MAA OMWATI DEGREE COLLEGE HASSANPUR (PALWAL)

Notes

B.SC 5th Sem

Solid State Physics

Physics - 1

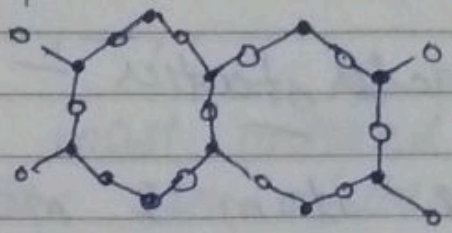
5th sem

Unit - 1

☆ Crystalline solids :-

The solid having the property of incompressibility and rigidity are known as crystalline substance. The crystalline solid are in which groups of atoms molecule or ions are arrange in a definite regular manner forming three dimensional pattern which may be obtain by a three-D repetition of a certain pattern unit.

eg → quartz, diamond



characteristics :-

1) The atoms, ions or molecules of crystalline solid are arranged in a definite geometric order

2) The orderly arrangement of atoms, ions and molecules in a crystals is extended over a large volume of the crystal. it mean crystaline solid shows a large range order

3) Crystalline solids are bounded by flat surface

4) Crystalline solids form uniform chemical composition throughout

☆ Amarphous (Glassy solids) :-

There are such substance such as ordinary glass, plasti lamp black, which look like solid in appe

but as far as their str is concerned. they can be consider as such as they can be consider as viscous liquid. The atoms of such substance are arrange in a irregular manner as shown in ? for two dimension but they have strong bonds b/w them. such solid are called amorphons solid.

characteristics :-

1) The atom & molecules are arrange in irregular manner
2) As the atoms or molecules in such solid are distributed randomly so such soli dare not bound by flat surface.
3) The glassy solids are isotropic
4) Glassy solid do not have sharp melting point

* Liquid crystals :-

The sub. exibited such as intermidate, mesomorphic phase are called liquid crystals. In a liquid crystal 3-D symmetry is not present

molecules are arrange in 1D & 2D
But they can flow to another directions
Most of the liquid crystals are organic
meterials composed of rigid moderately
large rod- like molecules typically
1-3 nm in length 0.3 to 1.0 nm across

Various type of liquid crystals are given as

* Smectic mesophase :-
The most ordered smetic crystals have a layer like str. Where molecules align themselves in parallel layers sliding on relative to the other. Thereby promoting fluidity. The longer axes of molecules lies up either normal to the plane of layers. as sh or incline at an angle ϕ with the normal to these plane. The value of ϕ depend upon temp of liquid crystal.

* Nematic ~~chatact~~ mesophase :-
In this case molecule also have parallel axes to each other but location of their centre of gravity is as irregular as in conventional liquid. Whole of nematic crystals has small regions each having its molecules align.

☆ Crystal translational vectors and crystals Axes :-

Let us consider an ideal crystals which is defined as a body composed of atoms arranged in a regular pattern so that the atoms arrangement at one location looks exactly the same in all respects

In the language of atom crystal in such a crystal there exist a smallest grp of atoms that repeat itself in all direction in the crystal by means of the translation operation defined as the displacement of a crystals parallel to itself by crystal translation Vector.

$$T = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \quad (1)$$

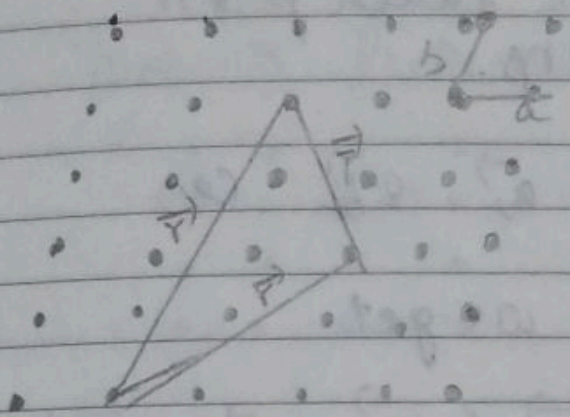
n_1, n_2, n_3 are arbitrary integers
$\vec{a}, \vec{b}, \vec{c}$ are vector.

the opp of the operation represented by eq^n (1) to any point $\vec{r}$ result in $\vec{r}'$

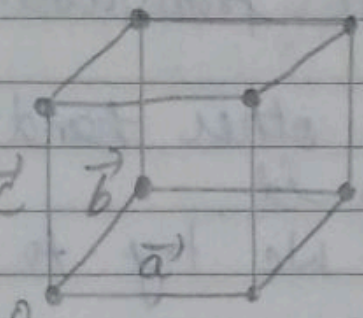
$$\vec{r}' = \vec{r} + \vec{T} = \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \quad (2)$$

which is identical in all respects to the original point $\vec{r}$. satisfy the feature of perfect crystal

for any arbitrary choice of n_1, n_2, n_3 and the vectors n_1, n_2, n_3 and the vector $\vec{a}, \vec{b}, \vec{c}$ are not translation vectors. it must be possible to find three translation vectors $\vec{a}, \vec{b}, \vec{c}$ which satisfy eqn (2). These translation vectors $\vec{a}, \vec{b}, \vec{c}$ are often called as crystal axis or basic vector.



crystal translation operation $\vec{T}$ & primitive translation vector $\vec{a}$ & $\vec{b}$ of two 2D lattice



crystal axis $\vec{a}, \vec{b}, \vec{c}$ making adjacent sides of a parallelopiped

Now there may be many ways of choosing these translation vectors

$\vec{c}$ & $\vec{b}$ illustrates two such choice such as $\vec{a_1}, \vec{b_1}$ & $\vec{a_2}, \vec{b_2}$ as translation vector.

$$\vec{T} = \vec{a_1} n_1 + \vec{b_1} n_2 \quad \text{--- (3)}$$

With some combination of n_1 & n_2. eg. We can get P' from P by using the operation $\vec{T} = 0.\vec{a_1} + 1.\vec{b_1}$ & can write

$$\vec{r}_p = \vec{r}_p + 0.\vec{a_1} + 1.\vec{b_1} \quad -(4)$$

such translation vector are called ~~p~~ primitive translation vectors.

on the other hand vector $\vec{a_2}$ & $\vec{b_2}$ can not do it.

If We try to do it we get

$$\vec{r}'_p = \vec{r}_p + 1/2\,\vec{a_2} + 1/2\,\vec{b_2} \quad (\because \vec{b_1} = 1/2\,\vec{a_2} + 1/2\,\vec{b_2}) -$$

which involve non integral coefficient of $\vec{a_2}$ & $\vec{b_2}$

Crystal lattice and Basis :-

Lattice :-

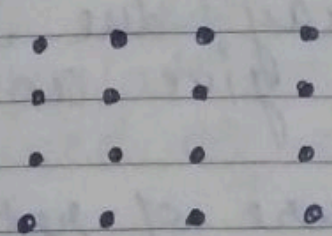
A crystal lattice is a purely geometrical concept. It is defined as a regular periodic arrangement of

points in three dimensions in which every point has surrounding or environments identicals to that of every other point.

The vector point in this lattice are connected by a translational vector $\vec{T}$

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}.$$

Two D Picture of lattic is given as



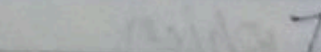
(5)

★ Basic :-

If we associated identically with every lattice point a structural or a building unit, a crystal structure is formed. is called basic

★ Periodicity in crystals :-

For understanding about lattice clearly we can see that a single translation given below produce an infinite 1d linear array of the repeated object.



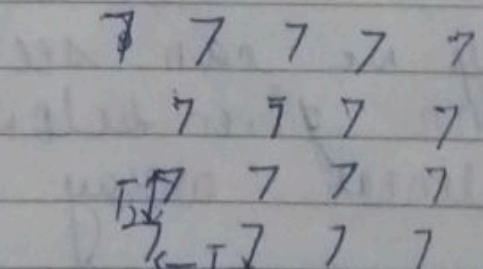
If such a linear translation T_1 is combined with another non-collinear translation T_2 the 2-D array is obtained.

If such a linear translation T_1 is combined with another non-collinear translation T_2 then a two repeated an infinite no. of times by the second T_2. Another way is that linear array due to T_2 is repeated by T_1 which give an imaginary character.

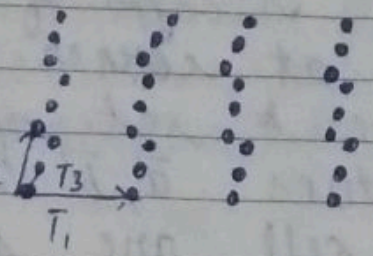
Further nature of repeated object does not effect the translation periodicity.

It is convectional to represent this periodicity by replacing each object in the array with a point. The resulting connection of periodic point are called lattice.

It may be notice that a point is an imaginary infinitesimal spot in space and so a lattice is also imaginary.



Further if 3rd translation is added to the plate lattice or the lattice as shown.



3rd translation repeat the plane at equal intervals T_3. & produce 3-D lattice array.

All lattice point are connected by translation operator T which is defined as under.

$$T = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

$\vec{a}, \vec{b}, \vec{c}$ funda transvect

n_1, n_2, n_3 = translation gp of crystals.

given the diagram of 2D lattice with vector $\vec{a} + \vec{b}$

geometrical arrangement

$$f(r) = f(r+T)$$

Unit cell :-

Unit cell of a lattice is the smallest block of geometric figure of a crystals which when repeated again & again along three definite direction in space forms the lattice str.

✯ Primitive cell :-

A type of unit cell contains lattice points at corner only and has a minimum volume & set of linearly independent vectors $\vec{a}, \vec{b}$ & $\vec{c}$ that define a primitive cell are called primitives basis vectors.

