ ,  $b$  and  $c$  respectively.

$$\vec{a} \cdot \vec{N} = aN \cos \alpha = 2a \sin \theta \cos \alpha$$

Similarly,  $\vec{b} \cdot \vec{N} = 2b \sin \theta \cos \beta$

$$\vec{c} \cdot \vec{N} = 2c \sin \theta \cos \gamma$$

$$\left[ \because N = 2 \sin \theta \right]$$

--- (4)

So from equations (3) by using the value of equation (4) —

$$\left. \begin{aligned} \vec{a} \cdot \vec{N} &= 2a \sin \theta \cos \alpha = nh\lambda \\ \vec{b} \cdot \vec{N} &= 2b \sin \theta \cos \beta = nk\lambda \\ \vec{c} \cdot \vec{N} &= 2c \sin \theta \cos \gamma = nl\lambda \end{aligned} \right\} \text{--- (5)}$$

The equations no. (6) are known as Laue equations and represent the condition for diffraction to occur.

■ We already know, for a orthogonal system,  $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ .  
If the value of  $h, k, l$  and  $n$  are known, the equations (5) determine unique value of  $\theta$  and  $\vec{n}$  which define a scattering direction.

### ■ Bragg's Law From Laue's Equations:-

From Laue equations, we find that for a fixed value of  $\theta$ , the direction cosine of scattering normal are proportional to  $h/a, k/b$  and  $l/c$ .

Also, the direction cosines of the normal to any arbitrary plane  $(hkl)$  are proportional to  $h/a, k/b$  and  $l/c$ .

From the above two statements, we can conclude that scattering normal ( $\vec{n}$ ) is the same as the normal to the plane  $(hkl)$ .

If  $d_{hkl}$  is the interplanar spacing between two adjacent planes of family  $(hkl)$ , then,

$$d_{hkl} = \frac{a}{h} \cos\alpha = \frac{b}{k} \cos\beta = \frac{c}{l} \cos\gamma$$

— (6)

Putting these values in Laue's Equation (5) we get -

$$\boxed{2d_{hkl} \sin\theta = n\lambda}$$

which is Bragg's Law.

## Atomic Scattering Factor ( $f$ ):-

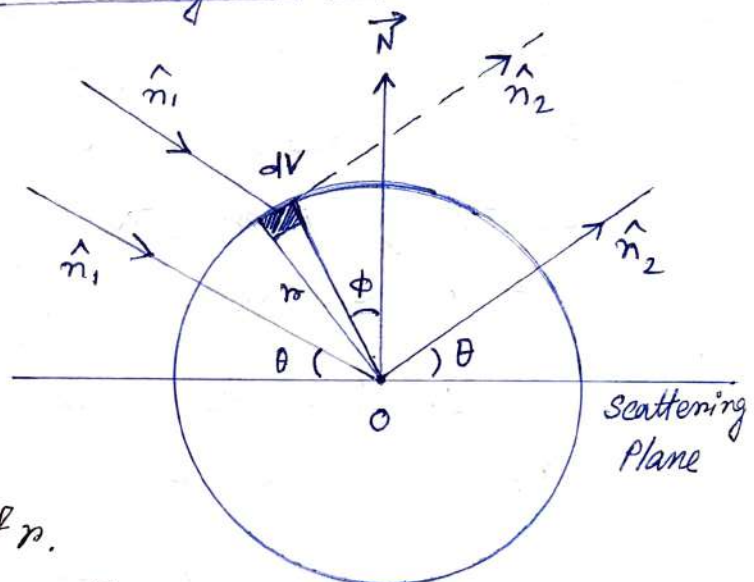
The atomic scattering factor or form factor ( $f$ ), describes the scattering power of a single atom in relation to the scattering power of a single electron.

$$f = \frac{\text{Amplitude of X-ray scattered by an atom}}{\text{Amplitude of X-ray scattered by an electron}}$$

In general,  $f < Z$  (atomic number). In limiting case,  $f$  approaches to  $Z$ .

## Expression of Atomic Scattering Factor ( $f$ ):

Let, an atom containing electrons arranged in a spherically symmetric configuration around its centre at origin  $O$ .



$r$  = radius of the atom.

$\rho(r)$  = charge density at  $r$ .

$dV$  = small volume element at  $r$ . [Fig:- Geometry of X-ray scattering for the calculation of 'f'.]

$\hat{n}_1$  = direction of incident X-ray beam.

$\hat{n}_2$  = direction of scattered X-ray beam.

$\vec{N}$  = scattering normal.

$\therefore$  Total change in the volume  $dV$ , =  $\rho(r) dV$

Now, phase difference between the wave scattered from the charge  $\rho(r) dV$  and that from an electron at origin  $O$  is -

$$\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{N})$$

Let, scattering amplitude from the electron at 0 in the direction  $\hat{n}_2$  is  $Ae^{i(kx - \omega t)}$ .

