Unit - I

CRYSTAL STRUCTURE

All matter condenses in solid state at sufficient low temperatures in practically. The study of the physical properties of matter in this state is called "Solid state Physics".

→ A solid material with such a regular atomic arrangements is said to be "Crystalline".

Ex:- NaCl, CsCl, Diamond etc.,

→ A solid material with out such a regular atomic arrangements is said to be "Non-Crystalline & Amorphous"

Ex:- Glass, Plastic etc.,

→ Amorphouses are also called as shapeless Crystalline, Most of solid matter is Crystalline. There are 20,000 Crystalline substances in the Crystal Kingdom.

"The study of the geometerical shape and Physical Properties of the solids using X-rays, Electron beams and neutron beams is known as Crystalography".

* Difference between Crystalline solids & Amorphous solids:-

Crystalline	Non-Crystalline
* symmetrical	* unsymmetrical
* more rigid	* less rigid
1. They will have regular Periodic arrangement of atoms (or) ions (or) molecules.	1. They do not have regular Periodic arrangement of atoms (or) Ions (or) molecules.
2. They will have definite melting & Boiling Points.	2. They donot have definite melting & Boiling Points.
3. Bond length between the atoms is identical (or) same	3. Bond length between the atoms are varying (or) changing.
4. They have an isotropic Physical Properties like Electrical Conductivity, thermal Conductivity & refractive index is in different directions. (Mechanical → different strength,	4. They have Isotropic Physical Properties like electrical conductivity, thermal conductivity and refractive index will be same in all directions.
	* Ex. Fibre glass, Napthalene, cell phones, Teflon, PVC

Coalition → thermal expansion

* Periodic Array of Atoms :-

Array means Pattern or arrangement of atoms in crystal that array of atoms gives structure of crystal.

Lattice :- Lattice is an imaginary arrangement of a regular Periodic array of Points in space which gives the shape of the crystal structure

The structure of all crystals can be described interms of a lattice.

Lattice Translation vectors :- When a lattice Point changes one translation Point to another Point, there is no change in the arrangement, that type of vector is called Lattice translation vectors. It is represented by $\bar{T}$.

The lattice is defined by 3- Fundamental translation vectors a_1, a_2, a_3 such that the atomic arrangement looks like the same in every respect when viewed from the Point "r" as when viewed from the Point "r'":

$$r' = r + u_1\bar{a}_1 + u_2\bar{a}_2 + u_3\bar{a}_3$$

Where u_1, u_2, u_3 are arbitary integers. The set of Points r' defined by u_1, u_2, u_3 defines a lattice.

Now, $\bar{T}$ interms of Fundamental translation vectors a_1, a_2, a_3 ~~a, b, c~~ as follows

$$\bar{T} = u_1a_1 + u_2a_2 + u_3a_3$$

The lattice and translation vectors a_1, a_2, a_3 are said to be Primitive if any two Points r, r' from which the atomic arrangement looks like the same, always satisfies with suitable integers u_1, u_2, u_3 that vectors are called "Primitive translation vectors".

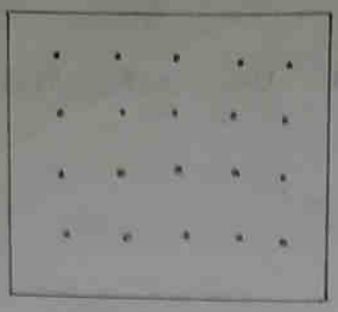


Fig a.
Lattice

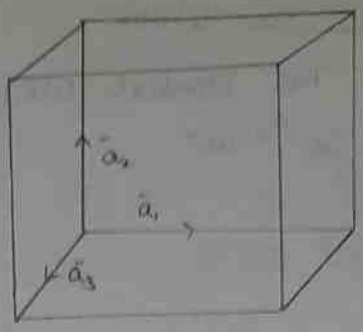


Fig b.
Lattice translation vectors in 2 & 3 dimensional crystal

* Symmetry operations :- A symmetry operation is one operation that leaves the crystal and its environment invariant.
Turn

Symmetry operations performed about a point or line is called point group symmetry & symmetry operations performed by translations as well as called "space group symmetry elements".

The following are the different point group symmetry elements exhibited by crystals.

i. Rotations :- A body is said to be possess rotational symmetry about an axis by some angle 'ϕ'. The body is left invariant as a result of Rotation.

The rotation angle ϕ must be an integral submultiple of 2π i.e.,

$$\phi_n = \frac{2\pi}{n}$$

Where "n" must be an integer is called multiplicity of rotation axis.

Fig:- Rotation through an angle ϕ.

The angles of ϕ_n restricted to 0° & 360°, 60°, 90°, 120° & 180° corresponding rotation axis 1, 6, 4, 3 & 2. This provides the crystal can have only 1, 2, 3, 4 & 6 fold axis of rotation and it can't have a five fold rotation.

ii. Reflection :-

A body is said to be possess reflection symmetry about a plane it is left unchanged in every where after being reflected in the plane. The below figure shows reflections by

using Notched wheel

The Symbol used to represent the reflection or mirror Symmetry is "m".