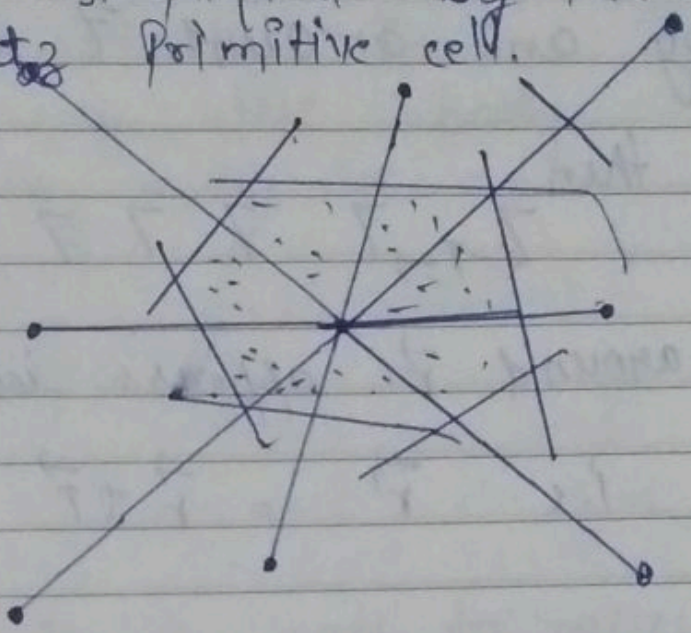
✯ Wigner sietz primitive cell :-

Another method of choosing a primitive cell of equal volume V_c is as under

1) First select any point on the lattice & connect this point to all nearby lattice points by drawing lines

2) At the mid point & normal to these lines draw new lines or planes The smallest volume enclose in this way is the new permitive cell & also their are is a density of one lattice point per permitive cell. The cell formed in this way is called Wigner sietz permitive cell.

In Wigner Sietz cell, the lattice point is at the centre of the primitive cell whereas in conventional primitive cell the lattice point is at the corner. All the theoretical cal. are simplified by the use of Wigned sietz primitive cell.



✱ Symmetry operation for a two-D crystals

A symmetric operation is one which transform the crystal to itself i.e leaves the crystals and its environment invarient under such a symmetry operation. We have seen that the translation fulfil this requirement. But these are not the only type of symmetry operation.

The addition of translation symmetry

1) Rotation about an axis
2) Reflection in a plane
3) Inversion about a point

★ Translation :-

The translation symmetry is the manifestation of the order of crystalline solid. Acc to it if we are at $\vec{r}$, and then translate the crystal by an amount $\vec{T}$ defined by

then

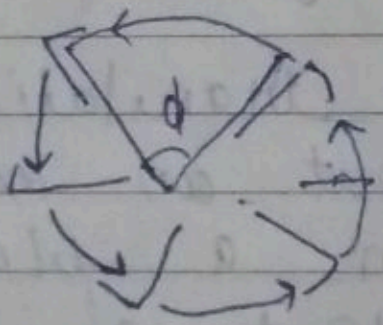
$\vec{r} \to \vec{r} \cdot \vec{r} \cdot \vec{r} \cdot \vec{r} \cdot \vec{r} \cdot \vec{r} \to$ new environment

around $\vec{r}$ appears identical to the old

i.e $\vec{r}' = \vec{r} + \vec{T}$

★ Rotations :-

A body is said to be possess the rotational symmetry about an axis of the rotational of the body about this axis by some angle ϕ leaves the body invariant. Then the rotation of body appears same as it was prior to rotation



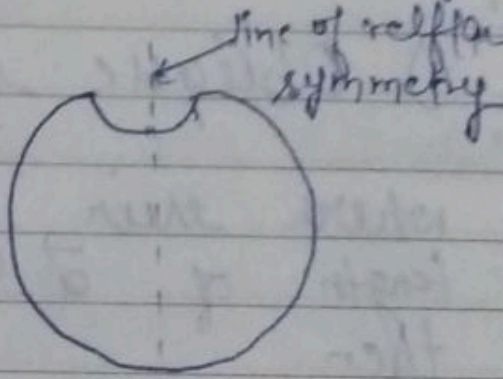
in single angle of rotation remains same after rotation at angle ϕ.

In order for the body to be truly invariant th by the rotation. their must be an integral number of such rotations in one complete revolution of the body. thus the angle 2π must be an integral multiple of ϕ

$$n\phi = 2\pi \text{ or } \phi = \frac{2\pi}{n}$$

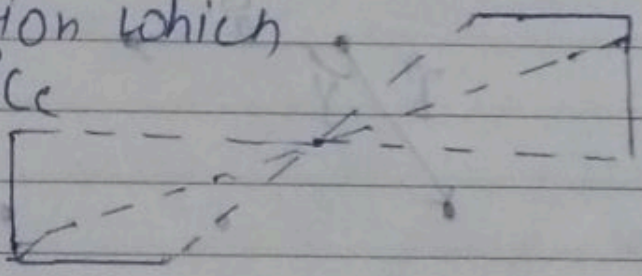
3) Reflection :-

A body is said to reflection symmetry if a plane can be drawn in the body dividing it into two reflection of the other half



4) Inversion :-

Inversion is a point operation which is applicable to 2-D lattice only.



In short, symmetry operations like translation & rotation leave the motif unchanged. Whereas reflection or inversion changes the character of the motif from right handed to left handed & vice-versa.

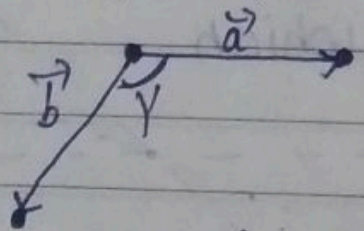
☆ Bravais Lattices in two dimensions

There are five distinct lattice type in two D. the oblic lattic & four special lattices. Bravais Lattice is the common phrase for a distinct lattice type & we say that there are five Bravais lattices in 2-D.

i) Oblique lattice :-

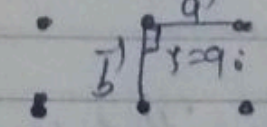
In a general lattice where there is no restriction on the length of $\vec{a}$ & $\vec{b}$ and on the angle γ b/w them

$$|\vec{a}| \neq |\vec{b}|, \quad \gamma \neq 90^\circ$$



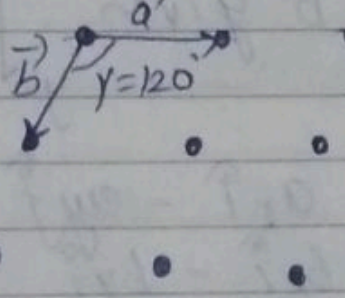
) Square lattice :-

In this Lattice $|\vec{a}| = |\vec{b}|$ and $\gamma = 90^\circ$. It is invarient under point operation 4



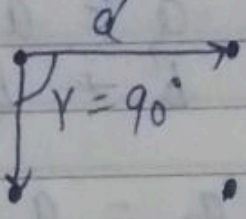
3) Hexagonal lattice :-

This lattice has $|\vec{a}| = |\vec{b}|$ and the angle $\gamma = 120^\circ$. This is invariant under a rotation $2\pi/6$ about an axis through a lattice point & normal to the plane.



4) Rectangular lattice :-

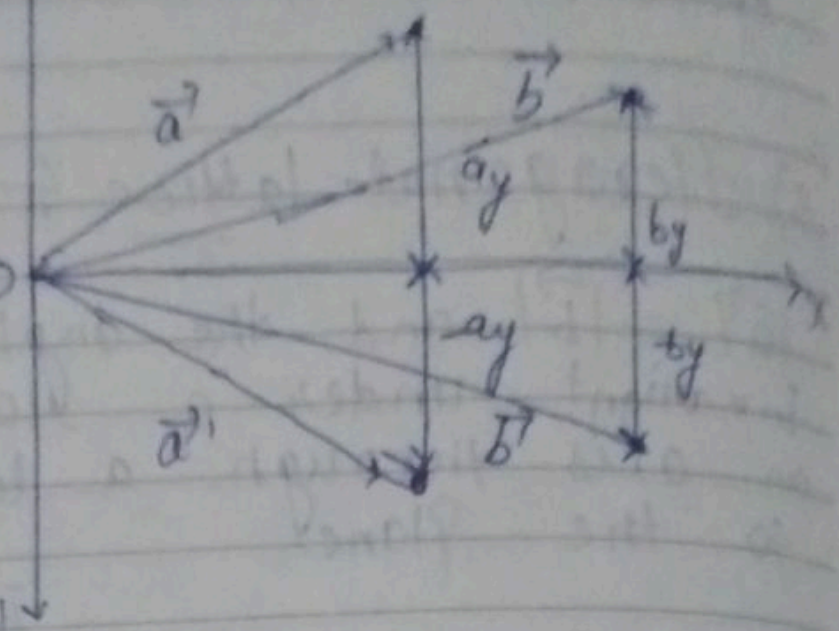
There are two important consequence if the lattice allow the mirror reflection m.



Let us consider an oblique lattice as show in fig
permitted translation vector $\vec{a}$ and $\vec{b}$.

Now the permitted translation vector $\vec{a}, \vec{b}$ in term of unit vector $\hat{i}, \hat{j}$ along the x & y axis

$$\vec{a} = a_x\hat{i} + a_y\hat{j}$$
$$\vec{b} = b_x\hat{i} + b_y\hat{j}$$ — (1)



If the primitive vector are mirrored in the x axis then $\vec{a}$ & $\vec{b}$ are transformed by the reflection operation into new vector $\vec{a}'$, $\vec{b}'$ given by

$$\vec{a} = a_x\hat{i} - a_y\hat{j}$$
$$\vec{b} = b_x\hat{i} - b_y\hat{j}$$ — (2)

then $\vec{a}'$, $\vec{b}'$ must also be lattice vectors they must be of the form: $n_1\vec{a} + n_2\vec{b}'$
n_1 & n_2 are integer

$$\vec{a} = a\hat{i}$$
$$\vec{b} = b\hat{j}$$ — (3)

Here $a_x = a$, $a_y = 0$
$b_x = 0$, $b_y = b$

using their result in eqn (2)

$$\vec{a}' = a\hat{i} \quad , \quad \vec{b}' = -b\hat{j}$$

Thus $\vec{a}' = \vec{a}$ & $\vec{b}' = -\vec{b}$ so lattice is carried it self. mean $\vec{a}$, $\vec{b}$ are primitive translation vectors thus we get resulting perm. trans. rec lattice

$$|\vec{a}| \neq |\vec{b}| \quad , \quad \gamma = 90^\circ$$

5) Central Rectangular lattice :-

The choice of $\vec{a}, \vec{b}$ other than given by eqn (3) give another type of lattice. which is invarient under reflection. $\vec{b}'$ will be lattice vector if

$$\vec{b}' = \vec{a} - \vec{b}$$

$$b'_x\hat{i} + b'_y\hat{j} = (a_x - b_x)\hat{i} + (a_y - b_y)\hat{j} \quad \text{---(4)}$$

from eqn (2)

$$\vec{b}' = b'_x\hat{i} + b'_y\hat{j} = b_x\hat{i} - b_y\hat{j} \quad \text{---(5)}$$

& compairing eqn (4) & (5)

$a_x - b_x = b_x$

$a_y - b_y = -b_y$

$2b_x = a_x$ or $b_x = \frac{a_x}{2}$

$a_y = 0$

these eqn have a soln if

- $a_y = 0$, $b_x = (1/2)a_x$

$$\vec{a} = a_x \hat{i}$$

$$\vec{b} = \frac{1}{2} a_x \hat{i} + b_y \hat{j} = \frac{1}{2} a\hat{i} + b_y \hat{j}$$

☆ BRAVIS Lattices in three dimensions

In 3-D the picture become complicated due to additional symmetry elements & due to the added dimensional itself

It is possible to prove that there are thirty two different three dimensional points groups permissible in a 3-D crystals

We first discuss following points

1) Rotation axes :-

One-, two-, three-, four- and six fold rotation axes are permissible corresponding to rotation by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$, $2\pi/6$ radians. there rotation axes are denoted by the symbols 1, 2, 3, 4 and 6.