Then, the scattering amplitude from the charge  $\rho(r) dV$  in the same direction  $\hat{n}_2$ , will be proportional to the magnitude of charge and will contain the phase factor  $e^{i\phi_n}$ , so the amplitude is of the form -  

$$Ae^{i(kx - \omega t) + i\phi_n} \cdot \rho(r) dV$$

$\therefore$  The ratio of the amplitude of scattered x-ray from volume element  $dV$  and that scattered by a point electron at origin -

$$df = \frac{Ae^{i(kx - \omega t) + i\phi_n} \cdot \rho(r) dV}{Ae^{i(kx - \omega t)}} \\ = e^{i\phi_n} \cdot \rho(r) dV$$

again, The ratio of amplitude for the whole atom is

$$f = \int_V \rho(r) \cdot e^{i\phi_n} \cdot dV$$

Now, using the spherical polar co-ordinate -

$$dV = 2\pi r^2 \sin\phi \, d\phi \, dr$$

$$\text{and, } \phi_n = \frac{2\pi}{\lambda} \cdot rN \cos\phi = \frac{2\pi}{\lambda} \cdot r \cdot 2\sin\theta \cdot \cos\phi \\ = \left(\frac{4\pi}{\lambda} \sin\theta\right) r \cos\phi \\ = \mu r \cos\phi$$

$$\left[ \text{as, } |\vec{N}| = 2\sin\theta \text{ and let } \mu = \frac{4\pi}{\lambda} \sin\theta \right]$$

$$\therefore f = \int_{r=0}^{\infty} \int_{\phi=0}^{\pi} \rho(r) e^{i\mu r \cos \phi} \cdot 2\pi r^2 \sin \phi \cdot d\phi \cdot dr$$

$$\text{or, } \boxed{f = \int_0^{\infty} 4\pi r^2 \rho(r) \frac{\sin \mu r}{\mu r} dr}$$

$$\left[ \because \int_0^{\pi} e^{i\mu r \cos \phi} \cdot \sin \phi \cdot d\phi = \frac{2 \sin \mu r}{\mu r} \right]$$

This is the general expression for atomic scattering factor.

▣ The variation of  $f$  with  $\frac{\sin \theta}{\lambda}$  for Magnesium ( $Z=12$ ) is shown in the figure.

When,  $\theta \rightarrow 0$ ,  $f \rightarrow Z$ .

The same result is also satisfy the theoretical expression -

when,  $\theta \rightarrow 0$ ,  $\mu (= 4\pi \frac{\sin \theta}{\lambda}) \rightarrow 0$

and  $\frac{\sin \mu r}{\mu r} \rightarrow 1$

$$\therefore f = \int_0^{\infty} 4\pi r^2 \rho(r) dr = Z$$

ie,

The integral represents, the charge inside the spherical shell of radius  $r$  and thickness  $dr$ . The total charge inside a atom is  $Z$ .

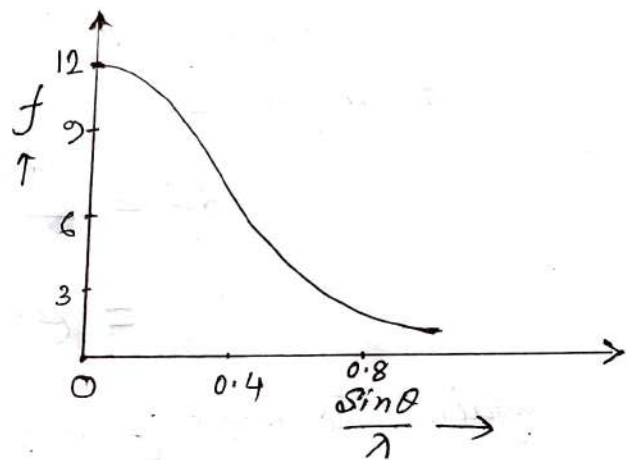


Fig:- Atomic scattering factor vs  $\frac{\sin \theta}{\lambda} (\text{\AA}^{-1})$  for Mg.

## Geometrical structure Factors :-

The intensity of an x-ray beam diffracted from a crystal not only depends on atomic scattering factors of the various atoms but also on the numbers, type and distribution of atoms within the unit cell.

### Definition :-

The ratio of the amplitude of the wave scattered by all the atoms in the unit cell to that scattered by a free electron for the same incident beam of same wave length.

### General Expression :-

The total scattering amplitude  $F(hkl)$  from the reflection  $(hkl)$  is given by -

$$\begin{aligned} F(hkl) &= \sum_j f_j e^{i\phi_j} \\ &= \sum_j f_j e^{i \cdot (2\pi/\lambda) \cdot (\vec{r}_j \cdot \vec{N})} \end{aligned}$$

where,  $f_j$  = The atomic scattering factor for  $j$ th atom

$\phi_j$  = Phase difference between the scattered x-ray from  $j$ th atom of unit cell to that from electron at origin.

$$= \frac{2\pi}{\lambda} (\vec{r}_j \cdot \vec{N})$$

$\vec{N}$  = scattering normal.

$\vec{r}_j$  = position of  $j$ th atom.

If the coordinate of the  $j$ th atom is  $(u_j, v_j, w_j)$ .

$$\therefore \vec{r}_j = u_j \vec{a} + v_j \vec{b} + w_j \vec{c}$$

$$\therefore (\vec{r}_j \cdot \vec{N}) = \lambda (u_j h + v_j k + w_j l)$$

$$\text{as, } \frac{2\pi}{\lambda}(\vec{a} \cdot \vec{N}) = 2\pi h$$

$$\text{or, } \vec{a} \cdot \vec{N} = h\lambda, \text{ similarly, } \vec{b} \cdot \vec{N} = k\lambda \text{ and } \vec{c} \cdot \vec{N} = l\lambda$$

$$\therefore F(hkl) = \sum_j f_j e^{i \cdot 2\pi (u_j h + v_j k + w_j l)}$$

For identical atoms, all the  $f_j$  have same value. let it is  $f$ . so the above equation takes a simple form -

$$F(hkl) = f S$$

$$\text{where, } S = \sum_j e^{2\pi i (u_j h + v_j k + w_j l)}$$

The expression  $S$  is the geometrical structure factor as it depends on the geometrical arrangements of atoms within the unit cell.