Fig (ii)

Fig (iii)

Fig (iii). shows the reflection Symmetry using notched wheel

Fig (iii). shows the reflection across a line.

(iii) Inversion :- Inversion is a Symmetry operation similar to reflection with only difference that reflection occurs in a plane through lattice Point, while Inversion occurs through a Point. An Inversion centre is equivalent to reflection is denoted by the Symbol "C".

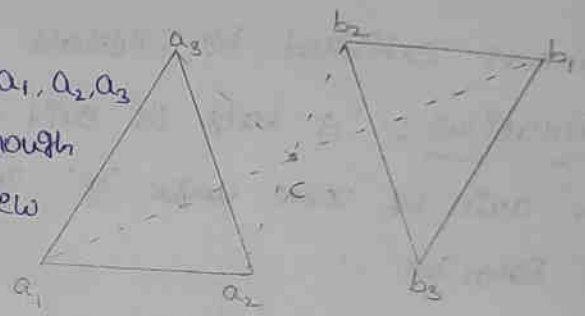


Fig. Shows Inversion Points a_1, a_2, a_3 of a triangle being reflected through the Point "C" and Producing the new Points b_1, b_2, b_3.

The different Symmetry Elements can also be combined if they are able to exist compatible. A combined rotation-Inversion operation is known as an improper rotation and corresponding axis as an improper axis.

Basis and Crystal Structure :-

Basis :- The combination of one or more number of atoms at the lattice Point is called "Basis".

The arrangement and Orientation of the base at the lattice Point must be identical by translating the base in all directions the total crystal can be obtained.

Let us consider a two-dimensional space lattice.

Fig (a)
Space lattice

Fig (b)
Basis containing two different ions.

In which the Environment about the Each Point is same. Fig (b) represents Basis, Big Circle shows one type of atom and small Circle shows another type of atom so the basis contains two atoms.

Crystal structure:-

The regular arrangement of atoms at the lattice Points inside the crystal is called crystal structure. It can be studied using space lattices.

The simple relation between lattice basis and crystal structure can be expressed as

Lattice + Basis = Crystal structure.

* Fundamental types of lattices:-

There are two types of Fundamental lattices They are

1. Two dimensional lattice types
2. Three dimensional lattice types.

1. Two Dimensional Bravais lattice:-

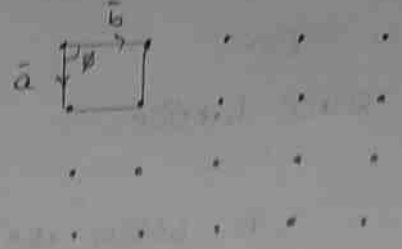
There are various way of positioning structure less Points in space such that all Points have identical surroundings these are called "Bravais lattices".

There are five Bravais lattice in Two-dimensions.

i. Oblique :-

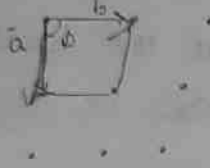
$\bar{a} \neq \bar{b}$ ϕ = arbitary

ii. Square :-



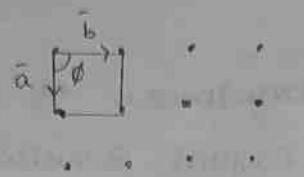
$\bar{a} = \bar{b}$; $\phi = 90^\circ$

iii. Hexagonal :-



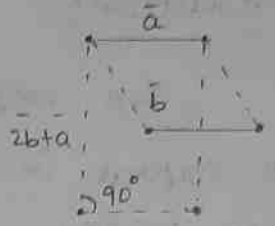
$\bar{a} \neq \bar{b}$; $\phi = 120^\circ$

iv. Rectangular :-



$\bar{a} \neq \bar{b}$, $\phi = 90^\circ$

v. Centered Rectangular :-



i. For Primitive cell $\bar{a} \neq \bar{b}$, $\phi = 90^\circ$

ii. For Non Primitive cell

$\bar{b} \neq \bar{a}$; $\phi = 90^\circ$

	Lattice	Conventional unit cell	Crystal axes	System	Point group
1	Oblique	Parallelogram	$a \neq b$; $\phi \neq 90$	Oblique	1, 2
2	Square	Square	$a = b$, $\phi = 90^\circ$	Square	4, 4mm
3	Hexagonal	Rhombous	$a \neq b$; $\phi = 120$	Hexagonal	3, 3m ; 6mm
4	Primitive rectangular	Rectangle	$a \neq b$; $\phi = 90^\circ$	Rectangle	1m, 2mm
5	Centered rectangular	Rectangle	$a \neq b$; $\phi = 90$	Rectangle	1m, 2mm

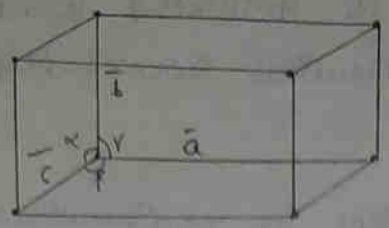
Bravais lattices in 3-dimensions:

There are various ways of positioning structureless points in space such that all points have identical surroundings. These are called "Bravais lattices".