2) Reflection plane :-

Mirror reflection is in a plane through the lattice point. It is denoted by m.

3) Inversion centre :-

A crystal possesses an inversion centre if the crystal str. is left-invarient by the operation $\vec{r} \to -\vec{r}$ where $\vec{r}$ is the vector position of an orbitary point in the crystal referred to the lattice point. An inversion centre is denoted by I.

4) Rotation inversion axis :-

A crystal str. possesses a rotation inversion axis if it is combined rotation & inversion.

This operation of combaen rotation & inversion is also known as an improper rotation & corresponding axis as an improper axis. crystal can possess one-, two-, three-, four-, six-fold rotation inversion axes

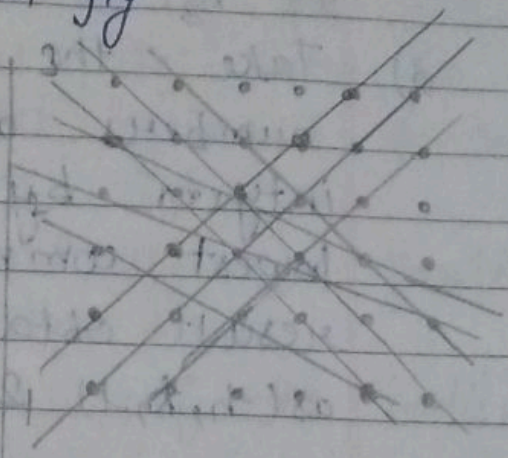
UNIT-2

UNIT -2

chapter-2

Crystal Planes :-

The lattice point forming a space lattice may be considered as occupying various sets of parallel planes some of are given in fig



The line shown in fig will apear as plane when geometry is extended 3-D.

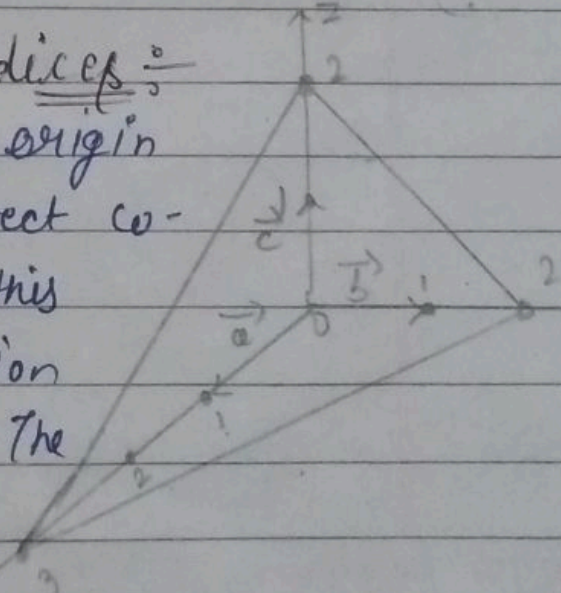
The position and orientation of a crystal plane are found by any three points in the plane provided the points are not collinear.

Miller indicas :-

It was more useful for crystal str. analysis to specify the orientation of a plane by another set of thre D called Miller indices.

Rule to found indices :-

Take any atom as a origin in the crystal and erect co-ordinate axes from this atom in the direction of crystal $\vec{a}, \vec{b}, \vec{c}$ The axis may be permitive or Non permitive



2) Choose one plane of the set of intercept and find its intercept on the three co-ordinate axes in terms of lattice const. a, b, c such that $x = n_1 a$, $y = n_2 b$ $z = n_3 c$

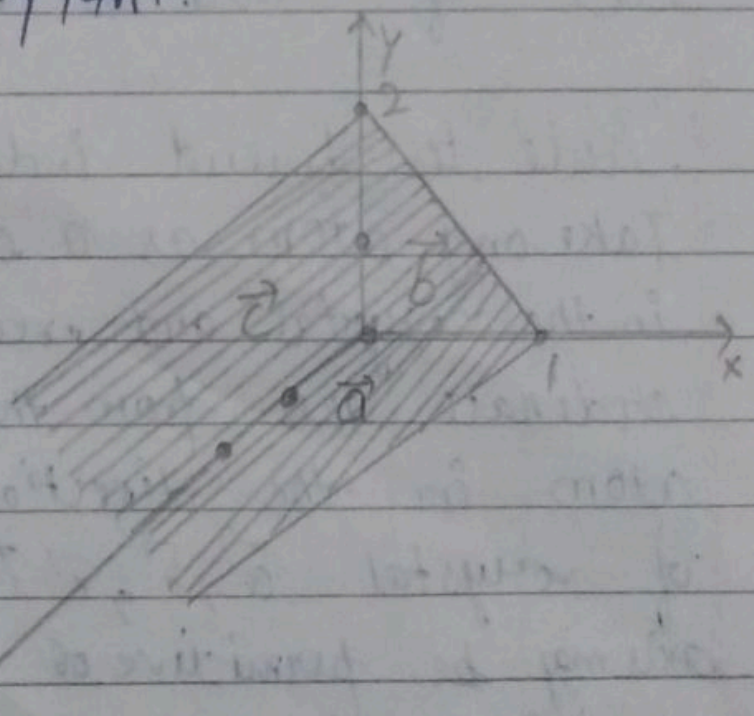
3) Take the reciprocal of thes three numbers and reduce them into three integers by multiplying with their lowest common denominator. So the result obtained is enclosed in parenthesis as (h, k, l) & called mirror indices.

intercepts are $\infty, \vec{b}, 2\vec{c}$

Reciprocals $\frac{1}{\infty}, \frac{1}{1}, \frac{1}{2}$

indices $0, 2, 1$

Thus the mirror indices of the plane are (021) Thus the plane is a (021) plane.



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Important features of Miller indices:-

i) All equally-spaced parallel planes have the same index no.

ii) A plane parallel to one of the ~~plane~~ co-ordinate axes has an intercept of infinity and index of zero for that axes.

iii) Miller indices do not define a particular plane but a parallel plane.

iv) It is only the ratio of the indices which is of important

v) A plane passes throug the origin is defined in terms of parallel plane having non-zero intercept.

vi) The angle θ

$$\cos\theta = \frac{u_1u_2 + v_1v_2 + w_1w_2}{(u_1^2+v_1^2+w_1^2)^{1/2} (u_2^2+v_2^2+w_2^2)^{1/2}}$$

vii) The distance d b/w adjacent plane of a set of parallel plane of the indices is given by

$$d_{hkl} = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$

where a is edge of prism.

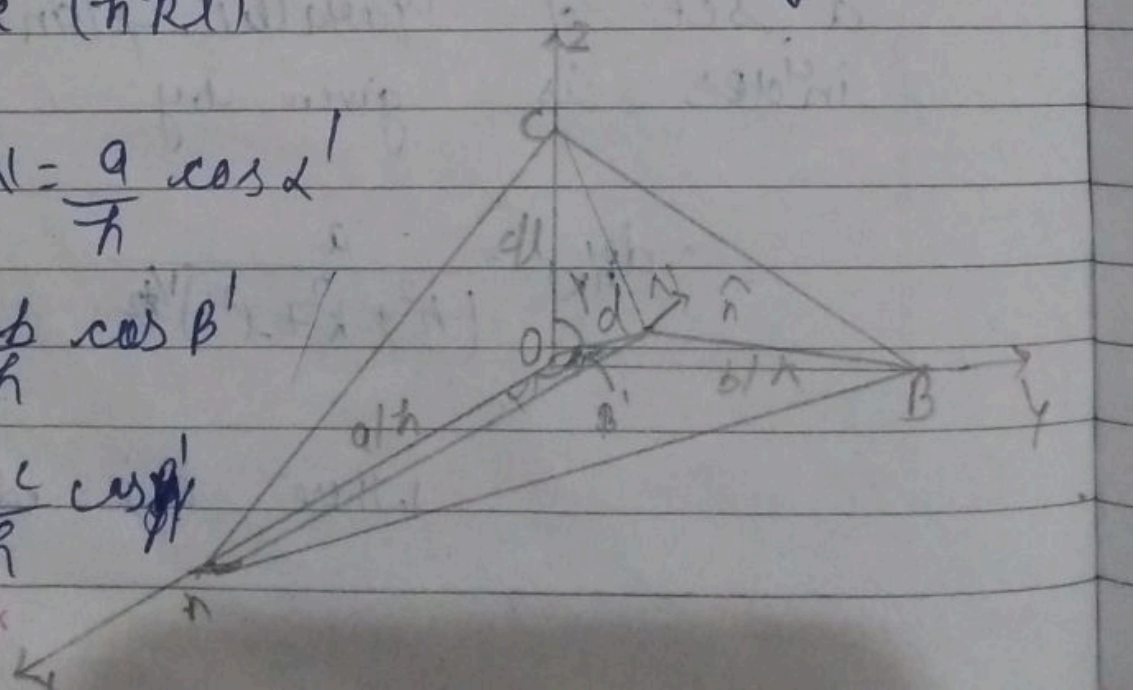
INTer Planer Spacing :-

Consider any simple unit cell in which the coordinate axes are orthogonal. the origin O is taken at any lattice point and co-ordinate axes x, y, z along in $\vec{a}$-, $\vec{B}$- $\vec{c}$-- direction. Now consider a family of parallel planes defined by miller indices with reference plane passing through the origin. the interplaner spacing is the perpendicular distance b/w the origin & the plane which is nearest to this origin. This plane would obviously cut the intercepts a/h, b/k, c/l on x(a-), y($\vec{b}$-), z(c-) axes respectively. A normal ON = d is drawn on the plane ABC from the origin. d the length of normal & distance b/w adjecent plane (hkl)

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

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

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



Now using law of direction cosines

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

Putting the value of $\cos\alpha'$, $\cos\beta'$, $\cos\gamma'$

$$d^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right) = 1$$

$$\therefore d = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2}} \quad \text{(1)}$$