### ▣ Structure Factor ( $S$ ) for Simple Cubic (sc):-

In simple cubic, number of atoms per unit cell is one. Let, it lies at origin  $(0, 0, 0)$ .

$$\begin{aligned} \therefore S &= e^{2\pi i (0 \cdot h + 0 \cdot k + 0 \cdot l)} \\ &= e^0 \\ &= 1 \end{aligned}$$

$$\therefore F(hkl) = f$$

$$\text{and intensity, } I = |F|^2 = F * F = f^2$$

so, Intensity does not depend on  $h, k, l$  i.e., any particular type of planes.

### Structure factor for BCC:-

The effective number of atoms in a BCC unit cell is two. If co-ordinate of the any corner atom is  $(0,0,0)$ , then the centered atom has co-ordinate  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

$$\begin{aligned}\therefore S &= [e^{2\pi i(0+0+0)} + e^{2\pi i(\frac{h}{2} + \frac{k}{2} + \frac{l}{2})}] \\ &= [1 + e^{\pi i(h+k+l)}]\end{aligned}$$

where,  $S$  depends on  $h, k, l$ . So intensity ( $I$ ) depends on particular type of plane.

Conditions:-

(a) If  $(h+k+l) = \text{even}$ .

$$\therefore e^{\pi i(h+k+l)} = 1$$

$$\therefore \boxed{S=2} \text{ and } F(hkl) = 2f$$

(b) If,  $(h+k+l) = \text{odd}$ .

$$e^{\pi i(h+k+l)} = -1$$

$$\therefore \boxed{S=0} \text{ and } F(hkl) = 0$$

$$\therefore \text{Intensity } (I) = 4f^2 \text{ ( } h+k+l = \text{even) }$$

$$= 0 \text{ ( } h+k+l = \text{odd) }$$

$\therefore$  Reflection allowed for even values of  $(h+k+l)$ .

### Structure factor of FCC:-

An FCC unit cell has four identical atoms. One of these atoms is contributed by corners and its coordinate is  $(0,0,0)$ . Other three atoms are face centred and their co-ordinates  $(\frac{1}{2}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(0, \frac{1}{2}, \frac{1}{2})$ .



$$\therefore s = [e^{2\pi i(0+0+0)} + e^{2\pi i(\frac{h}{2} + \frac{k}{2})} + e^{2\pi i(\frac{h}{2} + \frac{l}{2})} + e^{2\pi i(\frac{k}{2} + \frac{l}{2})}]$$

$$= [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

So,  $s$  depends on the values of  $h, k, l$ .

● Condition:-

(a) If  $(h, k, l)$  are all odd or all even.

$$s = [1 + 1 + 1 + 1]$$

$$= 4$$

$$\therefore F(hkl) = 4f$$

Intensity,  $I = 16f^2$   
 so, Reflections of the type  $(111), (200), (220)$  are present.

(b) If  $(h, k, l)$  are mixed.

suppose,  $(100)$  type of reflection-

$$s = 1 + e^{i\pi} + e^{i\pi} + e^0$$

$$= 1 - 1 - 1 + 1$$

$$= 0$$

$$\therefore F(hkl) = 0$$

$$I = 0$$

so, reflection of the type  $(100), (110), (211)$   
 are absent for FCC crystal.

● Extinction Rules For cubic crystal:-

Crystal	Reflection allowed for
Simple cubic (sc)	all possible values of $h, k$ and $l$ .
Body centered cubic (bcc)	even values of $(h+k+l)$
Face centered cubic (fcc)	all odd or all even values of $h, k$ and $l$ .

## ▣ Vibration of One Dimensional Diatomic Lattice :-

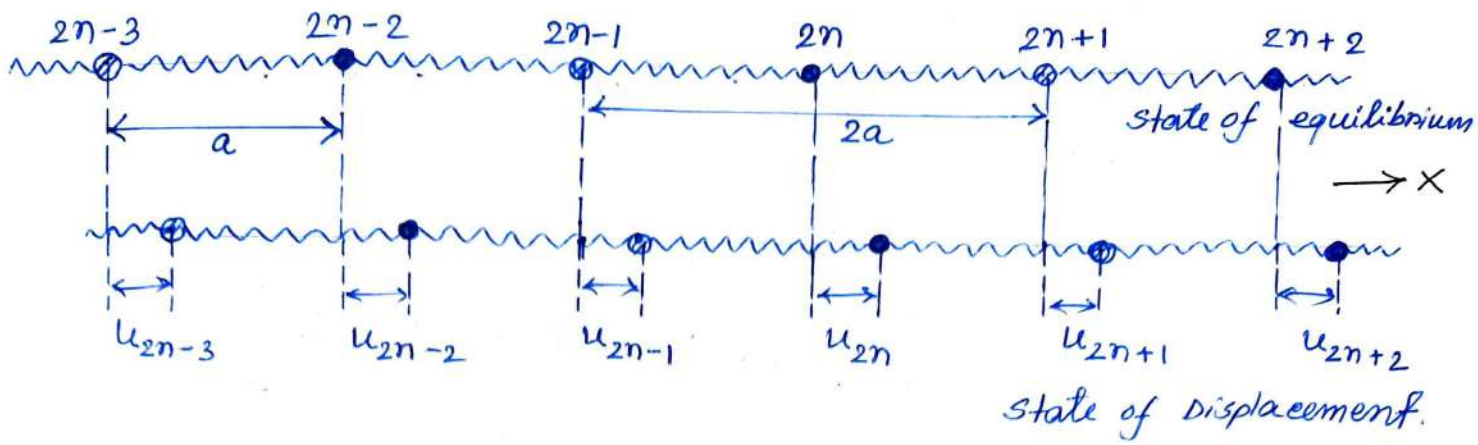


Fig- Linear Diatomic lattice in equilibrium and disturbed states.