There are 14 Bravais lattices in 3-dimensions. These 14 Bravais lattice (1 general & 13 special) are grouped into seven crystal systems according to the seven conventional unit cells.

Crystal system	Characteristic symmetry Elements	Bravais lattice & symbol	unit cell axes & angle	Example
Triclinic	None	Simple (P)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$FeSO_4 \cdot 5H_2O$ $CuSO_4$, $K_2Cr_2O_7$
Monoclinic	one 2-fold rotational axis	Simple (P) Base centered (C)	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	$LiSO_4 \cdot H_2O$ Gypsum
Orthorhombic	3 mutually ⊥ 2-fold rotation axes.	Simple (P) Base centered (C) Body centered (I) Face centered (F)	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ = \beta$	KNO_3, K_2SO_4 Ga, $PbCO_3$ Borax
Tetragonal	one 4-fold & 2-fold axes normal to 4-fold axis.	Simple (P) Body centered (I)	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	β-Sn white SnO_2
Cubic	Four 3-fold rotation axes.	Simple (P) Body centered (I) Face centered (F)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Au, Ag, Cu, Fe Diamond, NaCl
Hexagonal	one 6-fold rotation axis	Simple	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Zn, Cd, Mg Graphite, Ni
Trigonal	one 3-fold rotation axis	Simple	$a = b \neq c$ $\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$	As, Cd, Quartz Calcite, Bi, Sb

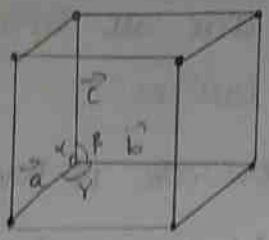
1. Triclinic :-



Simple (P)

$\bar{a} \neq \bar{b} \neq \bar{c}$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$

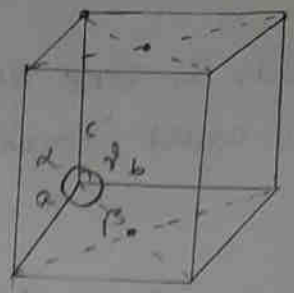
2. Monoclinic :-



Simple (P)

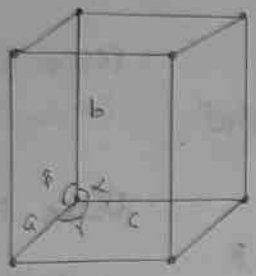
$\bar{a} \neq \bar{b} \neq \bar{c}$

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

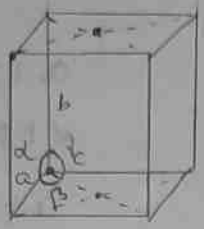


Base centered (C)

3. Orthorhombic :-

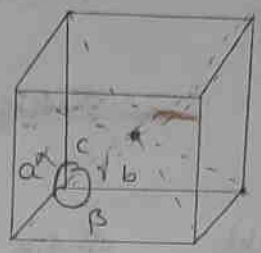


Simple (P)

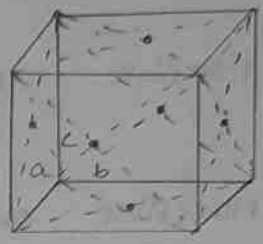


Base centered (C)

$\vec{a} \neq \vec{b} \neq \vec{c}$; $\alpha = \beta = \gamma = 90^\circ$

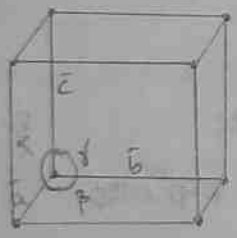


Body centered (I)



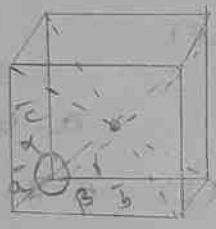
Face centered (F)

4. Cubic Crystal :-



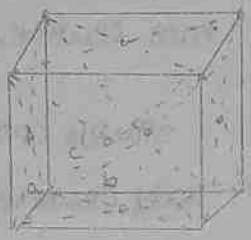
Simple (P)

$\bar{a} = \bar{b} = \bar{c}$;



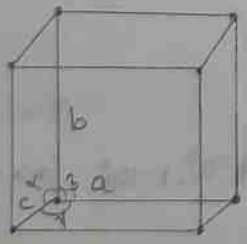
Body centered (I)

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



Face centered (F)

