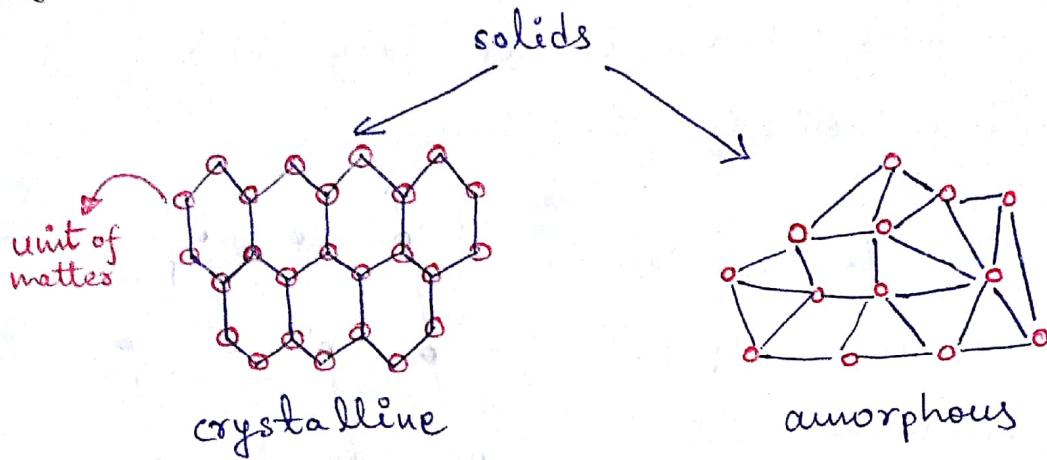


SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holy grail



(iv) Amorphous solid : no order in arrangement of unit of matter (atoms, molecules etc). XRD shows "liquid like" properties.

what's "solid"? \rightarrow elasticity

$$\text{But } \frac{1}{2} k \bar{x^2} = \frac{1}{2} k_B T$$

(Equipartition
theorem)

$$F = -l^2 K \frac{x}{l}$$

↖

$$= -Klx = -Kx,$$

$$\sigma = K \frac{x}{l}$$

$$\therefore \bar{x}^2 = \frac{k_B T}{K} = \frac{k_B T}{K\ell}$$

So if $K \rightarrow 0$, $\frac{1}{K} \rightarrow \infty$

amorphous solids

→ "rigidity"

highly viscous, supercooled liquids.

Example pitch, plastic,
silicate glass.

SALIENT

FEATURES

- (i) molecular motion is irregular but distance is more or less same with elastic solid.
 - (ii) no regular shape \rightarrow conductivity, elasticity, tensile strength is isotropic
 - (iii) no long range order. short range / medium range order possible.
 - (iv) no sharp melting point.

There are polycrystalline substances which are composed of many small domains/regions of single crystals. Crystalline substances are distinguished from amorphous solids by their anisotropic behaviour (direction dependent).

Ideal crystal: infinite repetition of identical structure in space.

Periodic arrangement of unit (atoms, molecules, ions) in a crystal is called the lattice, defined by three fundamental translation vectors $\vec{a}, \vec{b}, \vec{c}$. / basis vectors

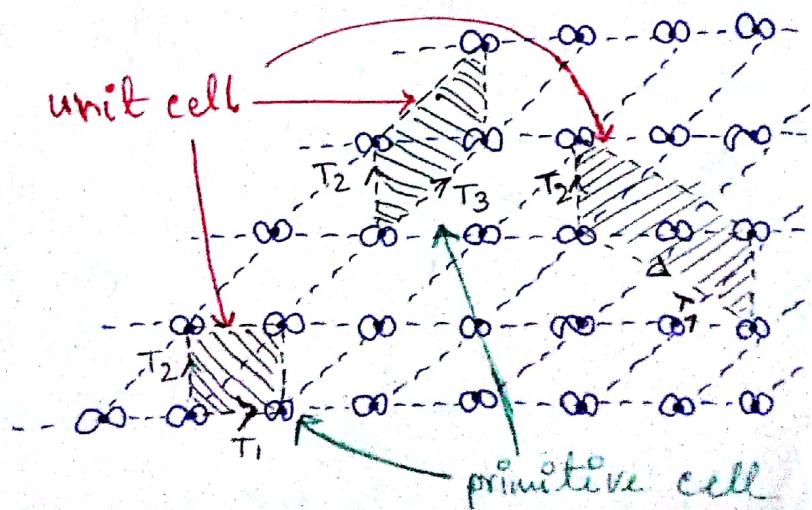
$$\text{Atomic position vector } \vec{r}' = \vec{r} + \vec{T} \\ = \vec{r} + n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

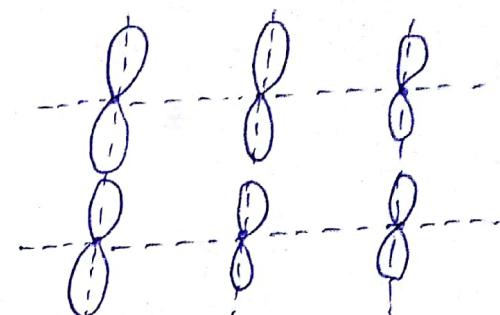
Unit cell is volume from which entire crystal can be constructed by translational repetition. (OABC parallelogram)

primitive cell is a type of unit cell that contains 1 lattice point at corners & minimum in volume = $|(\vec{a} \times \vec{b}) \cdot \vec{c}|$



Basis In crystal structure, every lattice point is associated with an unit assembly of atoms/molecules/ions. This unit is called basis.

crystal structure = lattice + basis



Basis can contain even hundreds & thousands of molecules.

