CRYSTAL DIFRACTION AND RECIPROCAL LATTICE

The x-rays are not reflected on normal Plane grating because x-rays are difracted if the grating has 40 million lines per centimeter C.M. Practically it is not Passible to construct these lines on normal grating.

Generally the grating has 6,000 lines per C.M. So x-rays are difracted on crystal it is Experimentally verified on 1912 by van Lave's crystal has 3D 3d atomic arrangement.

The condition for diffraction of x-rays is the Wave length of x-rays is comparable with interspacing of atoms in the lattice Plane of the crystal.

* Bragg's law :-

"W.L. Bragg" Presented a simple Explanation of the observed angles of the difracted beams from a crystal.

Consider a series of Parallel rows in which the atoms are arranged in given Plane of crystal. Suppose a Parallel beam of x-rays incident in direction making a glancing angle "θ" with the surface of Planes.

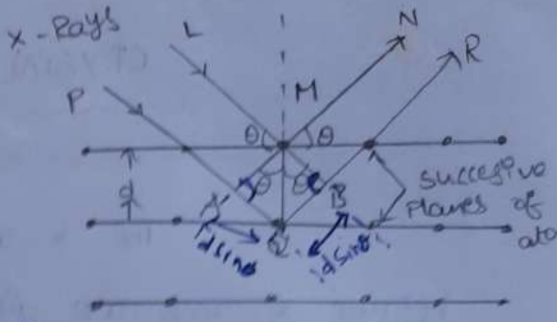
→ x-rays are much more Penetrate than ordinary line. the condition for reflected fronts are in same Phase, the Path difference between the reflected wave from one layer and that next layer must be an Exact wave length or, integral multiple of wave length.

→ let us consider two Parallel rays Planes LMN & PQR which are reflected by two atoms M & Q in adjcent layers is as shown in figure.

→ The atom Q is vertically below "M" The length of the Path PQR is greater than the length of the Path LMN

The Path difference is

$$QA + QB = n\lambda \quad -(1)$$



From figure $QA = QB = d\sin\theta$

$$2d\sin\theta = n\lambda \quad -(2)$$

∴ Reflection of x-rays from series of atomic layers in given Equation (2). gives condition for reflection of x-rays from series of atomic layers in given Plane. The "λ" is fixed Eqn (2) has a set of solutions.

$$\theta_1 = \sin^{-1}\left(\frac{\lambda}{2d}\right) \quad \text{if } n=1$$

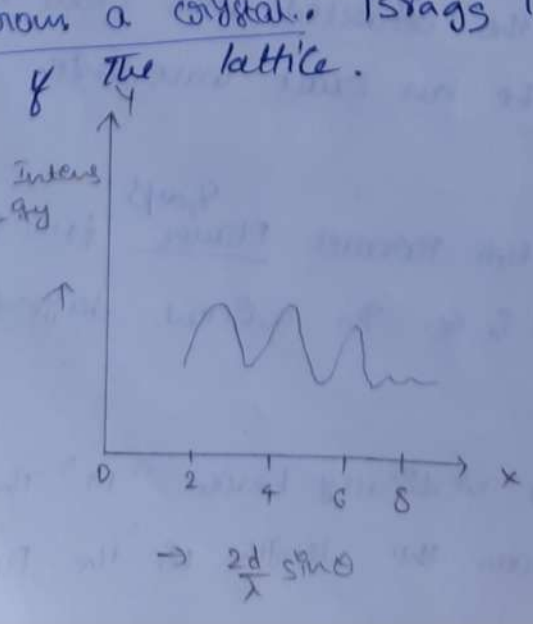
$$\theta_2 = \sin^{-1}\left(2\frac{\lambda}{2d}\right) \quad \text{if } n=2.$$

These are known as 1, 2, 3 - - etc. reflections according to n - Bragg's reflection can be occure only for wave length "λ" lessthan or equal to 2d.