5. Tetragonal :-



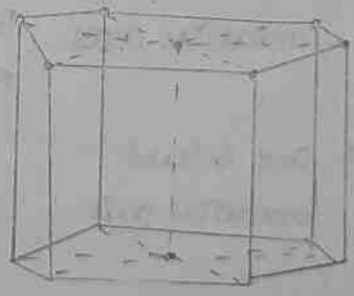
Simple (P)

$\bar{a} = \bar{b} \neq \bar{c}$

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

Body Centered (I)

6. Hexagonal :-



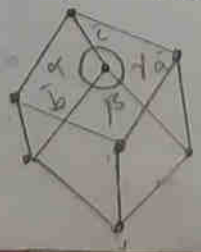
Primitive (P)

$\bar{a} = \bar{b} \neq \bar{c}$

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

$\gamma = 120^\circ$.

7. Trigonal :-



Primitive (P)

$\bar{a} = \bar{b} \neq \bar{c}$

$\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$.

Simple crystal structures:

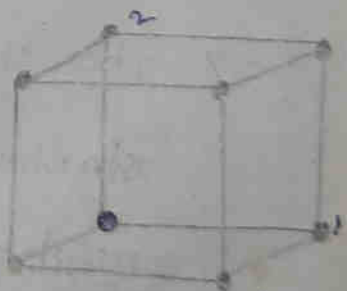
There are several types of crystal structures. The simplest one is the simple cubic lattice (SC). Two other cubic lattices are the Body Centered (BCC) and the Face Centered (FCC) cubic lattice.

Simple cubic:

→ In the structure, the atoms situated at the corners of the unit cubes, touching eachother along the edges.

→ Each atom is surrounded by '6' nearest neighbours, the coordination number is '6'.

→ The atomic radius 'r' is $a/2$, where 'a' is distance between two nearest neighbours and also called "Lattice constant".



ff: Simple cubic ~~lattice~~

→ Atomic radius is defined as "half the distance between the nearest neighbours.

→ The number of atoms per unitcell is '1'.

→ The volume of unitcell is a^3

→ The volume of atoms in the unit cell is $\frac{4}{3}\pi r^3$.

→ Therefore packing factor (or) packing density is $\frac{\text{volume of atom in unit cell}}{\text{volume of unit cell}} = \frac{4/3\,\pi r^3}{a^3} = \frac{\pi}{6}$. $\left[\because r = \frac{a}{2}\right]$

→ only one element polloneium (Po) at a certain below the 75° temp region exhibits this crystal structure.

Face centered cubic:

→ It is a cubic and an atom occupies each corners of the cube and the centre of each face hence the name is face centered cubic.

→ This structure is symmetrically w.r.to rotation by 90° above any one of the cube edge.

→ The structure is also called "closed packed' crystal structure because each atom as '12' nearest neighbours. Therefore the coordination number is 12

No. of atoms per unit cell – 4 & Volume a3

→ Elements possessing this structure are Cu, Ag, Au, Al, Pb & Pt.

fig

closed-packed-face centred cubic str

→ some transition elements and Rare earth elements crystaline in FCC structure.

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

Body centered cubic:

→ The unitcell is cubic and cell consists one atom at each corner and one atom in the centre of Body cubic E

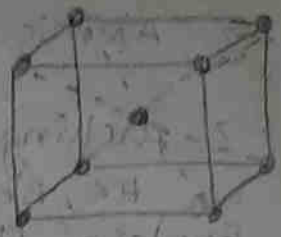


fig. The body centered cubic lattice

→ Each atom has only '8' atoms are nearest neighbours. so that the co-ordination number is '8'. Therefore we don't call it is a closed-packed structure.

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

→ Elements possess body centered cubic structure are like Na, k, Cr, Mo, W & ordinary modification of Fe. etcertra

• They are two atoms per unit cell of volume a^3

Hexagonal close packed structure: (HCP)

→ Mg, Zn, cd, Be, Rm crystals possess this structure.

→ It is a close-packed structure because this structure having highest packing density (or) packing factor and also co-ordination number is 12.

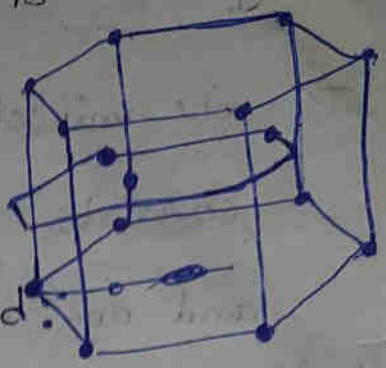
→ There it have '12' nearest neighbouring atoms and '6' atoms will be in its plane, three atoms in a plane above and three atoms in plane below.