Let, a one dimensional lattice with basis consisting of two atoms of masses  $m$  and  $M$  ( $m < M$ ) are placed alternatively along  $x$  axis with an interatomic distance  $a$ . In the state of equilibrium the atomic position are shown in the figure and the displacement of atoms are also shown at any instant during vibratory motion of atoms.

Equation of motion for the lighter atom of mass  $m$  -

$$F_{2n} = m \frac{d^2 u_{2n}}{dt^2} = \beta (u_{2n+1} + u_{2n-1} - 2u_{2n})$$

similarly, for heavier atom of mass  $M$  - ①

$$F_{2n+1} = M \frac{d^2 u_{2n+1}}{dt^2} = \beta (u_{2n+2} + u_{2n} - 2u_{2n+1})$$

Let, the periodic trial solution of the above equation - ②

$$u_{2n} = A e^{i(\omega t - 2Kna)}$$

$$u_{2n+1} = B e^{i[\omega t - (2n+1)ka]}$$

similarly,

$$u_{2n+2} = A e^{i[\omega t - (2n+2)ka]}$$

$$u_{2n-1} = B e^{i[\omega t - (2n-1)ka]}$$

③

$$\text{Now, } \frac{d^2 u_{2n}}{dt^2} = -\omega^2 A e^{i[\omega t - k2na]}$$

$$\text{and } \frac{d^2 u_{2n+1}}{dt^2} = -\omega^2 B e^{i[\omega t - k(2n+1)a]}$$

Now substituting all the values in equation (1) we get -

$$-\omega^2 A m e^{i[\omega t - k2na]} = \beta \left[ B e^{i[\omega t - k(2n+1)a]} + B e^{i[\omega t - k(2n-1)a]} - 2A e^{i[\omega t - k2na]} \right]$$

$$\text{or, } -m\omega^2 A = \beta [B(e^{ika} + e^{-ika}) - 2A]$$

$$\text{or, } m\omega^2 A = \beta [2A - 2B \cos ka]$$

$$\text{or, } (2\beta - m\omega^2) A - (2\beta \cos ka) B = 0 \quad \text{----- (4)}$$

similarly, from equation (2) we get -

$$(2\beta - M\omega^2) B - (2\beta \cos ka) A = 0 \quad \text{----- (5)}$$

For, non trivial solution of equation (4) and (5), the determinant of coefficient matrix must be vanishes -

$$\begin{vmatrix} 2\beta - m\omega^2 & -2\beta \cos ka \\ -2\beta \cos ka & 2\beta - \omega^2 M \end{vmatrix} = 0$$

$$\text{or, } (2\beta - m\omega^2)(2\beta - M\omega^2) - 4\beta^2 \cos^2 ka = 0$$

$$\text{or, } 4\beta^2 + Mm\omega^4 - 2\beta(M+m)\omega^2 - 4\beta^2 \cos^2 ka = 0$$

$$\text{or, } Mm\omega^4 - 2\beta(M+m)\omega^2 + 4\beta^2 \sin^2 ka = 0$$

$$\begin{aligned} \therefore \omega^2 &= \frac{2\beta(M+m) \pm \sqrt{4\beta^2(M+m)^2 - 4Mm \cdot 4\beta^2 \sin^2 Ka}}{2} \\ &= \frac{2\beta\left(\frac{1}{M} + \frac{1}{m}\right) \pm \sqrt{4\beta^2\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{16\beta^2}{Mm} \sin^2 Ka}}{2} \\ &= \beta\left(\frac{1}{M} + \frac{1}{m}\right) \pm \sqrt{\beta^2\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4\beta^2}{Mm} \sin^2 Ka} \\ &= \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) \pm \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 Ka} \right] \end{aligned}$$

$\omega^2$  has two values and each gives again two values for  $\omega$ .  
Now considering only positive values -

$$\left. \begin{aligned} \omega_+ &= \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) + \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 Ka} \right]^{1/2} \\ \omega_- &= \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) - \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 Ka} \right]^{1/2} \end{aligned} \right\} \text{--- (6)}$$

These are the dispersion relation for a linear diatomic lattice.

### ▣ Dispersion Curve :-

1. ● When  $K=0$ ,  $\sin^2 Ka = 0$ , then,  $\omega_+ = \text{maximum} = \omega_{+ \max}$ .

$$\omega_{+ \max} = \sqrt{2\beta\left(\frac{1}{M} + \frac{1}{m}\right)}$$

$$\omega_{- \min} = 0$$

So, the condition is -

$$\sin^2 Ka = 0$$

$$\text{or, } \sin Ka = \sin(2\eta \cdot \frac{\pi}{2})$$

$$\text{where, } \eta = 0, \pm 1, \pm 2, \dots$$

$$\therefore K = 0, \pm \frac{2\pi}{2a}, \pm \frac{4\pi}{2a}, \pm \frac{6\pi}{2a}, \dots$$

2. ● When,  $\sin^2 Ka = 1$ , then,  $\omega_+ = \text{minimum}$  and  $\omega_- = \text{maximum}$

$$\therefore \omega_{+ \min} = \sqrt{\frac{2\beta}{m}} \quad \text{and} \quad \omega_{- \max} = \sqrt{\frac{2\beta}{M}}$$

Condition:-  $\sin^2 Ka = 1$

or,  $\sin Ka = \sin (2n+1) \frac{\pi}{2}$

where,  $n = 0, \pm 1, \pm 2, \dots$

$\therefore k = \pm \frac{\pi}{2a}, \pm \frac{3\pi}{2a}, \pm \frac{5\pi}{2a}, \dots$

Summary:-

$\omega_{+max} = \sqrt{2\beta \left( \frac{1}{M} + \frac{1}{m} \right)}, \quad \omega_{+min} = \sqrt{\frac{2\beta}{m}}$