A translation operation leaves the crystal invariant.

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

physical significance : number density $n(\vec{r}) = \sum_{\vec{T}} \delta(\vec{r} - \vec{T})$
(point mass atom)

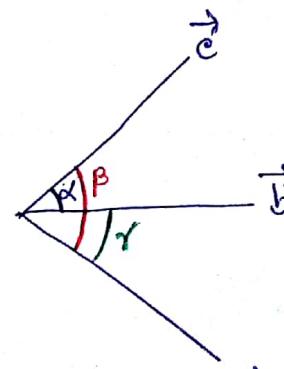
$$\text{density } \rho(\vec{r}) = \sum_{\vec{T}, \alpha} m_{\alpha} \delta(\vec{r} - \vec{T} - \vec{c}_{\alpha})$$

where m_{α} is mass of atom at lattice site \vec{c}_{α} .

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

for cubic structure $|\vec{a}| = |\vec{b}| = |\vec{c}|$

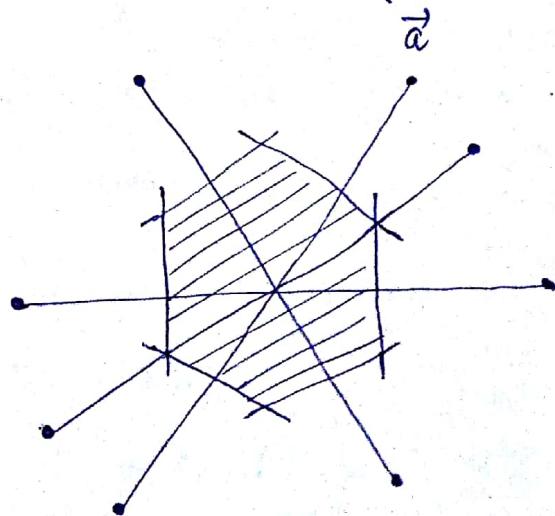
$$\alpha = \beta = \gamma = \frac{\pi}{2}$$

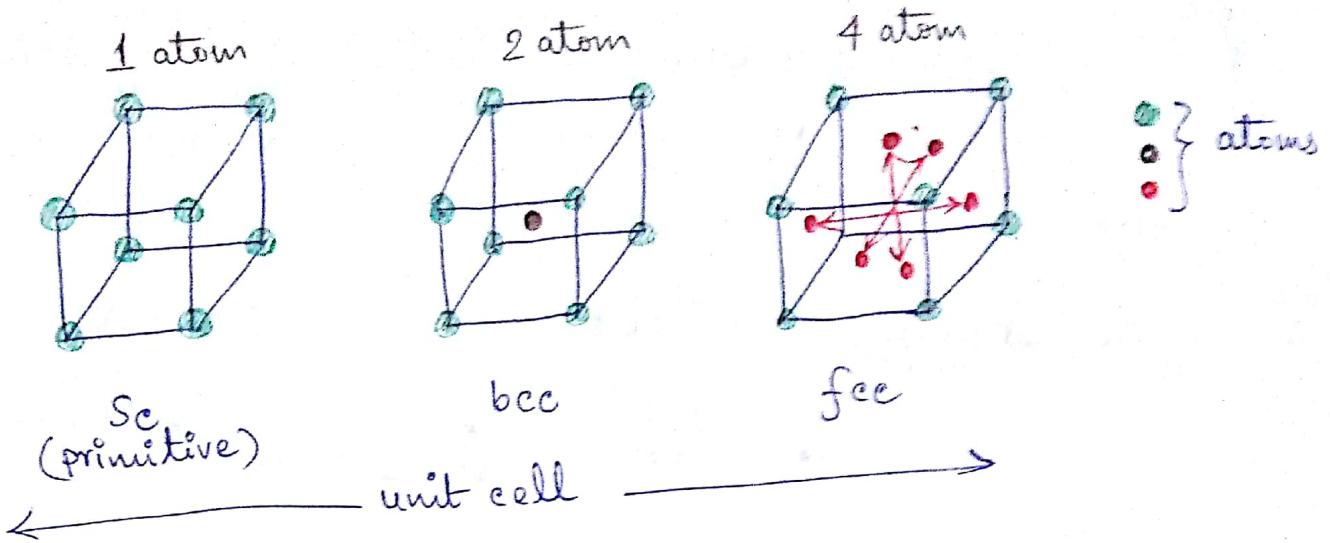


Wigner-Saitz primitive cell

1. Draw lines connecting nearby lattice points.
2. Draw planes/lines at midpoint of line & perpendicular to it.

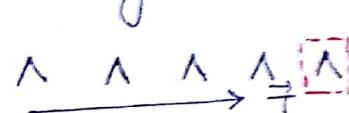
This is WS primitive cell.