HCP

→ The number of atoms in unitcell is '6'

→ Atomic radius 'r' = $a/2$

→ packing factor = $\frac{\sqrt{2}}{6}\pi$ = 0.74

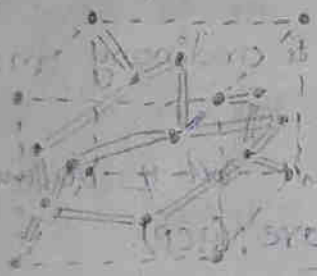


eg: He, Be, Mg, Ti, Zr.

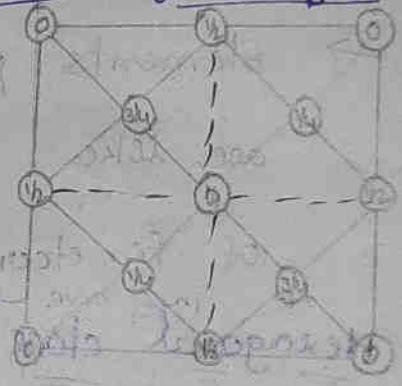
Explain the structure of diamond.

The diamond lattice can be formed by two interpenetrating FCC lattices along the body diagonal by 1/4 of the length of the body diagonal (one sub lattice as its origin at (0,0,0) and other at $[a/4, a/4, a/4]$. Basis Contain two atoms are identical in Diamond. But this two atoms are different in Zinc-Blende structure. (Zinc sulfide)

(projection of Diamon lattice points on the Base..



Atomic positions in the cubic cell of diamond



Basic projection of Diamond structure.

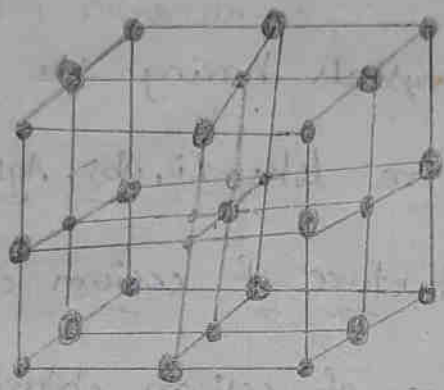
* The diamond structure is loosely packed since each atom has only four nearest neighbouring atoms. so the co-ordination number is four and 12 next nearest neighbours.

* The atomic packing density (or packing factor is 0.34 as compared to a value of 0.74 for the case of closed packed structure.

* carbon, silicon and germanium crystallize in diamond structure. In this structure the type of the bonding is covalent bonding.

Explain the structure of sodium chloride :-

The structure of the NaCl is also called "Rock salt structure" is as shown in fig.



Cl^- Ion
Na^+ Ion

structure

* The crystal can be constructed by arranging Na^+ ions and Cl^- ions alternatively at lattice points of a unit cube. The basis is a combination of one sodium ion and one chloride Cl^- ions seperated by distance, is equal to one half of the body diagonal of a unit cube.

* There are 4 units of NaCl in a unit cube, with Ions in the positions

$Na^+ \rightarrow (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\ (0,0,\frac{1}{2})\ (0,\frac{1}{2},0)\ (\frac{1}{2},0,0)$

$Cl^- \rightarrow (0,0,0)\ (\frac{1}{2},\frac{1}{2},0)\ (\frac{1}{2},0,\frac{1}{2})\ (0,\frac{1}{2},\frac{1}{2})$

Physical properties

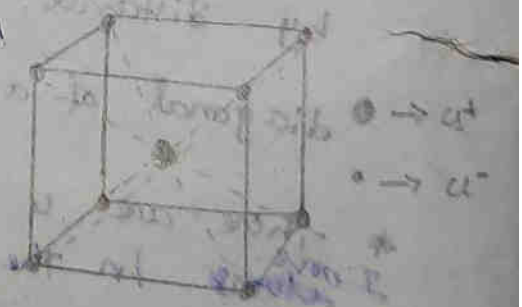
- High M.P & B.P
- Soluble in water
- Size, $Cl^- > Na^+$
- It is insoluble in organic compounds
- Electrical behaviour is - Insulator.
- Brittle

Each atom has six nearest neighbouring atoms of opposite kind i.e., the co-ordination number is '6' and next nearest neighbouring atoms are 12 of the same kind. In this structure the type of bonding is ionic bonding. chloride ion bigger than sodium ion. The atomic radius $a = 5.63\ A^\circ$ (each cation surrounded by 6- Cl⁻ Ions) ∴ coordination number is '6'.

The crystals having the NaCl type arrangement are like Li, PbS, AgBr, MgO, MnO, etc.

Explain the structure of cesium chloride :-

* The structure of cesium chloride is body centered cubic structure.
* The Cs^+ ions will be kept at '8' corners of a unit cube with the chloride ion located at the body of the centered the cube and vice versa.
* The Basis has one Cs^+ ion at (0,0,0) and one Cl^- ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, each atom is surrounded by '8' nearest neighbouring atoms and co-ordination no. is '8'. The compounds having the crystal structure like CsCl, NH₄Cl, LiHg, TlBr, BeCu, ZnS, etc.