This relation is applicable to primitive lattice in cubic, orthorhombic and tetragonal system.

for tetragonal $a = b \neq c$

$$d = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2}\right)^{1/2}} \quad \text{(2)}$$

for cubic system $a = b = c$

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad \text{(3)}$$

The spacing b/w (100), (111), (112), (011), (101) plane is a given below

$$d_{100} = \frac{a}{\sqrt{1^2+0+0}} = a$$

$$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$$

$$d_{112} = \frac{a}{\sqrt{1^2+1^2+2^2}} = \frac{a}{\sqrt{6}}$$

$$d_{011} = \frac{a}{\sqrt{0+1^2+1^2}} = \frac{a}{\sqrt{2}}$$

$$d_{101} = \frac{a}{\sqrt{1^2+0^2+1^2}} = \frac{a}{\sqrt{2}}$$

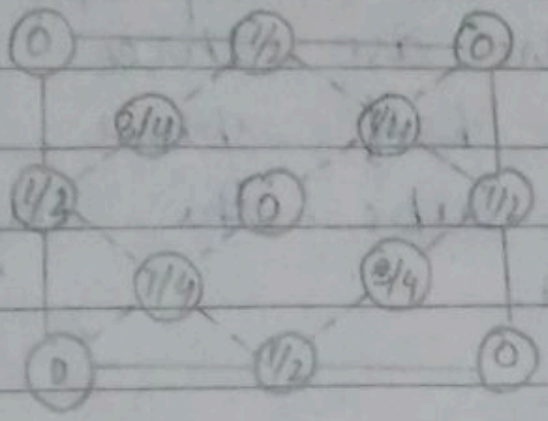
Above result is applicable to orthogonal lattices but not for non-orthogonal lattice.

☆ Some simple crystal structure

Diamond structure :

Diamond structure is a F.C.C. str with

a primitive base of two identical atoms, one located at (0,0,0) and another at (1/4, 1/4, 1/4) associated with each lattice point as in fig



The str may be viewed as resulting from the interpenetration of two face-centred sub-lattice. One sub lattice has it origin at the point (0,0,0) & another at (1/4, 1/4, 1/4) that is one quarter of the way along the body diagonal. The diamond cubic str is loosely packed since each atom has only four neighbours to which it is bounded by strong covalent bond. carbon, silicon, germanium & gray tin crystallize in the diamond str.

Packing fraction of Diamond str:-

No of sphere in one unit cell = 8
No. of diagonal = 8r.
if r is the radious of sphere. In diagonal there are three full sphere & two half sphre. If a is the side of cube. the diagonal will be $\sqrt{3}a$.

$$8r = \sqrt{3}\,a$$

$$a = \frac{8r}{\sqrt{3}}$$

volume of cube $= a^3 = 8\left(\frac{8r}{\sqrt{3}}\right)^3$

Packing fraction (f):-

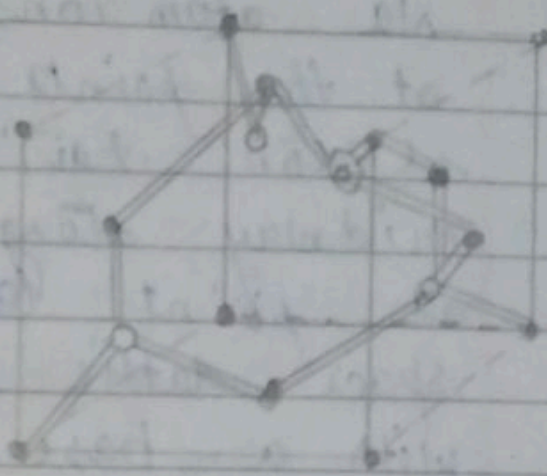
$\Rightarrow$ $\frac{\text{volume occupied by atoms in unit wx}}{\text{Total volume of cube.}}$

$$\Rightarrow \frac{8 \times \frac{4}{3}\pi r^3}{\left(\frac{8r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}}{16}\pi$$

$$= 0.34 = 34\%.$$

Zinc Blend structure :-

Zinc blend str is very closely related to the str of diamond. The cubic zinc sulphide str. results when zn atoms are placed on f.c.c lattice & S atom on the other f.c.c. lattice as shown in figure



Therefore also a true face centred cubic str. with a base of two different atoms There are four unit of ZnS per unit cell

Crystal str of Z cubic zinc str. About each atom there are four equaly distance atoms of the opposite kind arranged at the corner of a regular tetrahedral This str is loosely packed.

Position of atoms is given by

$$Zn :- 000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0$$

$$S = \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4},\ \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4},\ \tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4},\ \tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4}$$

Sodium chloride str:-

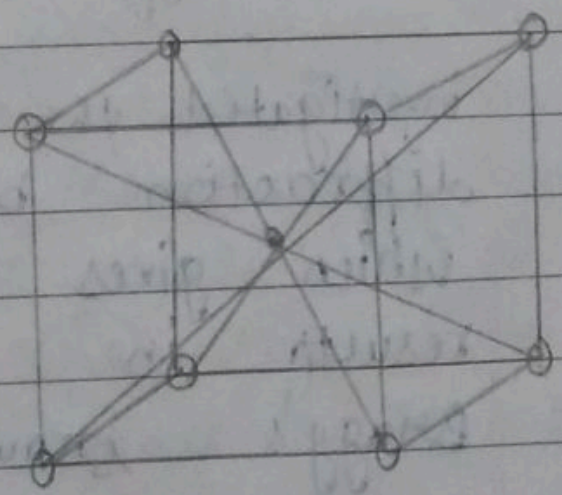
The Bravis lattic is F.cc. the basis consists of one Na atom & one Cl atom seprated by one half of the body diagonal of a unit cube. Therefore it can be considered as two F.cc sub lattice one of Na atom ions having its origin at the points 0(0,0,0) & the other Cl ion having its origin midway along a cube edge say at point (a/2, 0, 0) Thus the space lattic is truly FCC with a base of one Na ion & one Cl ion seperated by one half of the body diagonal of a unit cube. There are four molecules of NaCl in each unit cube with ions in the positions.

Na 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$

Cl- $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$

This str may be viewed by composition composed of two type of ions arranged alternately at the lattice point of a simple cubic lattice each ion has six neighbours of the opposite kind.
Representatives crystals having the Nacl str. are LiH, KBr, KCl, AgBr, PbS, MnO.

Cesium chloride str :-
Another combination of cubic str. is that of CsCl. The lattic points of this compound are two interpenetrating simple cubic lattices the corner of one sub lattice is the body centre of the other One of the sub-lattice is ocupied by Cs ions. the other by Cl ions.



Chapter -3 Crystal diffraction

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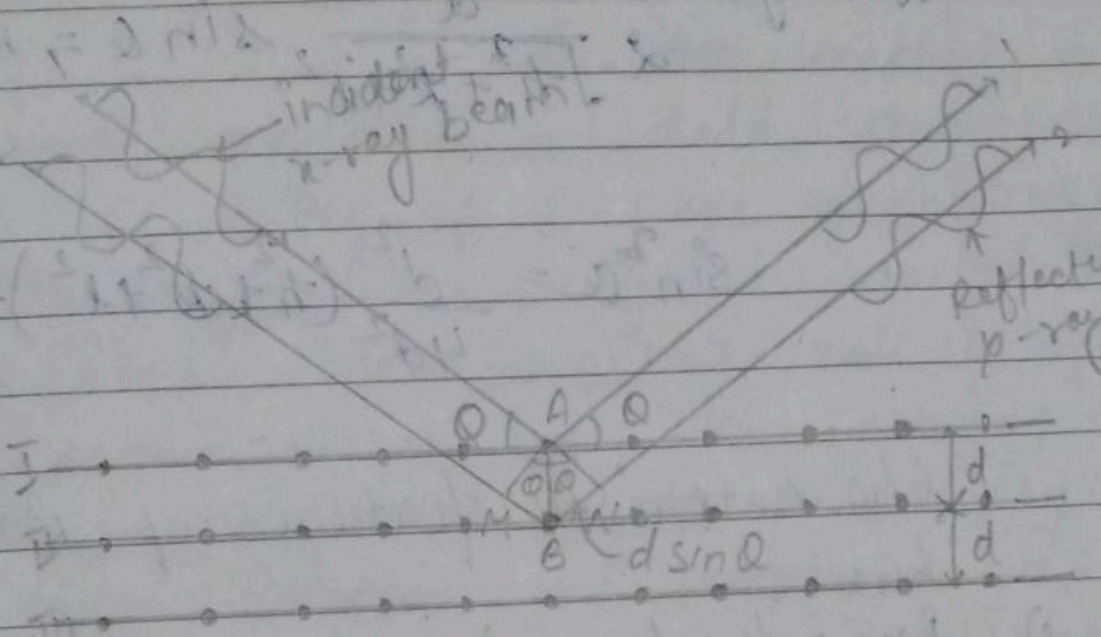
Diffraction of X-Ray :-

X-ray can be diffracted by crystal just in a similar manner as the visible light is diffracted by a diffraction grating In other words we can say that crystal can be used as diffraction grating for the diffraction of X-rays. The imp concept was first conceived by Laue in 1912 & later on tested by Freidrich & Knipping who demonstrated that x-rays beam after passing through a single crystal was broken up into a collection of diffracted beam.

✱ The Bragg's treatment :-

W.L Bragg's investigated the condition for x-rays diffraction by means of a model which gives correct mathematical results in a simple way. Bragg's shown that any

diffracted ray can be regarded as if it were reflected specularly from parallel atomic planes in the crystals with each plane reflecting only a very small fraction of radiation. The diffracted beam are found only when reflected from parallel plane of atoms interfere constructively. for obtaining the condition after reflaction of x-ray from a set of parallel layer



Draw perpendicular AM & AN on ray No 2
As two rays travel the same distance from points A & A onward it is obvious that ray No. 2 travels an extra distance = MB + BN

$$MB = BN = AB \sin\theta$$
$$= d \sin\theta.$$

Hence the path diff b/w two reflected beams

$$\therefore MB + BN = d\sin\theta + d\sin\theta$$
$$= 2d\sin\theta$$

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

If we substitute the value of d in terms of the millar indices of the planes for a cubic system we get

$$2\frac{a}{\sqrt{h^2+k^2+l^2}}\sin\theta = n\lambda$$

$$\sin^2\theta = \frac{\lambda^2}{4d^2}(h^2+k^2+l^2) \text{ for } n=1$$

Characteristic features of Bragg's law:-

i) Bragg's law is a consequence of the periodicity of the space lattice.

ii) This law do not represent the basis of atoms associated with its lattice point.

iii) The composition of basis determins

the relative intensity of the various order 'n' of diffraction from a given set of parallel planes.

iv) Bragg's reflection can be occur only for a wavelength $\lambda \leq 2d$, This is why visible wavelength can not be used in diffraction.