The observed intensities of diffracted beam will show a series of diffraction maxima.

If wave length is varied at fixed angle "θ" is shown in the figure.

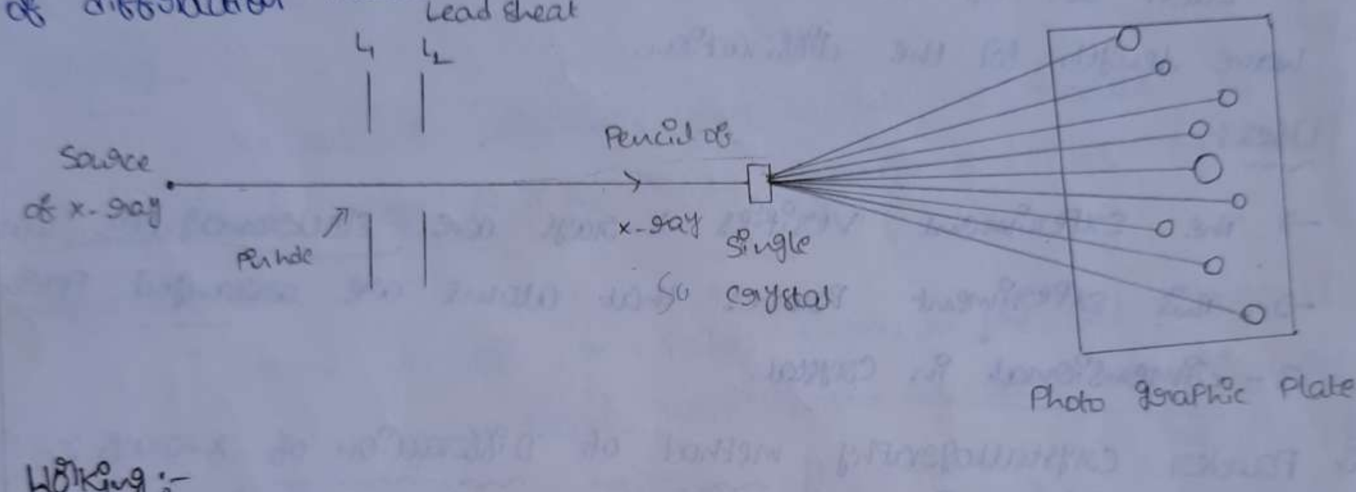
This law doesnot give any idea about the arrangement of atoms in the basis associated with each lattice Point. And * it Explain only observed angles of the diffracted beam from a crystal. Bragg's law is a consequence of the periodicity of the lattice.



* Experimental Diffraction Methods :-

1. Laue method of diffraction of x-rays :-

Description :- The operatus consists of coolidge tube maintains of 60,000 v btw Cathode and Anode. There are two Pin hold lead diaphrame and holder for setting the crystal. There will be a Photographic Plate for the Protection of diffraction Pattern.



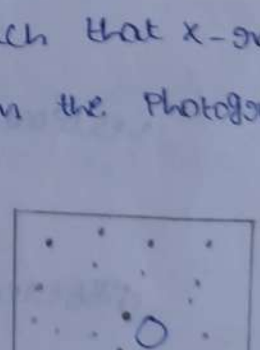
Working :-

The x-rays from coolidge tube will have continuous wave length. These x-rays passes through the led diaphrams to produce pencil of x-rays.

This pencil beam of x-rays fall on the crystal placed on the holder.

. The orientation of crystal is adjusted such that x-rays are diffracted. The diffraction pattern is obtained on the photographic plate.

In this experiment NaCl, $ZnSO_4$ are used.
(Single crystals are used)



Laue Pattern of cubic crystal.

observations:-

In this diffraction pattern there will be a centered bright spot "O". Around this spot many spots are produced symmetrically in series. This symmetrical pattern by a spots is called a "Laue's Pattern".