CRYSTAL DIFRACTION AND RECIPROCAL LATTICE

The x-rays are not reflected on normal plane grating because x-rays are diffracted if the grating has 40 million lines per centimeter (c.m). Practically it is not possible to construct these lines on normal grating.

Generally the grating has 6,000 lines per c.m. So x-rays are diffracted on crystal it is experimentally verified on 1912 by Von Laue'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 diffracted beams from a crystal

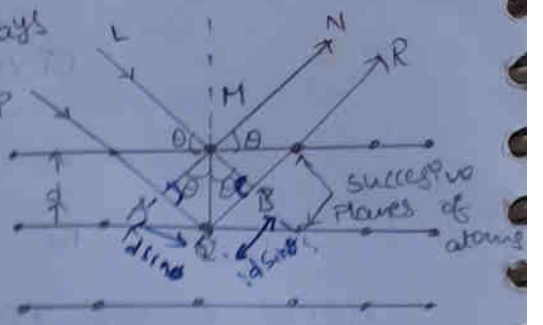
Consider a series of parallel rows in which the atoms are arranged in given plane of crystal. Suppose a parallel beam of x-rays incident in direction making a glancing angle "θ" with the surface of planes.

→ 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 planes (x-rays) 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



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

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

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

∴ 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

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

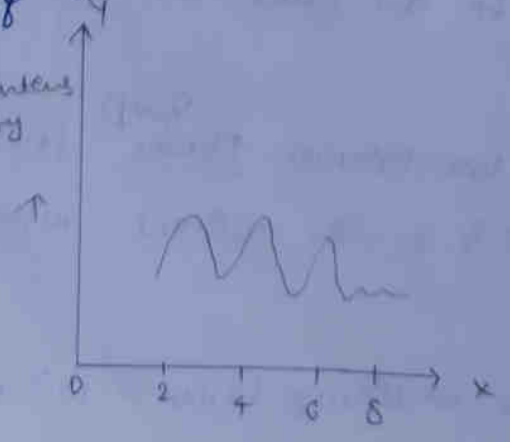
$$\theta_2 = \sin^{-1}\left(2\frac{\lambda}{2d}\right) \quad \text{if } n = 2.$$

These are known as 1, 2, 3 -- etc. reflections according to n - Bragg's reflection can be occure only for wave length "λ" less than 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" as 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 explains only observed angles of the diffracted beam from a crystal. Brags law is a consequence of the periodicity of the lattice.

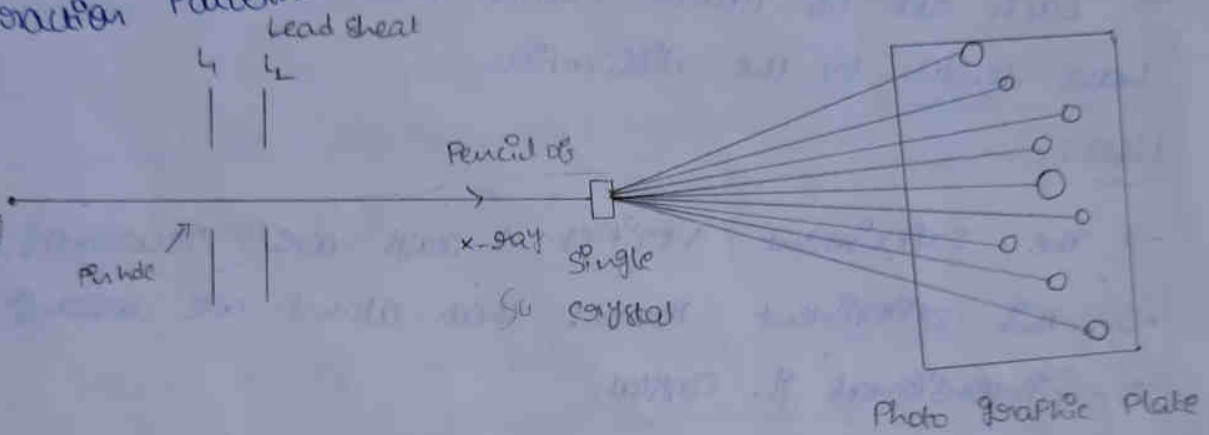


* Experimental Diffraction Methods :-

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 diaphrams and holders for setting the crystal.

There will be a Photographic Plate for the Protection of diffraction Pattern.



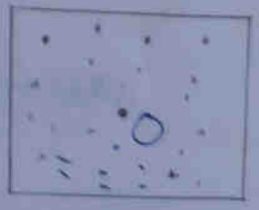
Working :-

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, KCl 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 mounted at 60,000V between anode & cathode. There will be filter "F" and two pin holded diaphragms. D_1 & D_2

The specimen in the form of powder stuck on a thin wire "p". There will be a photographic film on the inner circumference of a drum shaped cassette. The specimen is placed at the centre of cassette.