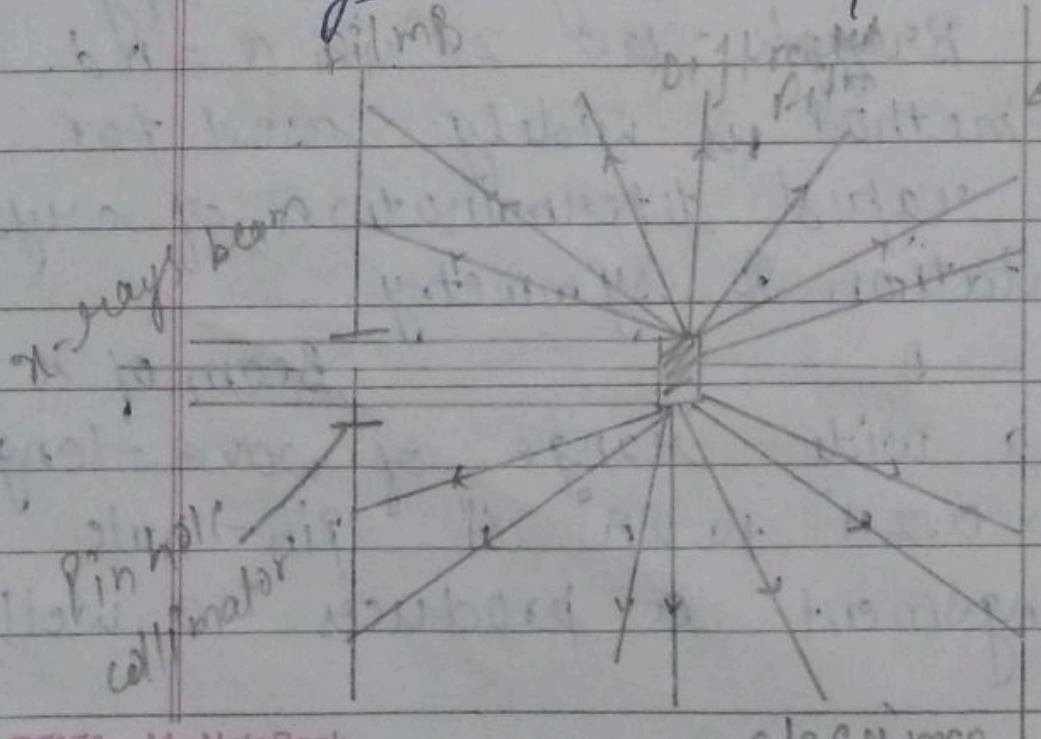
Experiment X-ray diffraction methods

1) Laue Method :-

In this method a single crystal is held stationary in a beam of X-rays of continuous wave length. The crystal selected & diffracts the discreate values of λ of which planes exist of spacing d & incidence angle θ satisfy the Bragg's law $2d \sin\theta = n\lambda$. This method is widely used for the rapid determination of crystal orientation & symmetry.

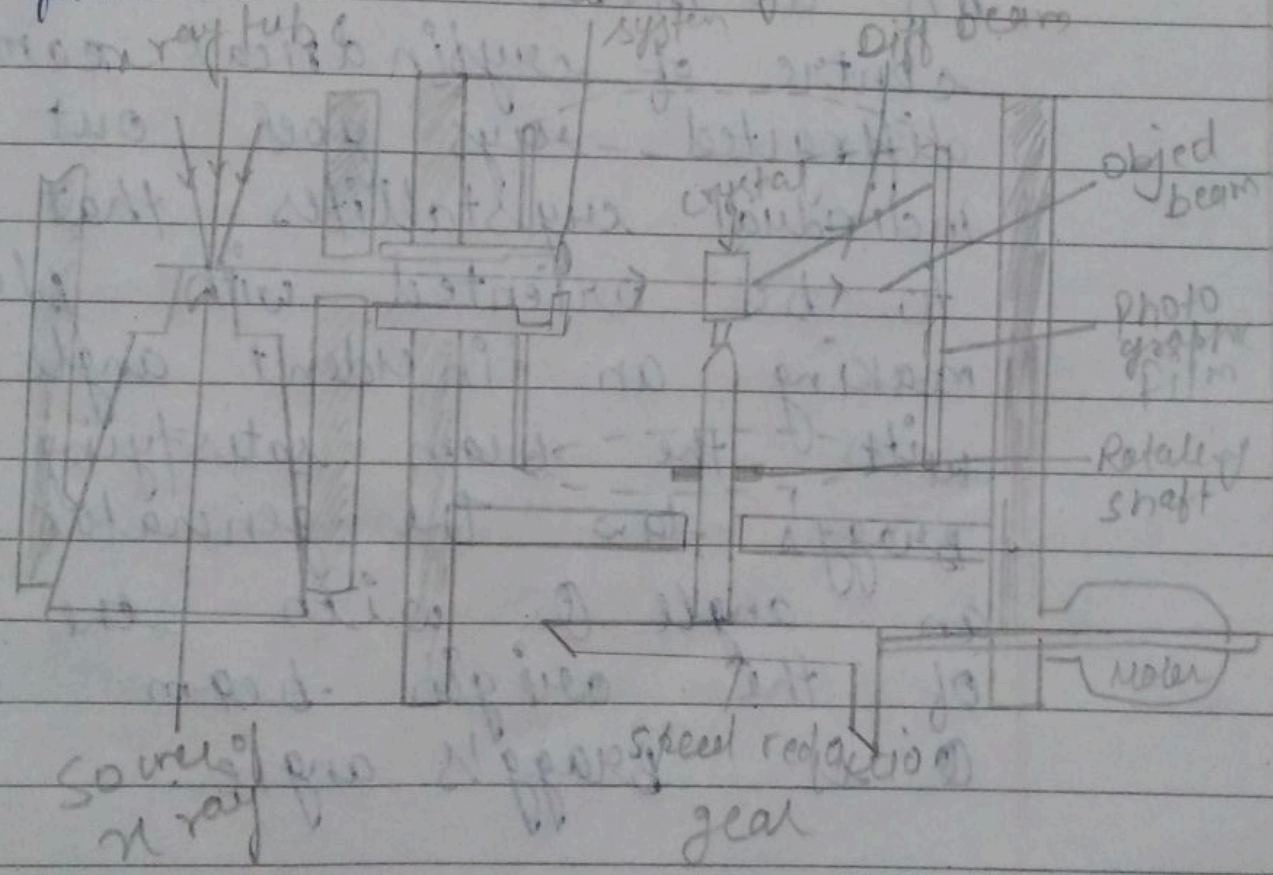
Beam of x-ray over a wide range of wave-lengths from 0.2Å to 2Å A pin-hole arrangement & produces a well

collimated narrow beam of x-rays. A single crystal specimen whose dimensions need not be greater then 1 mm. is placed stationary in a holder in the path of x-rays. A flate photographic plate is placed at a short distance from a crystal. For receiving the diffracted beam. Film B is used for back reflactio Laue pattern. The diffraction pattern consist of a series of spots. As indicated above each reflecting plane in the crystal selects from the incident beam. A wavelength satisfy Bragg's Law, the pattern will show the symmetry of the crystal. If a crystal has a four fold symmetry



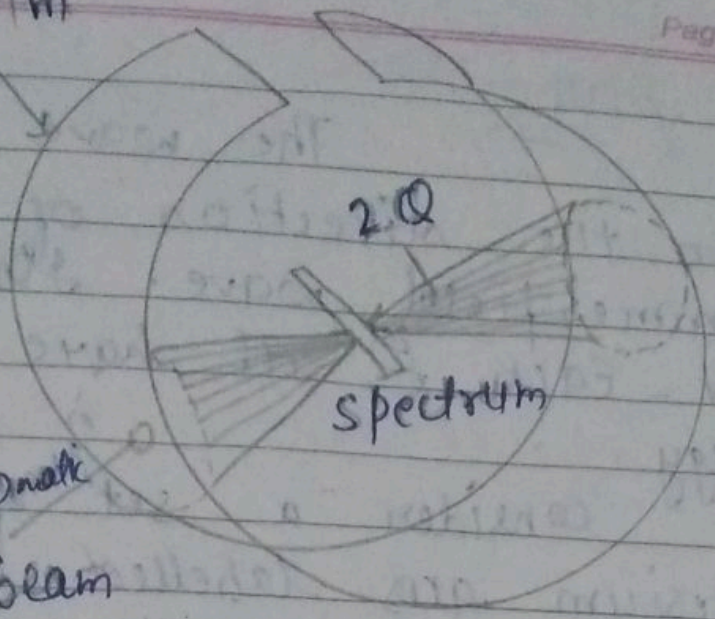
ii) Rotating crystal Method :

In this method a single crystal is rotated about a fixed axis in a beam of mono-chromic x-rays. The diffracted beam are recorded photographically on a plate or on a film mounted in a cylindrical holder concentric with a rotating spindle crystal mount. The incident x-ray beam is made monochromatic by a filter or by reflection from a earlier crystal. when during rotation the value of θ satisfies the Bragg's eqn. Plane with other orientations will reflect in layers above the below horizontal plane.



Powder Method :-

This methods described above employ a single-crystal The power method was devised by Debye & Scherrer in 1916. This method was used to study the phase-diagram of alloy system. In this method a narrow beam of monochromic radiation strikes a finally powdered specimen or a fine-grained polycrystalline specimen contained in a thin walled capillary tube, which is held on a movable mount at the centre of cylindrical cames diffracted rays goes out from individual crystallites that happen to be oriented with planes making an incident angle θ with the beam satisfying the Bragg's law. The generator make an angle θ with the direction of the origin beam where θ is Bragg's angle.