$\omega_{-max} = \sqrt{\frac{2\beta}{M}}, \quad \omega_{-min} = 0$

$[\omega_{+min} > \omega_{-max} \quad \text{as} \quad M > m]$

When,  $k = 0, \pm \frac{2\pi}{2a}, \pm \frac{4\pi}{2a}, \dots \quad \omega_{+} = \text{max}, \omega_{-} = \text{min.}$

$k = \pm \frac{\pi}{2a}, \pm \frac{3\pi}{2a}, \dots \quad \omega_{+} = \text{min.}, \omega_{-} = \text{max.}$

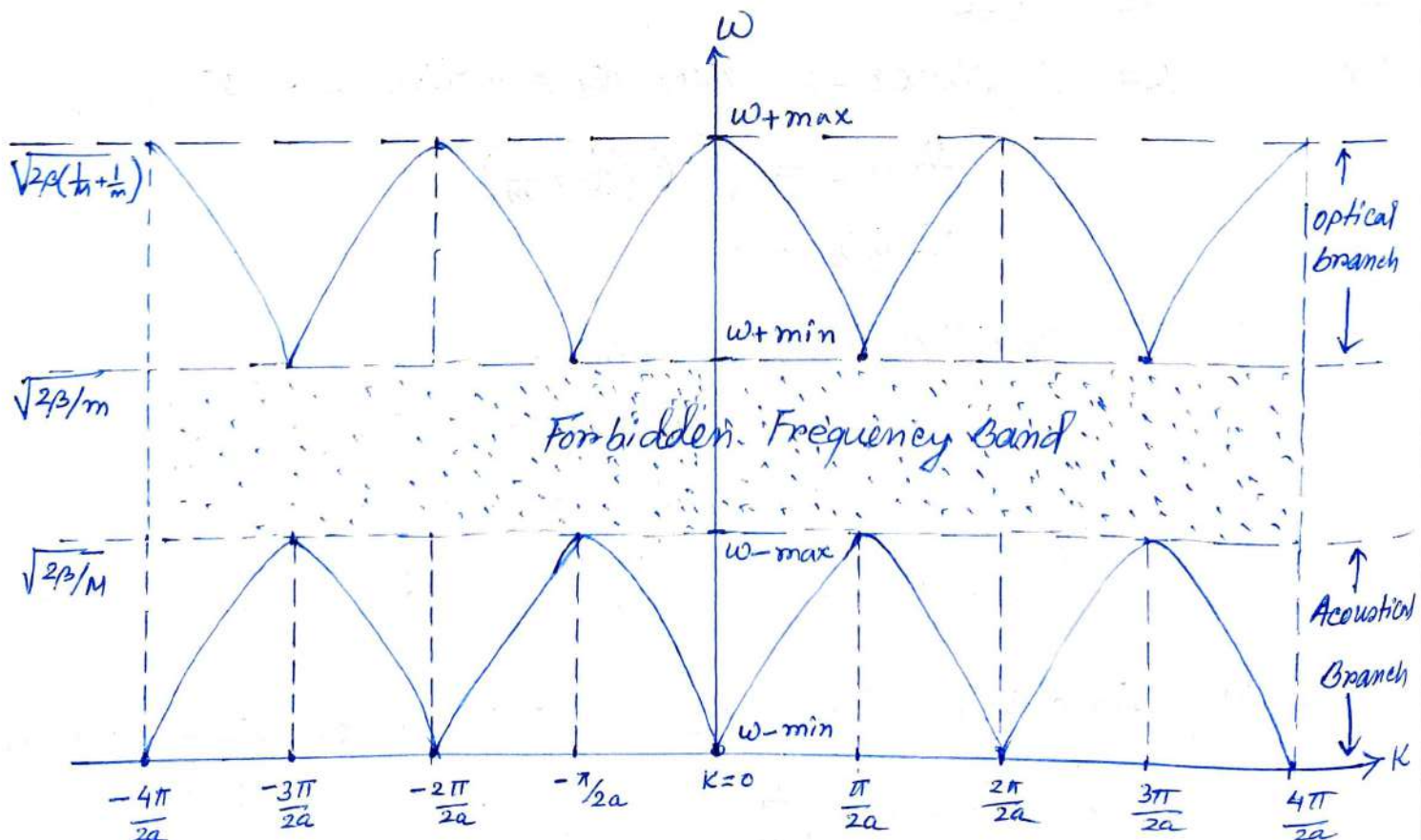


Fig:- Dispersion relations for linear Diatomic lattice.

## ELEMENTARY LATTICE DYNAMICS

A crystal lattice is regarded as a regular arrangement of atoms which are joined together by elastic springs. So motion of any single atom is shared by all the atoms. So the motion of the atoms are coupled. The lattice may vibrate freely due to its internal energy. The vibrations yield information about thermal properties of solid, such as specific heat and thermal conductivity.