According to Bragg's law x-rays are diffracted by the atoms in the lattice planes of the crystal.

* Each set of lattice planes will have its own inter planer spacing distance "d". Different sets of lattice planes will have different glancing angles.

→ x-rays are diffracted by different set of lattice planes simultaneously to produce "Laue's Pattern".

→ Each set of lattice planes fixed out x-rays of corresponding wave length for the diffraction.

Uses:-

→ The experiment verifies x-rays are electromagnetic waves.

→ This experiment proves that atoms are arranged periodically 3-dimensional in crystal.

2. Powder crystallography method of Diffraction of x-rays :- (or)

Debye - scherrer method :-

In this powder method there will be millions of micro crystals and always many crystals with their lattice planes oriented so as to satisfy Bragg's law for the diffraction of x-rays. for the same values of n, θ & d,

The scattered beam produces a cone with semi vertical angle 2θ about the direction of incident x-rays.

For different values of "d" and "n" there will be different cones for a glancing angle θ.

The scattered ray or diffracted ray will be deviated by an angle 2θ.

Description :-

The apparatus consists of coolidge tube mainted at 60,000V between anode & cathode. There will be filter "F" and two Pin ~~halded~~ hole diaphrams. D_1 & D_2

The specimen in the form of powder struck on a thin wire "P". There will be a photographic film on the inner circum ference of a drum shaped cassatte. The specimen is placed at the center of cascatte.

Working :-

X-rays of different wave lengths are produced by the coolidge tube, these X-rays passes through a filter "F" give a monochromatic X-rays.

These X-rays are passes through the led diaphram give a pencil of X-rays beam. These pencil X-rays beam fall on the specimen powder P. X-rays pattern is observed on the photographic plate.

Point "A" on the film corresponds to glancing angle 2θ. The point "O" on the film corresponds to central maxima

Observation :-

From the photographic plate, the intersecting of different cones with the photographic film produces concentric circular rings due to narrow width of the film. The circular rings are cuts into ~~~~ arcs

If the glancing angle increases arcs ~~arcs~~ will be produced on the screen. If glancing angle reaches 90°, cones ~~between~~ become flat and straight lines are produced on the film.

If the glancing angle increases above 90° arcs are reversed. If the glancing angle reaches 180°, again circular rings are formed.

Let d_1, d_2 and d_3 be the distance between symmetrical lines on the film. Let "D" be the diameter of the photographic film.

$$\frac{4\theta}{d} = \frac{360^\circ}{\pi D}$$

$$\theta = \frac{90^\circ}{\pi D} \cdot d$$

$$\theta_1 = \frac{90^\circ}{\pi D} d_1 \; ; \; \theta_2 = \frac{90^\circ}{\pi D} d_2 \; ; \; \theta_3 = \frac{90^\circ}{\pi D} d_3 \; ; \ldots$$

Substitute $\theta_1 ; \theta_2 \,\&\, \theta_3 \ldots \theta_n$ the Bragg's law then the inter planar distance (d) is calculated.

For example cubic crystal taken in this experiment for given (h, k, l) plane, there will be 28 sets of lattice planes

* Derivation of Scattered Wave Amplitude :-

Let us consider incase of a plane wave which is incident on a small crystal. Let in the free space at point "x" the amplitude be F then

$$\boxed{F(x) = F_0 \, e^{i(kx - \omega t)}} \quad \text{--- ①}$$

* At point x=0 is an origin. Now Eqn ① represents a travelling wave having wave vector "k"; angular frequency "ω" and the wave length

$$\boxed{\lambda = \frac{2\pi}{k}}$$

* Now we place the crystal in the beam with origin "O" choose any where with in the crystal.