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

$$\frac{\Delta(n\lambda)}{\Delta\theta} = \frac{2\Delta d}{\Delta\theta} \sin\theta + 2d\cos\theta$$

for monochromatic x ray

$$\frac{\Delta}{\Delta\theta}(n\lambda) = 0$$

$$\Delta d \sin\theta + d\cos\theta \Delta\theta = 0$$

$$\frac{\Delta\theta}{\Delta d} = -\frac{\tan\theta}{d}$$

Thus the variation in θ for a given variation Δd in d is larger when θ approaches

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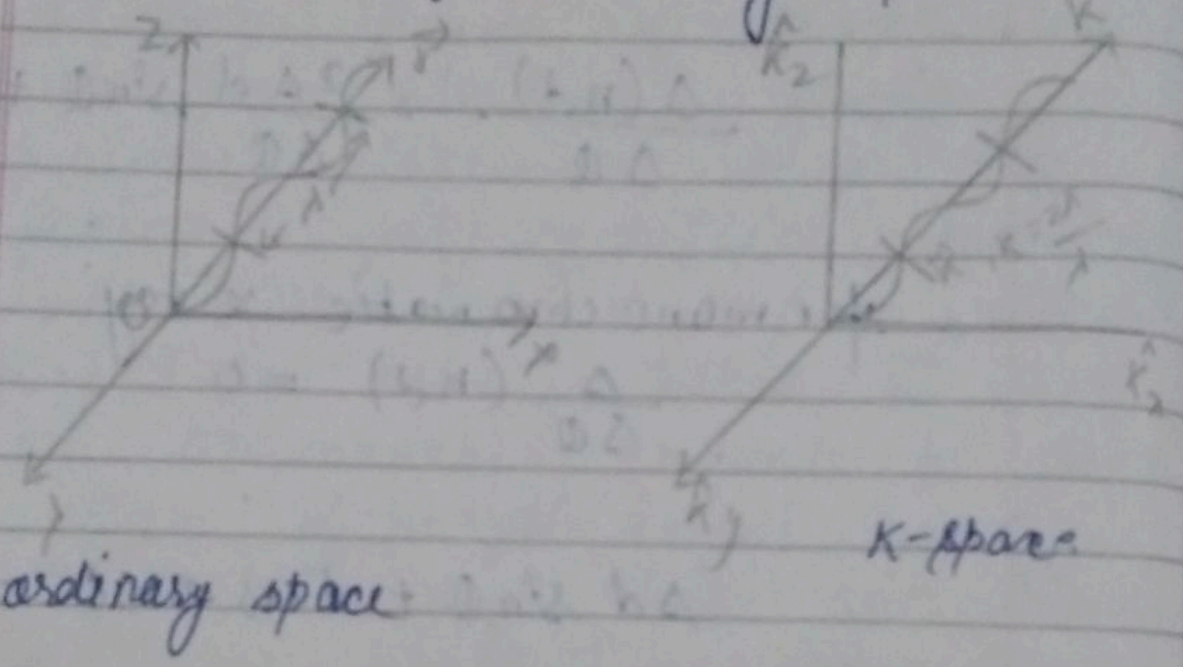
* K-space :-

The wave vector $\vec{k}$ given the direction of the sommerfield wave. Its magnitude $2\pi/d$. Each ℓ all have its own energy.

consider a set of three cartesium axes labelled k_x, k_y, k_z and situated parallel to the x, y, z axes of ordinary space.



ordinary space K-space

spherical surface in K-space, centred on the origin, will consist of points representing states of the same energy

$$E = \frac{\hbar^2 k^2}{2m}.$$

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Reciprocal Lattice :-

The molecules in a crystalline solid are periodically arranged the electrons in the solid have properties which are also periodic. for e.g → the electron density of crystalline solid should have the periodicity of the crystal lattice since any periodic function can be expressed as a fourier series so we express the electron density of a periodic solid as

$$n(\vec{r}) = \sum_G n_G e^{-i \vec{G} \cdot \vec{r}} \quad (1)$$

where n_G are the fourier co-efficient corresponding to G's which are known as reciprocal lattice vectors to be discussed later

$$n(\vec{r} + \vec{T}) = \sum_G n_G e^{-i \vec{G} \cdot (\vec{r} + \vec{T})} \quad (2)$$

where $\vec{T}$ is translation vector equal to $n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$ Due to periodicity of lattice.

equate eqn (1) to eqn (2)

$$n(\vec{r}) = n(\vec{r} + \vec{T})$$

$$\sum_G n_G e^{-i \vec{G} \cdot \vec{r}} = \sum_G n_G e^{-i \vec{G} \cdot (\vec{r} + \vec{T})}$$

from eq (1)

$$e^{i \vec{G} \cdot \vec{T}} = 1$$

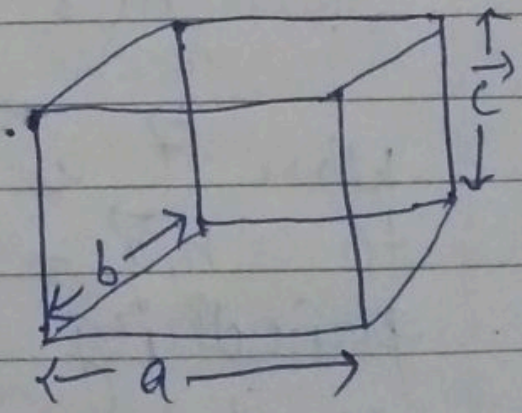
$$e^{i \vec{G} \cdot \vec{T}} = 1 = e^{i 2\pi N}$$

Where N is an integer (= 0, ± 1, ± 2

$$\vec{G} \cdot \vec{T} = 2\pi N$$

Reciprocal lattice vector for general crystal axes :-

For any type of crystal axis with lattice parameter $\vec{a}$, $\vec{b}$ & $\vec{c}$ as show in fig



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

Where v_0 is the volume of the unit cell.

Thus the relation

$$\vec{G} \cdot \vec{T} = 2\pi \times \text{integer}$$

can be satisfied if we put

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

where h, k, l are integers and $\vec{A}, \vec{B}, \vec{C}$ the primitive translation vector of the reciprocal lattice

where $$\vec{A} = 2\pi \frac{\vec{b} \times \vec{c}}{v_0}$$

$$\vec{B} = 2\pi \frac{\vec{c} \times \vec{a}}{v_0}$$

$$\vec{C} = 2\pi \frac{\vec{a} \times \vec{b}}{v_0}$$

where we can see that

$$\vec{a} \cdot \vec{A}^{*} = 2\pi = \vec{b} \cdot \vec{B} = \vec{a} \cdot \vec{C}$$

$$\vec{a} \cdot \vec{B}^{**} = 0 = \vec{a} \cdot \vec{C} = \vec{b} \cdot \vec{A} = \vec{b} \cdot \vec{C} = \vec{c} \cdot \vec{A} = \vec{c} \cdot \vec{B}$$

it is to be noted that the reciprocal translation vector bear a simple relation ship to the crystal translation vector

$\vec{A}$ is normal to $\vec{b}$ & $\vec{c}$
$\vec{B}$ is normal to $\vec{c}$ & $\vec{a}$
$\vec{c}$ is normal to $\vec{a}$ & $\vec{b}$

Construction of Reciprocal lattice

1) Take origin at same arbitrary point
2) from the origin draw perpendicular to every set of parallel planes of the direct lattice. The direction of the perpendicular specifies the orientation of the plane & thus a two dimensional plane is represented by the normal drawn on it which has only one dimensions.
3. Now take the length of each perpendicular equal or 2π times the reciprocal cal of the

interplaner spacing for the correspondi set of planes.

iv) The terminal points of these perpendicular represent the reciprocal lattice because the distance in these lattices are the reciprocal to those in the direction crystal lattice.

also Diagrams

A Need for Reciprocal Lattice :-

We can seen that x-rays diffraction is equivalent to reflection by the sets of parallel lattice planes in a crystal. Now since in a crystal there exists many sets of interpenetrating planes with different orientations & spacing that can diffracts a given beam of x-rays. This require the consideration of several sets of parallel planes.

Each set of parallel planes on a direct lattice can be represent by a normal to these planes, having length proportnal to their interplaner spacing

i.e proportnal of $\frac{1}{d_{hkl}}$.

We might more promptly think in terms of such normals. These normals are drawn with reference to any arbitrary origin and points are marked at their ends, The marked terminal points of all such possible normal corresponding to all sets of parallel planes form a regular arrangement This regular arrangement of these points is called reciprocal lattice Because the distance in this lattice are reciprocal to those in the crystal.

* Reciprocal lattice vector for general crystal axes :-

* Physical significance of Reciprocal lattice

We have already mentained that the K-space is equi- to momentum space which is reciprocal of the ordinary space. Inside a crystal the ordinary space has a lattice whose points are occupied by atoms and molecules

so the $e^{\ominus}$ belonging to those atoms & molecules have also periodicity of the lattice although they are moving around the atomic nucleus inside the solid or moving inside the solid or moori as a result of this they more in a momentum space which is also periodic A periodic lattice in K-space is the reciprocal lattice, thus a crystal has two types of lattices.

i) Direct lattice where the lattice points are separated by the integral multiple of lattice parameters $\vec{a}, \vec{b}$ & $\vec{c}$.

ii) Reciprocal lattice where the lattice points are seperated by integral multiple of reciprocal lattice parameters $\vec{A}, \vec{B}, \vec{C}$.

Properties of reciprocal lattice :-

1\ For every real lattice there is a reciprocal lattice & a direct lattice is the reciprocal lattice so its own reciprocal lattice. Simple cubic lattices is self reciprocal which b.c.c & f.cc. lattice are reciprocal to each other

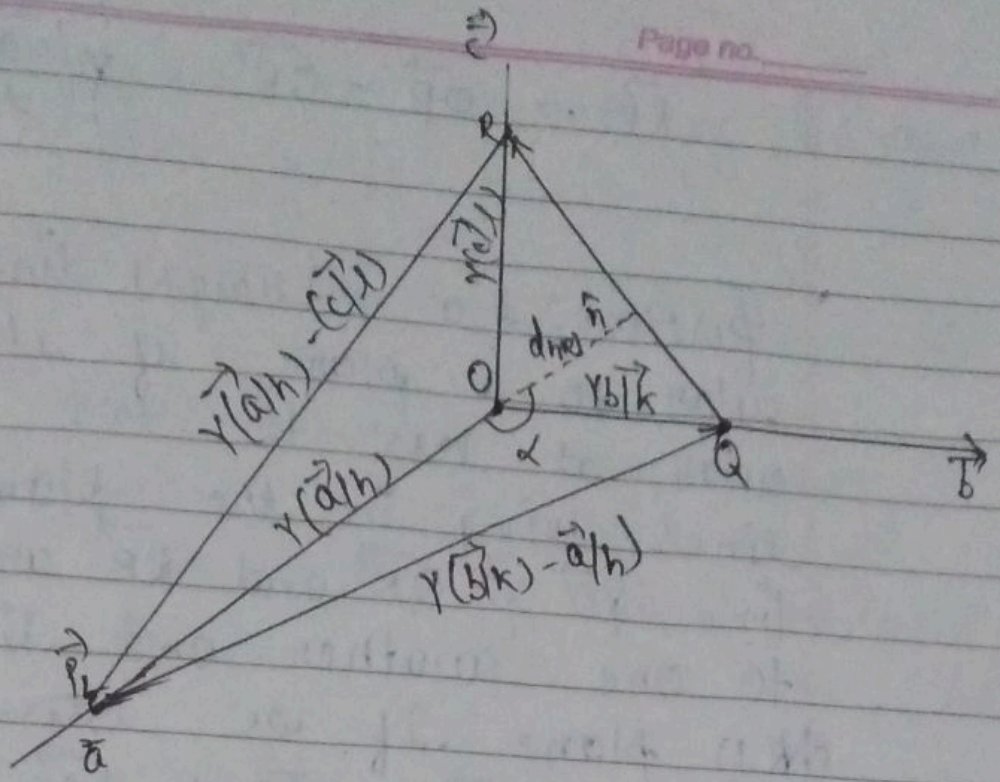
2) Each point in a reciprocal lattice corresponds to a particular set of parallel planes of the direct lattice