### ■ Vibration of Linear monoatomic chain of Atoms :-

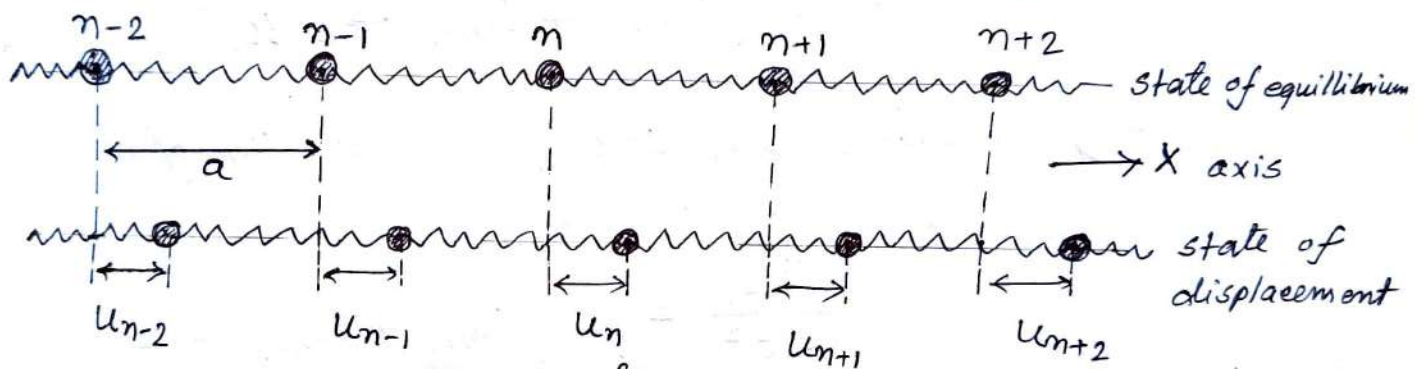


Fig - 1-D monoatomic Lattice in equilibrium and excited state.

Let, a one dimensional chain of atoms of mass  $m$  are arranged periodically along  $x$  axis. The atoms are attached to another by massless springs and spaced at a distance  $a$  in equilibrium state. But when they are excited, atoms execute periodic motion about their equilibrium position.

Let, at any instant of time, displacement of  $n$ th atom is  $u_n$ . Similarly, displacement of  $(n+1)$ th,  $(n+2)$ th,  $(n-1)$ th and  $(n-2)$ th atoms are  $u_{n+1}$ ,  $u_{n+2}$ ,  $u_{n-1}$  and  $u_{n-2}$  respectively.

Assuming nearest neighbour interaction and elastic force is proportional to the displacement, if  $u$  be the displacement of a spring with spring constant  $\beta$ , the force exerted by a spring on a atom -

$$\boxed{F = \beta u}$$

$\therefore$  Net force acting on the  $n$ th atom is

$$F_n = \beta (u_{n+1} - u_n) - \beta (u_n - u_{n-1})$$

$$\text{or, } F_n = \beta (u_{n+1} + u_{n-1} - 2u_n) \quad \text{--- (1)}$$

Using Newton's 2nd Law, the equation of motion is -

$$m \frac{d^2 u_n}{dt^2} = \beta (u_{n+1} + u_{n-1} - 2u_n) \quad \text{--- (2)}$$

Let, the periodic trial solution of the equation (2) is

$$u_n = u_0 e^{i(\omega t - k n a)} \quad \text{--- (3)}$$

where,  $k = \frac{2\pi}{\lambda}$  = wave vector.

$n a$  = x-coordinate of  $n$ th atom.

$\omega$  = angular frequency of the wave.

similarly, for  $(n+1)$ th and  $(n-1)$ th atoms -

$$\left. \begin{aligned} u_{n+1} &= u_0 e^{i[\omega t - k(n+1)a]} \\ u_{n-1} &= u_0 e^{i[\omega t - k(n-1)a]} \end{aligned} \right\} \text{--- (4)}$$

Now putting the values of (3) and (4) in equation (2) we obtain -

$$u_0 \cdot m \cdot (i\omega)^2 e^{i(\omega t - kna)} = \beta \left[ u_0 e^{i\{\omega t - k(n+1)a\}} + u_0 e^{i\{\omega t - k(n-1)a\}} - 2u_0 e^{i\{\omega t - kna\}} \right]$$

$$\text{or, } -m\omega^2 = \beta [e^{-ika} + e^{ika} - 2]$$

$$\text{or, } m\omega^2 = \beta [2 - (e^{ika} + e^{-ika})] \quad \left[ \text{as, } u_0 e^{i(\omega t - kna)} \neq 0 \right]$$

$$\text{or, } m\omega^2 = \beta [2 - 2\cos ka]$$

$$\text{or, } m\omega^2 = 2\beta \cdot 2 \sin^2\left(\frac{ka}{2}\right)$$

$$\text{or, } m\omega^2 = 4\beta \sin^2\left(\frac{ka}{2}\right)$$

$$\text{or, } \omega = \pm \sqrt{\frac{4\beta}{m}} \sin\left(\frac{ka}{2}\right)$$

since the angular frequency is not negative

$$\boxed{\omega = \sqrt{\frac{4\beta}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|} \quad \text{--- (5)}$$

### ▣ Dispersion Relation:-

Let,  $c = \text{longitudinal stiffness} = \beta a$

$\rho = \text{mass per unit length} = m/a$

From equation (5) becomes -

$$\omega = \frac{2}{a} \sqrt{\frac{c}{\rho}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

$$\text{or, } \omega = \frac{2}{a} v_s \left| \sin\left(\frac{ka}{2}\right) \right| \quad \text{--- (6)}$$

where,  $v_s = \sqrt{\frac{c}{\rho}} = \text{Constant for a given lattice.}$   
 $= \text{velocity of sound waves in solid.}$

$\omega$  and  $k$  are related by equation (6) and the equation is called dispersion relation.