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 θ

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 will be produced on the screen. If glancing angle reaches 90°, cones 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 l_1, l_2 and l_3 be the distance between symmetrical lines on the film let "D" be the diameter of the photographic film.

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

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

$$\theta_1 = \frac{90^\circ}{\pi D} l_1 \; ; \; \theta_2 = \frac{90^\circ}{\pi D} l_2 \; ; \; \theta_3 = \frac{90^\circ}{\pi D} l_3 \; ; \; \cdots$$

Substitute $\theta_1 ; \theta_2 \& \theta_3 \cdots \theta_n$ 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

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

* 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

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

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

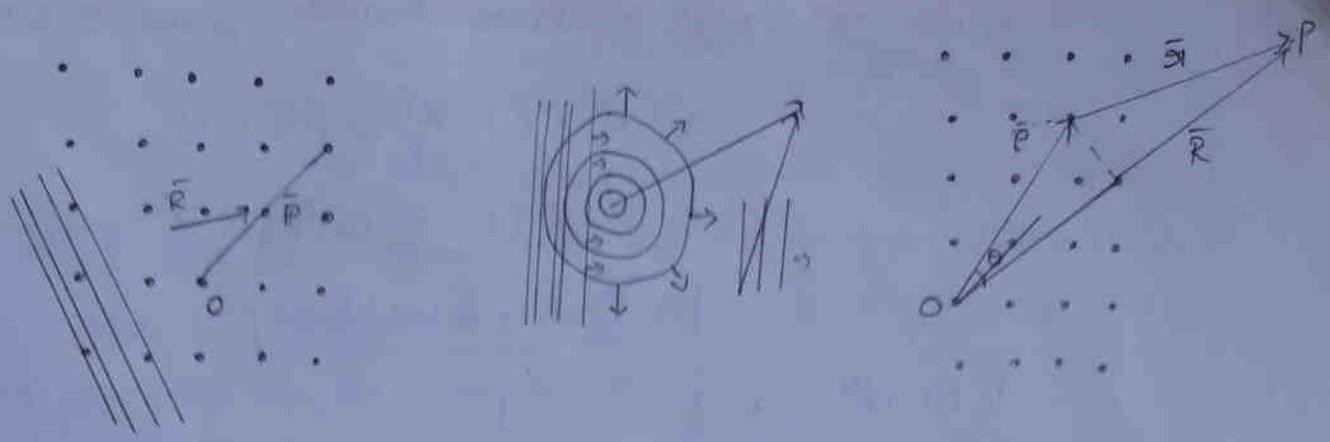


Fig i. shows

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

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

* 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 $(F_0 e^{ik\bar{S}})\left(\frac{e^{ikr}}{r}\right)$ —(3)

Where $F_0 \cdot e^{ik\bar{S}}$ 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

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

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

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

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

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

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

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

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

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

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

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

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

Eq^n (6) becomes

$$\boxed{\int dv\, n(\vec{\rho})\, e^{-i\bar{\rho}\Delta k}} \quad \text{— (7)}$$

Where;

$$ik\bar{\delta} - ik\bar{\delta}\cos(\bar{\delta}, R) \cong i\bar{\delta}(k - k')k' = k\cos(\rho, R) = -i\cdot\delta\Delta k$$

k' is wave vector in scattering direction R.,

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

Eq^n (7) gives the amplitude of scattered wave.

Reciprocal Lattice :-

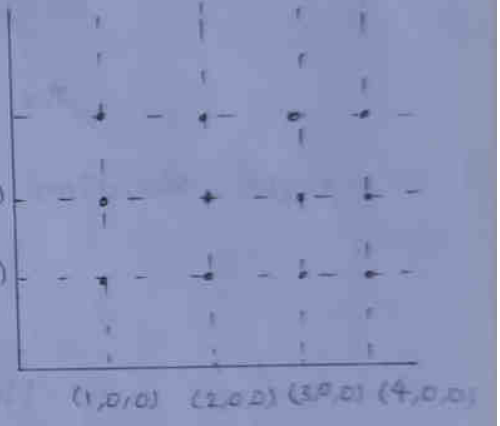
" It means that every plane in a real lattice becomes a point in the reciprocal lattice "

It is built from the direct crystal lattice by constructing normal drawn to each parallel 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

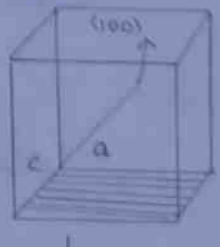


Consider a monoclinic crystal and all planes can be represented by a 2D - reciprocal lattice

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

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

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

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

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

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

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

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

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

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

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 $= a.(b \times c)$

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

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

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

Consider

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

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

$$= \frac{(b \times c)(b \times c).a^2}{a^3 (b \times c)^3}$$ [∵ By vector identity]

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

(Reciprocal lattice is a SC lattice)