3. If a, b, c are orthogonal
4. In real lattice $\vec{a}, \vec{b}, \vec{c}$ defines a primitive unit cell same is defined by $\vec{A}, \vec{B}, \vec{C}$ in reciprocal lattice. The unit cell of reciprocal lattice is not necessarily a parallelopiped
5. If we rotate $\vec{a}$. $\vec{A}$ will also be rotated

6 Reciprocal lattice translation vector $\vec{G_h} = h\vec{A} + k\vec{B} + l\vec{C}$ is perpendicular to hkl plane. i.e $G_{hkl} \perp (hkl)$ plane in a crystal lattice. It means that every reciprocal lattice vector is perpendicular to a direct lattice vector.

Proof :-

Let P, Q, R be the points of intersection of the plane (hkl) with the crystal axes which are not necessarily orthogonal. in fig intercepts along $\vec{a}, \vec{b}, \vec{c}$ axes



$$\vec{OP} = \frac{r\vec{a}}{h}$$

$$\vec{OQ} = \frac{r\vec{b}}{k}$$

$\vec{OR} = \frac{r\vec{c}}{l}$ respectively, where r is const

Therefore the vectors $\vec{PQ}, \vec{OR}, \vec{RP}$ lying in plane (hkl) are

$$\vec{PQ} = \vec{OQ} - \vec{OP} = r\left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right)$$

$$\vec{QR} = \vec{OR} - \vec{OQ} = r\left(\frac{\vec{c}}{l} - \frac{\vec{b}}{k}\right)$$

$$\vec{RP} = \vec{OP} - \vec{OR} = Y\left(\frac{\vec{a}}{h} - \frac{\vec{c}}{l}\right)$$

further a straight line is perpendicular to a plane if it is perpendicular at least to two non-parallel lines lying in the plane. straight line $\vec{PQ}$, $\vec{QR}$ and $\vec{RP}$ are not parallel to one another and lie in the (hkl) plane. If we can prove that $\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$ is perpendicular to all of $\vec{PQ}$, $\vec{QR}$ & $\vec{RP}$ then $\vec{G}$ is $\perp$ to (hkl) plane.

Now consider scalar product of $\vec{PQ}$ with $\vec{G}$ i.e $\vec{G} \cdot \vec{PQ}$ oo

$$(h\vec{A} + k\vec{B} + l\vec{C}) \cdot Y\left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right)$$

$$\Rightarrow Y\left[\frac{h}{k}\vec{A}\cdot\vec{b} - \frac{h}{h}\vec{A}\cdot\vec{a} + \frac{k}{k}\vec{B}\cdot\vec{b} - \frac{k}{h}\vec{B}\cdot\vec{a} + \frac{l}{k}\vec{C}\cdot\vec{b} - \frac{l}{h}\vec{C}\cdot\vec{a}\right]$$

$$\therefore \Rightarrow Y[0 - 2\pi + 2\pi - 0 + 0 - 0] = 0 \quad \text{--(1)}$$

$$\left(\because \vec{a}\cdot\vec{A} = \vec{b}\cdot\vec{B} = 2\pi\right)$$

and $\vec{A}\cdot\vec{b} = \vec{B}\cdot\vec{a} = \vec{C}\cdot\vec{b} = \vec{C}\cdot\vec{a} = 0$

Similarly scalar product of $\vec{QR}$ and $\vec{RP}$ with G is

$$\vec{G} \cdot \vec{QR} = 0 = \vec{G} \cdot \vec{RP} \quad \text{——} (2)$$

Since eq^n (1) and (2) conclude that $\vec{G}$ is normal to $\vec{PQ}$, $\vec{QR}$ and $\vec{RP}$, so it is normal to the plane containing these vectors i.e to the plane (hkl)

I) The right of vector $\vec{G}$ i.e $|\vec{G}|$ is equal to $2\pi/d_{hkl}$ is $d_{hkl} = 2\pi/|G_{hkl}|$

Proof :-

For proving this we note that in view of the above property, $\hat{n}$ the unit vector normal to plane (hkl) is parallel to $\vec{G}$ so that $\vec{G}$ can be written as.

$$|\vec{G}_{hkl}|\hat{n} = h\vec{A} + k\vec{B} + l\vec{C}$$

$$\hat{n} = \frac{h\vec{A} + k\vec{B} + l\vec{C}}{|\vec{G}_{hkl}|}$$

The length of the inter-planar spacing of the (hkl) plane shown in

$$d_{hkl} = \frac{a}{h}\cos\alpha$$

$$\Rightarrow \frac{\vec{a}\cdot\hat{n}}{h} = \frac{\vec{a}}{h}\cdot\frac{(h\vec{A}+k\vec{B}+l\vec{C})}{|G_{hkl}|}$$

$$= \frac{\vec{a}\cdot\vec{A}}{|G_{hkl}|} = \frac{2\pi}{|\vec{G}_{hkl}|} \quad (\because \vec{a}\cdot\vec{A} = 2\pi,\ \vec{a}\cdot\vec{B} = \vec{a}\cdot\vec{C} = 0)$$

for orthogonal axes $\vec{a} \perp \vec{b} \perp \vec{c}$
so we get $\vec{A} \perp \vec{B} \perp \vec{C}$

$$\vec{A} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot(\vec{b}\times\vec{c})} = \frac{2\pi}{a}\hat{i}$$

Similarly

$$\vec{B} = \frac{2\pi}{b}\hat{j}$$

$$\vec{c} = \frac{2\pi}{c}\hat{k}$$

$$G_{hkl}^2 = \vec{G}_{hkl}\cdot\vec{G}_{hkl} = (h\vec{A}+k\vec{B}+l\vec{C})\cdot(h\vec{A}+k\vec{B}+l\vec{C})$$

$$= h^2A^2 + k^2B^2 + l^2C^2$$

$$= 4\pi^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)$$

$$d_{hkl} = \frac{2\pi}{2\pi\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}} = \frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}}$$

* Volume of unit cell of Reciprocal lattice-

The reciprocal lattice unit cell is spanned by the vector $\vec{A}, \vec{B}$ & $\vec{C}$ its volume would be $(\vec{A}\cdot\vec{B}\times\vec{C})$ substituting the values of $\vec{A}, \vec{B}, \vec{C}$ terms of $\vec{a}, \vec{b}$ & $\vec{c}$. so here

$$\vec{A}\cdot(\vec{B}\times\vec{C}) = \frac{(\vec{b}\times\vec{c})\cdot\{(\vec{c}\times\vec{a})\times(\vec{a}\times\vec{b})\}\times(2\pi)^3}{(\vec{a}\cdot\vec{b}\times\vec{c})^3}$$

$$= \frac{(\vec{b}\times\vec{c})\cdot[\{\vec{c}\cdot\vec{a}\times\vec{b}\}\vec{a} - \{\vec{c}\cdot(\vec{a}\times\vec{a})\}\vec{b}]\times 8\pi^3}{(\vec{a}\cdot\vec{b}\times\vec{c})^3}$$

$$= \frac{[\vec{a}\cdot(\vec{b}\times\vec{c})]^2\times 8\pi^3}{(\vec{a}\cdot\vec{b}\times\vec{c})^3} = \frac{8\pi^3}{(\vec{a}\cdot\vec{b}\times\vec{c})}$$

$$= \frac{8\pi^3}{\text{volume of unit cell of the direct lattice}}$$

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

Reciprocal Lattice To S.C Lattice

The primitive translation vectors of a simple cubic lattice may be taken as the.

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

The volume of the cell is

$$\vec{a} \cdot \vec{b} \times \vec{c} = (a\hat{i}) \cdot (a\hat{j}) \times a\hat{k}) = a^3.$$

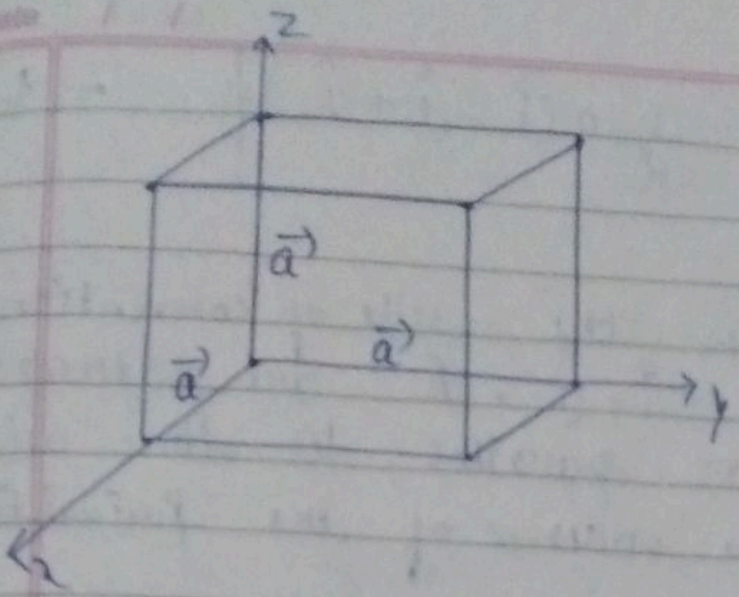
The fermitive translation of the reciprocal lattice are found from

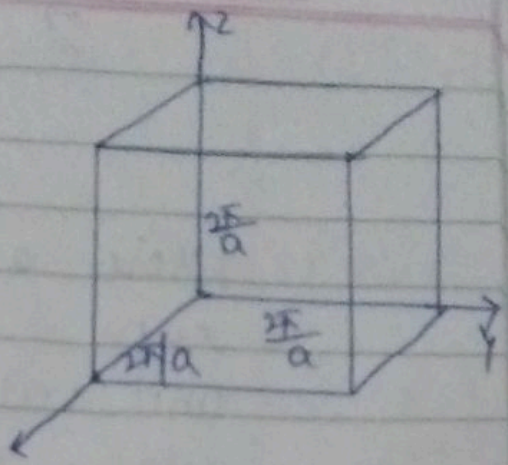
$$\vec{A} = \frac{2\pi \vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}} = \frac{2\pi a^2 \hat{j} \times \hat{k}}{a^3 \hat{i} \cdot \hat{j} \times \hat{k}} = \frac{2\pi}{a}\hat{i}$$

similarly.