## Dispersion curve :-

$$\omega = \sqrt{\frac{4\beta}{m}} \left| \sin \frac{Ka}{2} \right|$$

When,  $\sin \frac{Ka}{2} = 1$ , then  $\omega = \omega_{\max} = \sqrt{\frac{4\beta}{m}}$

$$\therefore \omega = \omega_{\max} \left| \sin \frac{Ka}{2} \right|$$

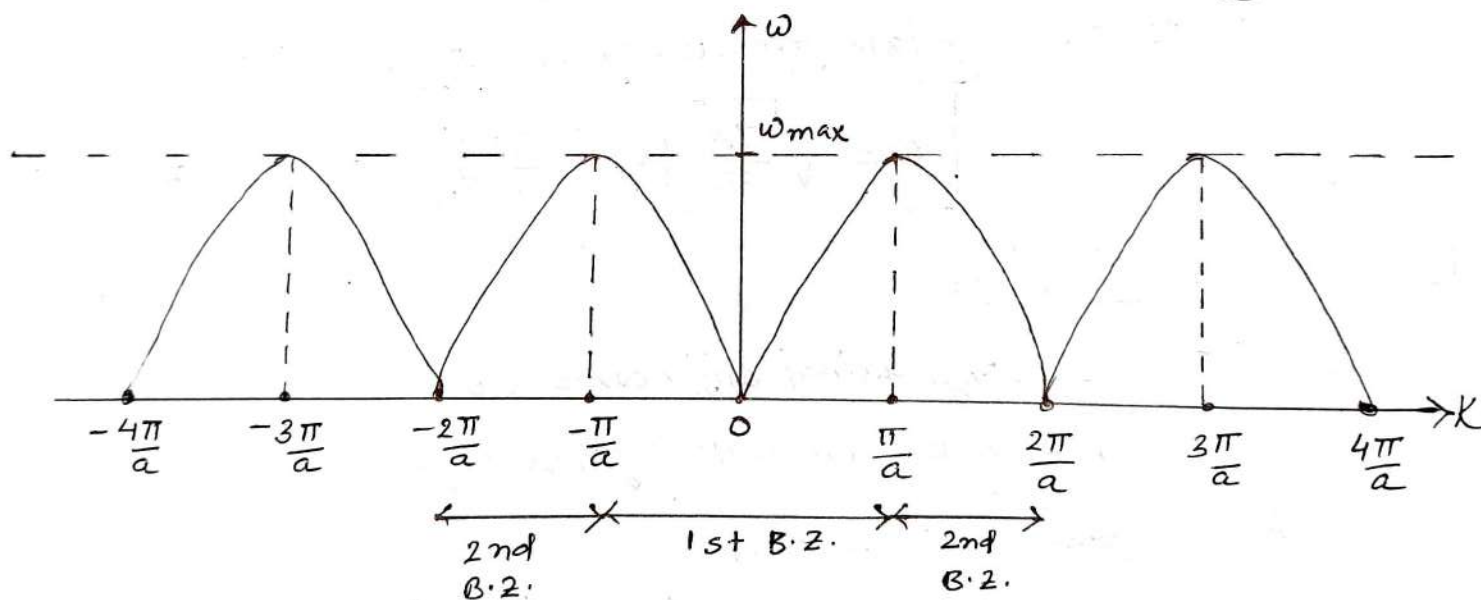
Condition for maxima,  $\left| \sin \frac{Ka}{2} \right| = 1$

or,  $\sin \frac{Ka}{2} = \pm 1 = \sin (2n+1) \frac{\pi}{2}$

or,  $K = (2n+1) \frac{\pi}{a}$ , where,  $n=0, \pm 1, \pm 2, \dots$

$\therefore \omega$  is maximum, when,  $K = \pm \frac{\pi}{a}, \pm \frac{3\pi}{a}, \pm \frac{5\pi}{a}, \dots$

$\omega$  is minimum when,  $K = 0, \pm \frac{2\pi}{a}, \pm \frac{4\pi}{a}, \dots$



### Brillouin Zones:-

1st Brillouin Zones:  $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a}$

2nd Brillouin Zones:  $-\frac{2\pi}{a} \leq K \leq -\frac{\pi}{a}$  and

$$\frac{\pi}{a} \leq K \leq \frac{2\pi}{a}$$

3rd Brillouin Zones:  $-\frac{3\pi}{a} \leq K \leq -\frac{2\pi}{a}$

and  $+\frac{2\pi}{a} \leq K \leq \frac{3\pi}{a}$

## Discussions:-

### (i) At Low frequency:-

At very low frequency,  $k \rightarrow 0$ . Hence  $\sin \frac{ka}{2} \rightarrow \frac{ka}{2}$

Dispersion relation,  $\omega = \frac{2}{a} v_s \left| \sin \frac{ka}{2} \right|$

or,  $\omega = \frac{2}{a} v_s \cdot \frac{ka}{2}$

or,  $\omega = v_s k$

(a) Phase velocity,  $v_p = \frac{\omega}{k} = v_s = \text{constant}$ .

(b) Group velocity,  $v_g = \frac{d\omega}{dk} = v_s = \text{constant}$ .

(c) The phase and group velocity are equal and independent of wavelength. Then the solid medium behaves like a non dispersive medium.

(d) For long wavelength or low frequency the atomic nature of solids is of little importance as far as the dynamical properties is concerned. This is due to the insensitiveness of the discrete medium to the waves of long wavelength.

### (ii) At high frequency:-

At high frequency,  $k \rightarrow \text{large}$ .

$$\omega = \frac{2}{a} v_s \left| \sin \frac{ka}{2} \right|$$

(a)  $v_p = \frac{\omega}{k} = \frac{2v_s}{ka} \left| \sin \frac{ka}{2} \right|$

$$v_g = \frac{d\omega}{dk} = v_s \left| \cos \frac{ka}{2} \right|$$

(b) Both  $v_p$  and  $v_g$  are function of frequency.

This refers the phenomena of dispersion and the medium is called the dispersive medium.