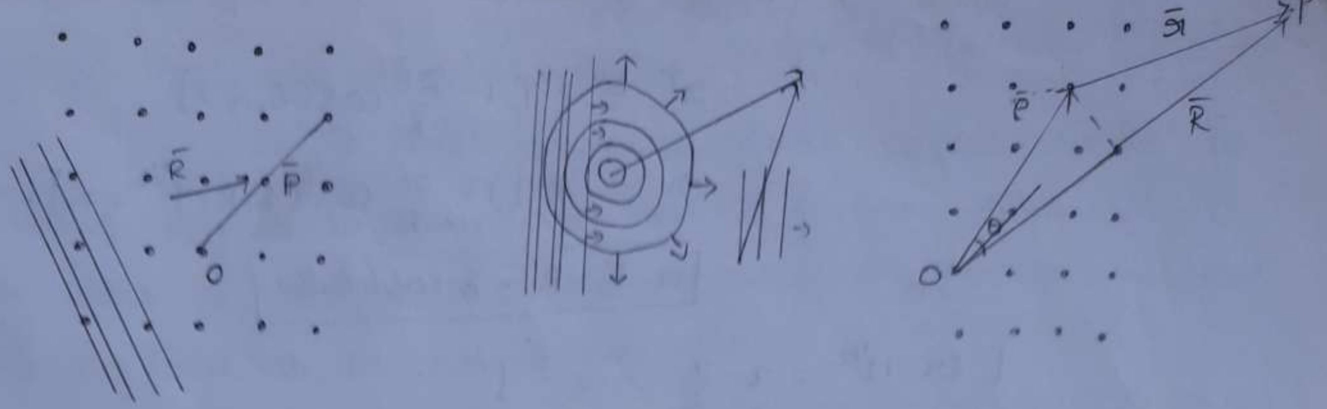


Fig i. shows

* At Point $\vec{P}$, the amplitude of incident wave is given by

$$F(\vec{P}) = F_0 e^{i(K\bar{\delta})} \quad \text{—(2)} \quad \text{at time } t=0.$$

* The atom at "$\bar{P}$" will be scatter some of radiation out of the incident beam.

From Fig ii, & iii. the amplitude of scattered radiation at Point "P".

$$\bar{R} = \bar{P} + \bar{r}$$

i.e., at a Point distance "r" from $\bar{P}$ outside the crystal will be Proportional to $(F_0 e^{ik\bar{\delta}})(\frac{e^{ikr}}{r})$ —(3)

Where $F_0 \cdot e^{ik\bar{\delta}}$ contains amplitude and Phase factor of the incident beam and second paranthesis $\frac{e^{ikr}}{r}$ describes spatial variations of the radiation scattered from $\bar{P}$.

The total Phase factor at "R" is given by

$$e^{ik\vec{\delta}} \cdot e^{ikr} = e^{ik\bar{\delta} + ikr} \quad \text{—(4)}$$

From figure iii, $r^2 = (R - \bar{\delta})^2$

$$= R^2 + \bar{\delta}^2 - 2R\bar{\delta}\cos(\bar{\delta}, R)$$

$$= R^2 \left[1 + \frac{\bar{\delta}^2}{R^2} - \frac{2\bar{\delta}}{R}\cos(\bar{\delta}, R)\right]$$

Where "R" is at a large distance $\frac{\bar{\delta}}{R} \ll 1$

$$r^2 \cong R^2 \left[1 - \frac{2\bar{\delta}}{R} \cos(\bar{\delta}, R) \right]$$

$$r \cong R \left[1 - \frac{2\bar{\delta}}{R} \cos(\bar{\delta}, R) \right]^{1/2} = R\left[1 - \frac{2\bar{\rho}}{R} \frac{\cos(\bar{\rho}, R)}{2} + \dots \right]$$

$$\boxed{r \cong R - \bar{\delta} \cos(\bar{\delta}, R)}$$

$$\left[(x-1)^{1/2} = x - \frac{x}{2} - \dots \right]$$

Now from Equation (4) the total Phase factor of the scattered wave at R is given by

$$e^{ik\bar{\delta} + ikR - ik\bar{\delta}\cos(\bar{\delta}, R)} \quad \text{--- (5)}$$

* Now assumed that the amplitude of the wave scattered from an Element of volume of the Crystal Proportional to Electron concentration $n(\bar{\delta})$ in volume Element.