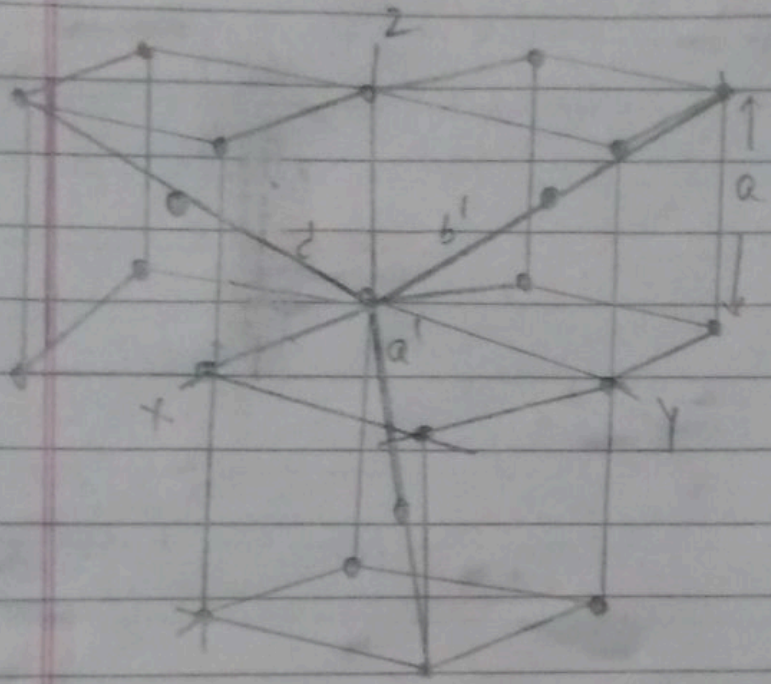
$$\vec{B} = \frac{2\pi}{a}\hat{j}, \quad \vec{c} = \frac{2\pi}{a}\hat{k}$$

Thus the reciprocal lattice to a S.C lattice is itself a simple cubic lattice, now of lattice const $\frac{2\pi}{a}$.





Reciprocal lattice for B.C.C Lattice.



The Primitive translation vector of the b.c.c lattice is

$$\left.\begin{aligned}\vec{a}' &= \frac{1}{2}a(\hat{i}+\hat{j}-\hat{k}) \\ \vec{b}' &= \frac{1}{2}a(-\hat{i}+\hat{j}+\hat{k})\end{aligned}\right]$$

$$\vec{c} = \frac{1}{2} a(\hat{i} - \hat{j} + \hat{k}) \quad \text{— eq}^{n}$$

Where a is the side of conventional cube & $\hat{i}, \hat{j}, \hat{k}$ are orthogonal unit vectors parallel to the cube edge. The volume of the primitive cell is

$$V = |\vec{a} \cdot \vec{b} \times \vec{c}| \left| \frac{1}{8} a^3 (\hat{i} + \hat{j} - \hat{k}) \cdot (-\hat{i} + \hat{j} + \hat{k}) \times (\hat{i} - \hat{j} + \hat{k}) \right|$$

$$= \left| \frac{1}{8} a^3 (\hat{i} + \hat{j} - \hat{k}) \cdot (\hat{k} + \hat{j} - \hat{k} + \hat{i} + \hat{j} + \hat{i}) \right|$$

$$= \left| \frac{1}{8} a^3 (\hat{i} + \hat{j} - \hat{k}) \cdot (2\hat{i} + 2\hat{j}) \right|$$

$$= \frac{1}{8} \left| a^3 (2 + 2) \right|$$

$$\Rightarrow \frac{1}{2} a^3 \quad \text{— eq}^{n}$$

The fermifire translation vector $\vec{A}, \vec{B}, \vec{C}$ of the reciprocal lattice are.

$$\vec{A} = \frac{2\pi}{V}(\vec{b} \times \vec{c}) = \frac{2\pi}{(1/2)a^3}\left[\frac{1}{2}a(-\hat{i}+\hat{j}+\hat{k}) \times \frac{1}{2}a(\hat{i}-\hat{j}+\hat{k})\right]$$

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

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

$$\Rightarrow \frac{2\pi}{a}(\hat{i} + \hat{j})$$

Similarly

$$\vec{B} = \frac{2\pi}{V}(\vec{c} \times \vec{a}) = \frac{2\pi}{a}(\hat{j} \times \hat{k})$$

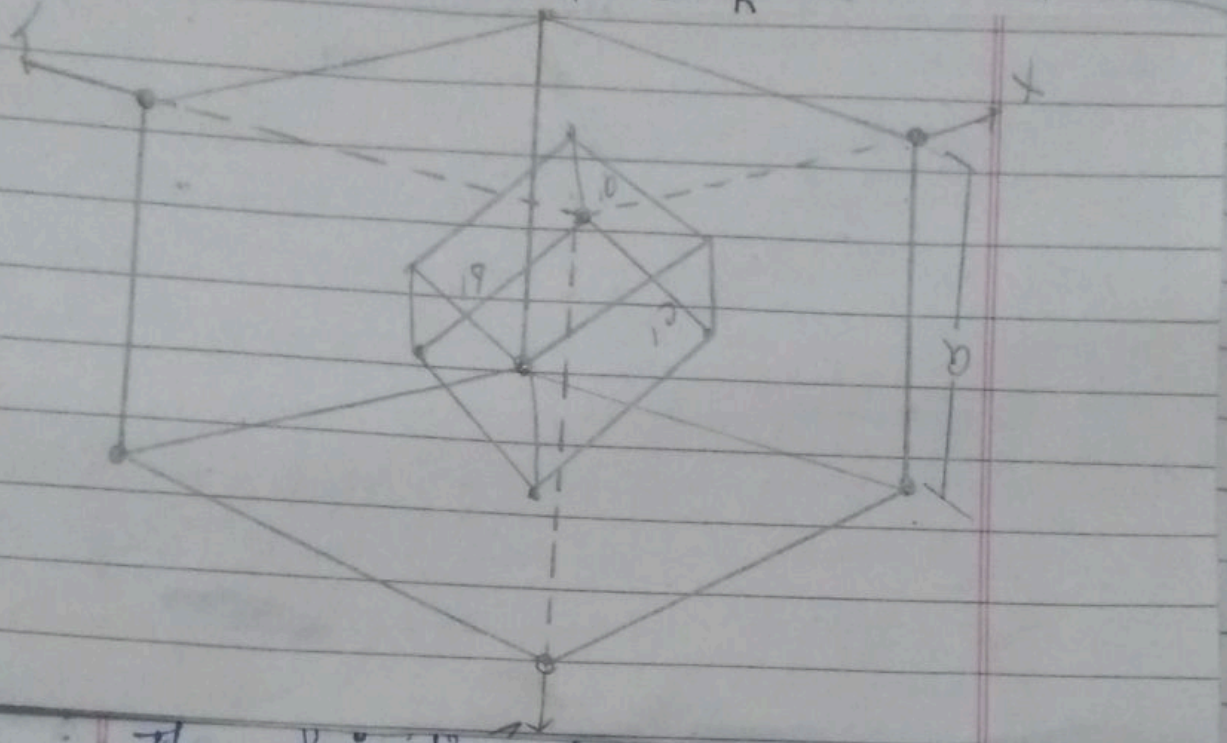
$$\vec{c} = \frac{2\pi}{V}(\vec{a} \times \vec{b}) = \frac{2\pi}{a}(\hat{i} + \hat{k})$$

It is imp to noted that we find that these are just the primitive vectors of the f.c.c lattice. Hence the f.c.c lattice is the reciprocal lattice of the b.c.c lattice If h, k, l are integers, then general reciprocal lattice vectors

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C} = \frac{2\pi}{a}\left[h(\hat{i}+\hat{j}) + k(\hat{j}+\hat{k}) + l(\hat{i}+\hat{k})\right]$$

$$= \frac{2\pi}{a}\left[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}\right]$$

* Reciprocal Lattice of FCC Lattice.



The primitive translation vectors of the f.c.c lattice shown

$$\left.\begin{aligned} \vec{a'} &= \frac{1}{2}a(\hat{i}+\hat{j}) \\ \vec{b'} &= \frac{1}{2}a(\hat{j}+\hat{k}) \\ \vec{c'} &= \frac{1}{2}a(\hat{k}+\hat{i}) \end{aligned}\right\} \quad (1)$$

The volume of the primitive cell is

$$V = |\vec{a} \cdot \vec{b} \times \vec{c}| = \frac{1}{8} a^3 |(\hat{i}+\hat{j}) \cdot (\hat{j}+\hat{k}) \times (\hat{k}+\hat{i})|$$

$$= \frac{1}{8} a^3 |(\hat{i}+\hat{j}) \cdot (\hat{i}-\hat{k}+\hat{j})| = \frac{1}{8} a^3 (1+1) = \frac{1}{4} a^3$$

the primitive translation vector $\vec{A}, \vec{B}, \vec{C}$ of the reciprocal lattice of the f.c.c lattice

$$\vec{A} = \frac{2\pi}{V} (\vec{b} \times \vec{c}) = \frac{2\pi}{(1/4) a^3} \left(\frac{1}{2} a(\hat{j}+\hat{k}) \times \frac{1}{2} a(\hat{k}+\hat{i}) \right)$$

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

Similarly

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

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

These are primitive translation vector of b.c.c lattice so that the b.c.c lattic is the reciprocal lattice of the f.c.c lattice.

If h, k, l are integers in general reciprocal lattice vectors is

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

$$= \frac{2\pi}{a}\left[(h-k+l)\hat{i} + (h+k-l)\hat{j} + (-h+k+l)\hat{k}\right]$$