(ii) At maximum frequency or shortest wavelength :-

At,  $\omega = \omega_{\max} = \sqrt{\frac{4\beta}{m}}$  = which represent the maximum angular frequency of vibration.

at,  $k \rightarrow \frac{\pi}{a}$  ,  $\omega = \sqrt{\frac{4\beta}{m}} = \omega_{\max}$ .

(a)  $k = \frac{2\pi}{\lambda} = \frac{\pi}{a}$

or,  $\lambda = 2a$

(b)  $v_p = \frac{\omega}{k} = \frac{a}{\pi} \sqrt{\frac{4\beta}{m}} = \frac{2v_s}{\pi} = \text{constant}$

$v_g = \frac{d\omega}{dk} = 0$

(c) At maximum frequency, refers there is no transfer of signal or energy. Hence the wave behave like a standing wave.

⊙ So from the above discussion, we can conclude that, the vibration of frequency  $\omega < \sqrt{\frac{4\beta}{m}}$  or  $\omega < \frac{2v_s}{a}$  can propagate through the lattice. So the lattice behave like a low-pass filter which transmits only if the frequency lies between zero and  $\frac{2v_s}{a}$ .

## ■ Discussions :-

(a) The allowed frequency range of propagation is split into two branches. The upper branch is called optical branch and the lower one is called acoustical branch.

### (b) Forbidden Frequency Band :-

The frequency range between the top of the acoustical branch and the bottom of the optical branch is forbidden band. It is not possible to excite vibration in a lattice at a frequency which lies inside this band.

The width of the forbidden band depends on the mass ratio  $M/m$ . If  $M=m$ , the optical and acoustical branches coincide at  $k = \pm \frac{\pi}{2a}$  and forbidden gap disappears.

Band width of forbidden frequency gap

$$= \omega_{+ \text{ min}} - \omega_{- \text{ max}}$$

$$= \sqrt{\frac{2\beta}{m}} - \sqrt{\frac{2\beta}{M}}$$

$$= \sqrt{2\beta} \left( \frac{1}{m} - \frac{1}{M} \right)$$

### (c) Acoustical Branch :-

The vibrations of the acoustical branch can be excited by a force which makes the atoms in a crystal move in the same direction. This type of effect may be produced, for example, by directing a beam of sound waves on the surface of a crystal. So the vibration is known as acoustical branch vibration. Monoatomic crystal respond to such vibration.

From dispersive curve, at  $k=0$ ,  $\omega = \omega_{- \text{ min}} = 0$   
(for acoustical branch.)

We can rewrite equation (A) -

$$(2\beta - m\omega^2)A - (2\beta \cos Ka)B = 0$$

Now, at  $K=0$   $\omega = \omega_{\min} = 0$

$$\therefore 2\beta A - 2\beta B = 0$$

or,  $\boxed{\frac{A}{B} = +1}$

This means that the two atoms of different masses moves in the same direction with the same amplitude.

There is a movement of their centre of masses as well.

This feature of acoustical branch holds for others  $K$  values too.



Fig: Acoustical mode of diatomic atoms.

#### (d) Optical Branch:-

The vibrations of the optical branch can be excited by a force which makes the two neighbouring atoms move in opposite directions. Optical radiations induce this type of vibrations in crystals. So these vibrations are called optical vibrations.

Ionic crystals comprising two type of opposite charged ions respond to such vibrations.

From dispersive curve - (optical branch)  
at  $K=0$ ,  $\omega = \omega_{\max} = \sqrt{2\beta \left(\frac{1}{m} + \frac{1}{M}\right)}$

Apply these values in equation (4) -

$$(2\beta - m\omega^2)A - (2\beta \cos Ka)B = 0$$

$$\text{or, } [2\beta - m \cdot 2\beta (\frac{1}{m} + \frac{1}{M})]A - 2\beta B = 0$$

$$\text{or, } (2\beta - 2\beta - 2\beta \frac{m}{M})A = 2\beta B$$

$$\text{or, } \boxed{\frac{A}{B} = -\frac{M}{m}}$$

This indicates that the two atoms move in opposite directions and their amplitudes are inversely proportional to their masses so that the centre of mass of the unit cell remains unchanged.

$$\text{If, } M=m, \quad \boxed{\frac{A}{B} = -1}$$

If masses are equal, the atoms always move in opposite directions.

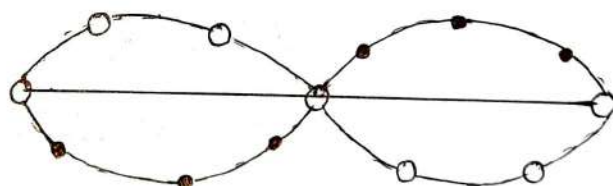


Fig:- Optical mode of vibration

### ▣ Phonons :-

The energy of an electromagnetic wave is quantized and this quantum of energy is called photon. Similarly, the energy of a lattice vibration or an elastic wave is also quantized and a quantum of this energy is known as phonon. Thermal vibrations are excited phonons, sound waves are acoustical phonons and optical

excitations of optical branch generates optical phonons.

- Energy of a phonon is given by,  $E = \hbar\omega$

where,  $\omega$  = angular frequency of a mode of vibration.

- If  $n$  is the number of phonons in a particular mode of vibration, the total energy of that mode is

$$E = n\hbar\omega$$

$n$  = zero or a positive integer.

- The number of phonons may change with temperature. The average number of phonons in a vibrational mode is

$$\bar{n} = \frac{1}{e^{(\hbar\omega/kT)} - 1}$$

$k$  = Boltzmann constant

$T$  = absolute temperature.

- Phonons are indistinguishable particles. So Bose-Einstein distribution function is required to describe their distribution in the allowed energy states of the system.

- Due to particle nature of phonon, they interact with other phonon or electron. This interaction is considered as a scattering collision between particles.