* Hence the amplitude of scattered radiation at "R" will be Proportional to

$$\int dv . n(\bar{\delta}) . e^{ik\bar{\delta} - ik\bar{\delta}\cos(\bar{\delta}, R)} \quad \text{--- (6)}$$

Where e^{ikR} is Emitted being constant over the volume

Eqn (6) becomes

$$\boxed{\int dv . n(\vec{P}) e^{-i\bar{\delta}\Delta k}} \quad \text{--- (7)}$$

Where ;

$$ik\bar{\delta} - ik\bar{\delta}\cos(\bar{\delta}, R) \cong i\bar{\delta}(k - k') \; k' = k\cos(P, R) = -i.\delta \Delta k.$$

k' is wave vector in scattering direction R.,

$$\Delta k = k' - k$$

Eqn (7) gives the amplitude of scattered wave.

Reciprocal Lattice :-

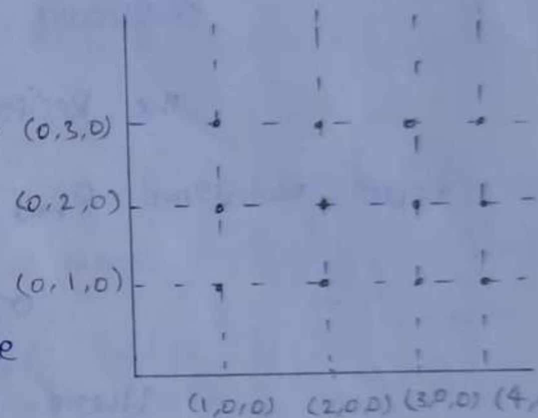
" It means that every plane in a real lattice becomes a point in the reciprocal lattice ".

It is built from the direct crystal lattice by constructing normal drawn parallel to each plane from a common origin with a length which is reciprocal of the interplanar spacing and then placing a point at the end of the normal.

The collection of the points is a lattice array and thus new lattice is called "Reciprocal lattice".

Graphical construction :-

The graphical construction of a reciprocal lattice is shown below.

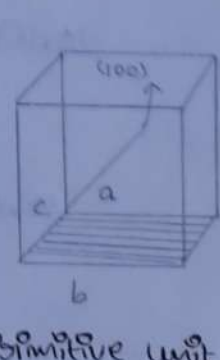


Consider a monoclinic crystal and all planes can be represented by a 2D - reciprocal lattice.

The example also shows the edge view of four (h,k,l) planes name (1,0,0) (1,1,0) (1,2,0) and (0,1,0) place a point on the normal to each plane (h,k,l) at a distance from the origin equal to $\left(\frac{1}{d_{hkl}}\right)$

Vector Development of the Reciprocal Lattice :-

The development of the reciprocal lattice by vector method is comparitively compact. The relationship betn the normal to a plane and crystallographic axes (a,b,c) by considering a primitive unit cell.



Primitive unit cell.

The premitive translation vectors of the direct lattice is a,b,c and primitive translation vectors of the reciprocal lattice are a^*, b^*, c^* are defined as

$$a^*\cdot b = a^*\cdot c = b^*\cdot c = b^*\cdot a = c^*\cdot a = c^*\cdot b = 0$$

$$\therefore a^* = \frac{b\times c}{a\cdot(b\times c)} ; \quad b^* = \frac{c\times a}{a\,(b\times c)} ; \quad c^* = \frac{a\times b}{a\cdot(b\times c)}$$

Now $a^*\cdot a = \dfrac{a\,(b\times c)}{a\,(b\times c)} = 1$

Similarly $b^*\cdot b = c^*\cdot c = 1$

$$\therefore a^* a = b^* b = c^* c = a . a^* = b b^* = c c^* = 1$$

The common denominator $a\cdot(b\times c)$ = vol^m of the direct lattice of the crystal.