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

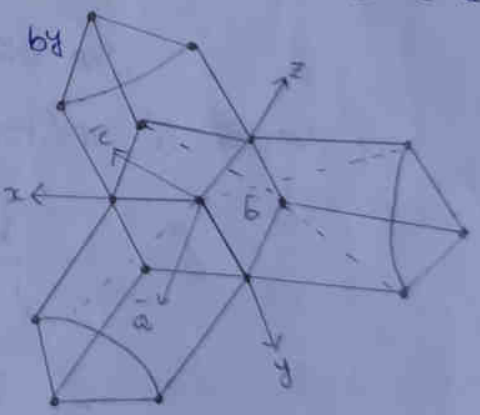
(4) ~~RPL~~ of FCC is BCC vice versa

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



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

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

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

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

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

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

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

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

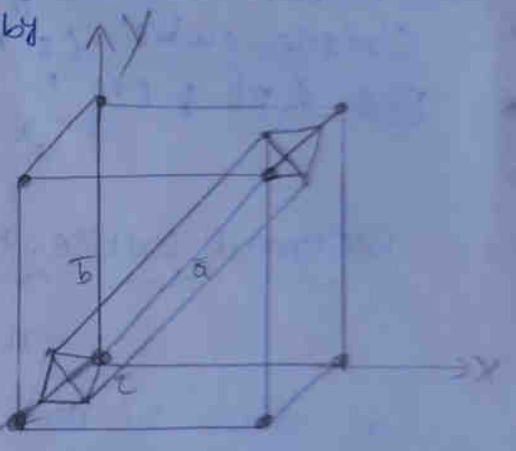
$= \frac{1}{2a}[2\bar{x}+2\bar{y}]$

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

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 Premitive translation vectors 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

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

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

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

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

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

Reciprocal Space :- 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.

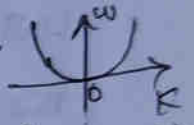
Brillouin zones:- A Brillouin zone is a particular choice of the unit cell of the reciprocal lattice. It is defined as the Wigner-Seitz cell of the reciprocal lattice.

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

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

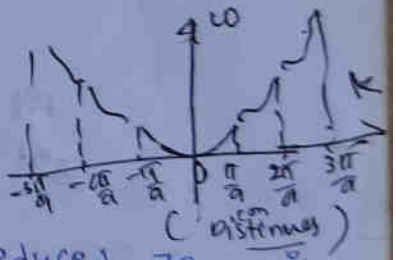
Where "n" is positive or negative integer.

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



(No discontinuities)

If we consider a line divided into energy discontinuities 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.



(Discontinuous)

Construction of zones:-

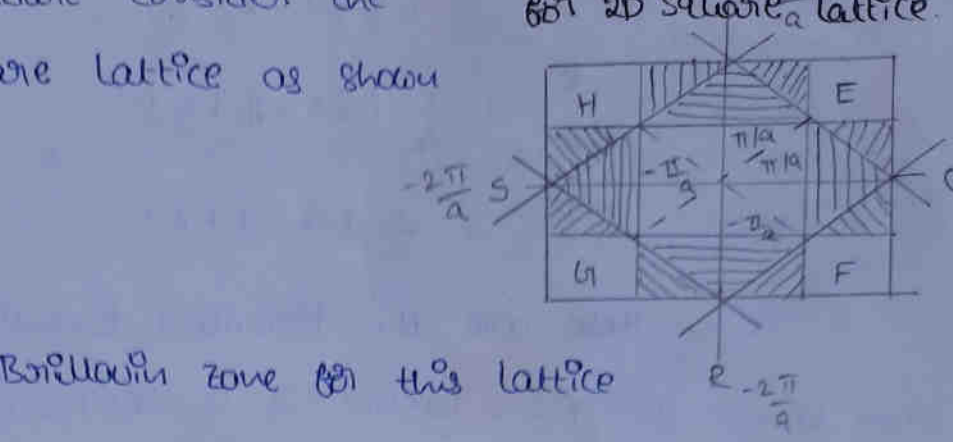
For many purposes only first or reduced zone is sufficient but sometime the higher zones are desirable.

The Brillouin zones are constructed from the planes which are the perpendicular bisectors of the reciprocal lattice vectors drawn 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.

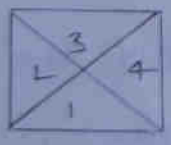


Fig (b)
2nd zone

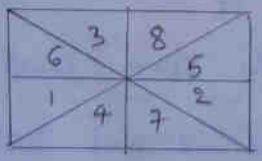


Fig (c)
3rd zone

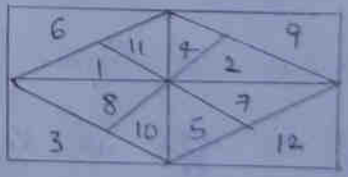


Fig (d)
4th zone

Figures shown the Reduced zones.