Similarly the volume of the reciprocal lattice = $a^*\cdot(b^*\times c^*)$

The Reciprocal lattice vector σ_{hkl} can be written in vector notation σ_{hkl} can be written in vector notation

$$\sigma_{hkl} = h a^* + k b^* + l c^*$$

Where h, k, l are integers.

Properties of Reciprocal lattice :-

1. The Reciprocal of reciprocal lattice is "direct Lattice". The form of reciprocal vector is a^*, the reciprocal of reciprocal lattice vector is $(a^*)^*$ $\quad a^* = \dfrac{b\times c}{a\cdot(b\times c)}$

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

Multiplying right side by $a . a^* = 1$ $\left(\because a\cdot a^* = 1\right)$

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

Similarly $(b^*)^* = b$ and $(c^*)^* = c$

The Reciprocal of Reciprocal lattice is the direct lattice.

2. The volume of the unit cell of reciprocal lattice is inversely proportional to the volume of the unit cell of the direct lattice.

W.K.T, vol^m of the direct lattice $= a\cdot(b\times c)$

vol^m of the reciprocal lattice $= a^*\cdot(b^*\times c^*)$.

Now, we have to prove that $a(b\times c) = \dfrac{1}{a^*\cdot(b^*\times c^*)}$

(i), $a^*(b^*\times c^*) = \dfrac{1}{a(b\times c)}$

Consider

$$a^*(b^*\times c^*) = \frac{b\times c}{a\cdot(b\times c)}\left[\frac{c\times a}{a(b\times c)}\times\frac{a\times b}{a(b\times c)}\right]$$

(Reciprocal lattice is it self a SC lattice

(3) The Reciprocal lattice of simple cubic lattice is Direct lattice of simple cubic. (same it self)

(4) RPL of FCC is BCC viceversa

$$= \frac{1}{[a(b\times c)]^3}\left\{b\times c\left[c\cdot(a\times b)\cdot a\right] - b\times c\left[a(a\times b)\cdot b\right]\right\}$$

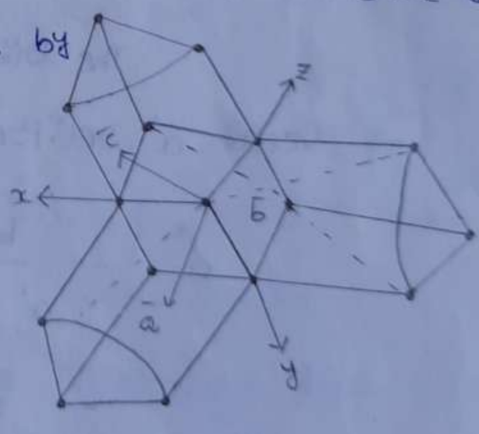
$$= \frac{(b\times c)(b\times c)\cdot a^2}{a^3(b\times c)^3} \quad [\because \text{By vector Identity}]$$

$$a^*(b^*\times c^*) = \frac{1}{a(b\times c)}$$

(i) FCC lattice is the reciprocal lattice of BCC
(ii) BCC lattice is the reciprocal lattice of FCC

Reciprocal Lattice to B.C.C lattice :-

The Primitive translation vectors of the B.C.C lattice as shown in the figure and are given by



$$a' = \frac{a}{2}\left[\bar{x}+\bar{y}-\bar{z}\right]$$

$$b' = \frac{a}{2}\left[-\bar{x}+\bar{y}+\bar{z}\right]$$

$$c' = \frac{a}{2}\left[\bar{x}-\bar{y}+\bar{z}\right]$$

Where "a" is the side of the conventional unit cube and $\bar{x}$, $\bar{y}$ & $\bar{z}$ are orthogonal unit vectors parallel to cubes edges.

W.K.T, the reciprocal lattice vectors

$$a^* = \frac{b\times c}{a(b\times c)}\ ; \quad b^* = \frac{c\times a}{a(b\times c)}\ ; \quad c^* = \frac{a\times b}{a(b\times c)}$$

Now $a^* = \frac{a}{2}[-\bar{x}+\bar{y}+\bar{z}] \times \frac{a}{2}[\bar{x}-\bar{y}+\bar{z}] \Big/ \frac{1}{2}a^3$

$$= \frac{1}{2a}\left[(-\bar{x}+\bar{y}+\bar{z})\times(\bar{x}-\bar{y}+\bar{z})\right]$$

$$= \frac{1}{2a}\left[\bar{z}+\bar{y}-\bar{z}+\bar{x}+\bar{y}+\bar{x}\right]$$

$$= \frac{1}{2a}\left[2\bar{x}+2\bar{y}\right]$$

$$a^* = \frac{\bar{x}+\bar{y}}{a}$$

Similarly $b^* = \frac{1}{a}(\bar{y}+\bar{z})$ and $c^* = \frac{1}{a}(\bar{z}+\bar{x})$

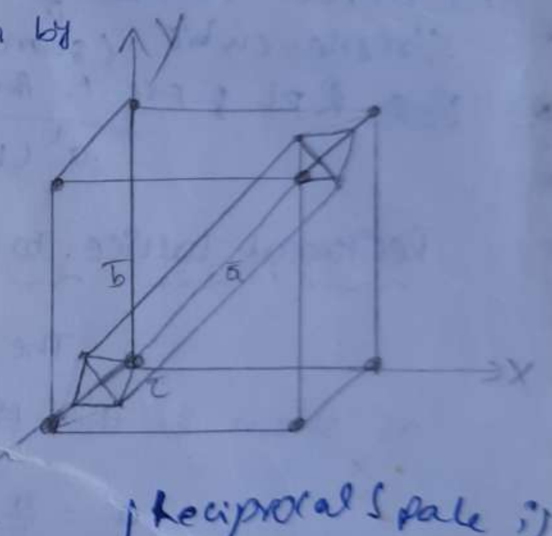
Reciprocal lattice to F.C.C Lattice :-

The Primitive translation vector of the F.C.C lattice are shown in the figure and given by

$$a' = \frac{a}{2}(\bar{x}+\bar{y})$$

$$b' = \frac{a}{2}(\bar{y}+\bar{z})$$

$$c' = \frac{a}{2}(\bar{z}+\bar{x})$$



The Primitive translation.

→ vector a' reciprocal Lattice a^* is

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

$$= \frac{\frac{a}{2}(\bar{y}+\bar{z})\times\frac{a}{2}(\bar{z}+\bar{x})}{\frac{a}{2}(\bar{x}+\bar{y})\left[\frac{a}{2}(\bar{y}+\bar{z})\times\frac{a}{2}(\bar{z}+\bar{x})\right]}$$

$$= \frac{2}{a}\,\frac{(\bar{y}+\bar{z})\times(\bar{z}+\bar{x})}{(\bar{x}+\bar{y})\left[(\bar{y}+\bar{z})\times(\bar{z}+\bar{x})\right]}$$

$$= \frac{2}{a}\,\frac{[\bar{x}+\bar{y}-\bar{z}]}{(\bar{x}+\bar{y})\left[(\bar{y}+\bar{z})\times(\bar{z}+\bar{x})\right]}$$

$$= \frac{2}{a}\cdot\frac{\bar{x}+\bar{y}-\bar{z}}{2}$$

Reciprocal space is also called as Fourier space, k-space or momentum space in opposite to the real space or direct space.

Similarly $a^* = \frac{1}{a}(\bar{x} + \bar{y} - \bar{z})$

$$b^* = \frac{1}{a}(-\bar{x} + \bar{y} + \bar{z})$$

and $c^* = \frac{1}{a}(\bar{x} - \bar{y} + \bar{z})$

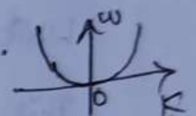
These are the Primitive translation vectors of B.C.C lattice and hence the F.C.C lattice is a reciprocal lattice of B.C.C Lattices.

Brillouin zones :- A Brillouin Zone is a particular choice of the unit cell of the reciprocal lattice. it is defind as the wigner - seitz cell of the reciprocal lattice.

In Kronig Penney Model that in one dimensional lattice the Energy discontinuetes occur when wave number "k" satisfies the condition

$$k = \frac{n\pi}{a}$$

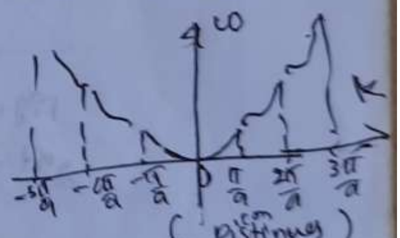
* The concept of Brillouin zone is particularly Imp in the consideration of the electronic structure of solids.



(no Discontinuties)

Where "n" is Positive or negative integer.

If we consider a line divided into Energy discontinuties into segments of length $\pm\frac{\pi}{a}$, then the first segment $+\frac{\pi}{a}$ to $-\frac{\pi}{a}$ is known as first "Brillouin zone" and similarly the segment $(+\frac{2\pi}{a}$ to $-\frac{2\pi}{a})$ is known as second Brillouin Zone.



(Distinues)

Construction of zones :-

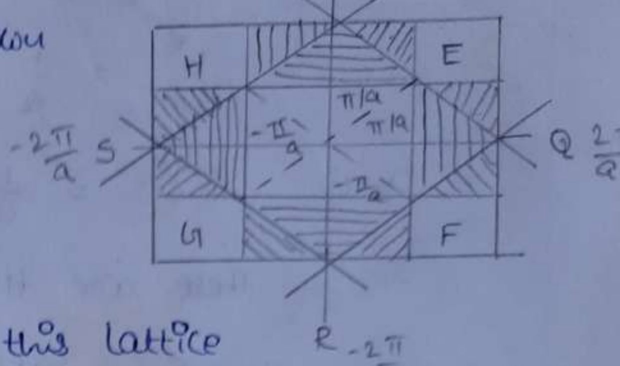
For many Purposes only first or reduced zone is sufficient but sometime the higher zones are desirable.

The Brillouin zones are constructed from the Planes which are the Perpendicular or bisectors of the reciprocal lattice vectors duran from the origin.

The first zone is the smallest volume about the origin enclosed by these Planes and similarly the second zone is the volume between the first zone and next set of Planes.

The Procedure consider the two dimensional square lattice as shown in figure.

Fig (a) : 3rd zone construction for 2D square lattice.



Reduction of zones :-

Each Brillouin zone for this lattice can be reduced into first zone. For example of second zone it has four separation sections. These four sections can be translated into the interior of first zone by moving the sections parallel to the axes by distances. Which are integral multiple of $\frac{2\pi}{a}$.

Four sections then fit together to form a square which is just an exact replica of first zone is shown in fig (b). This representation of second zone is known as reduced zone representation.

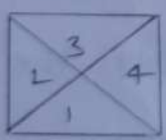


Fig (b)
2nd zone

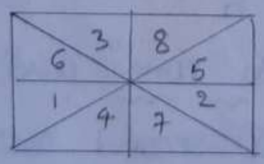


Fig (c)
3rd zone

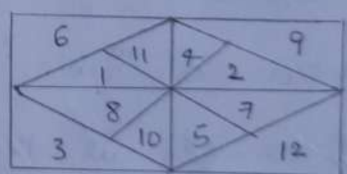


Fig. d
4th zone

Figures shown the Reduced zones.