Elements of symmetry

A symmetry operation transforms the crystal to itself.

(i) Translation $\vec{r}' = \vec{r} + \vec{\tau}$  $\xrightarrow{\text{motif}}$

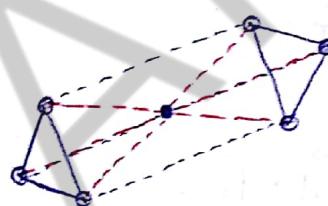
(ii) Rotation $n\phi = 2\pi$
 n = multiplicity of rotation axis.
 $= 1, 2, 3, 4, \cancel{5}, 6.$ A 2D square lattice has 4-fold rotational symmetry.

$$\begin{array}{c} \nearrow \downarrow \\ \leftarrow \rightarrow \\ \nwarrow \uparrow \end{array} \quad \phi = 60^\circ = \frac{2\pi}{6}$$

(iii) Reflection mirror image

(iv) Inversion

(only for 3D lattice)



Symmetry operations performed about a point / line are called point group symmetry. 3 types of point group (i) plane of symmetry (reflection), (ii) axis of symmetry (rotation), (iii) centre of symmetry (inversion)

5-fold rotational symmetry : quasicrystals.

But why 5-fold rotational symmetry is not permissible in crystal structure?

$$\begin{aligned} AB = a &= |\vec{a}| = |\vec{r}_1 - \vec{r}_2| \\ &= AA' = BB' \end{aligned}$$

Suppose $A'B' = q|\vec{a}|$ ($q = \text{integer}$)

$$\angle A'AC' = \angle D'BB' = \theta - \pi/2$$

$$A'C' = D'B' = |\vec{a}| \cos \theta$$

$$\therefore A'B' = |\vec{a}| + |\vec{a}| \cos \theta + |\vec{a}| \cos \theta$$

$$q|\vec{a}| = |\vec{a}| + 2|\vec{a}| \cos \theta \quad \text{or } |2\cos \theta| = \left| \frac{q-1}{2} \right|$$

as $\cos \theta < 1$, allowed values of q are $-1, 0, 1, 2, 3$

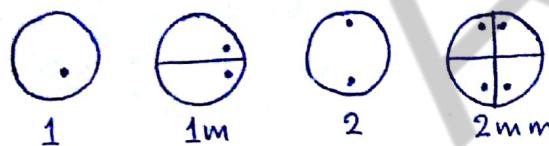
$$\left\{ q=-1, \theta = \frac{2\pi}{2} \right\}, \left\{ q=0, \theta = \frac{2\pi}{3} \right\}, \left\{ q=1, \theta = \frac{2\pi}{4} \right\}$$

$$\left\{ q=2, \theta = \frac{2\pi}{6} \right\}, \left\{ q=3, \theta = \frac{2\pi}{1} \right\}.$$

So, $n = 1, 2, 3, 4, 6 \rightarrow \text{hexad.}$
 ↓ ↗
 diad triad tetrad

Point group & space group

[translation, rotation, reflection] (point) point group.

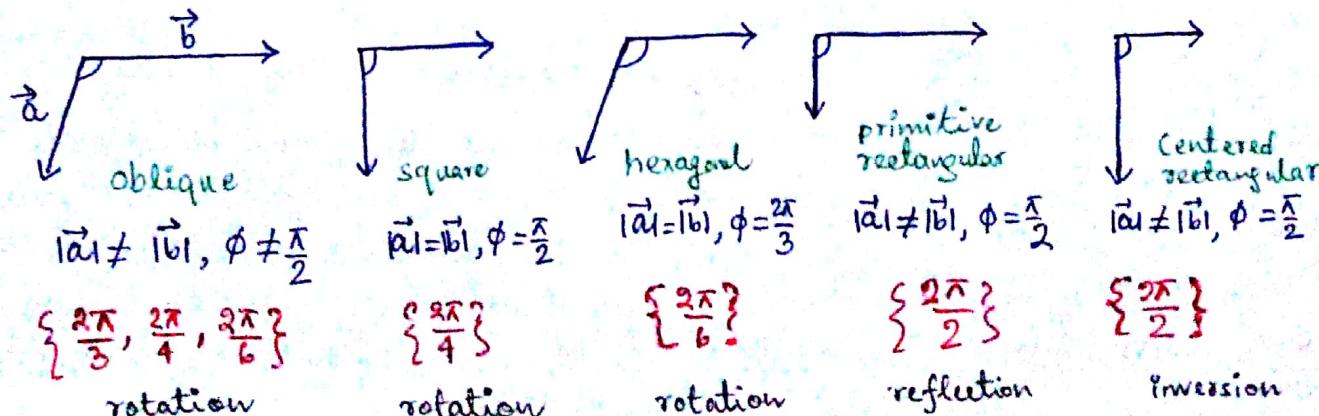


Total 32 point groups.

Group of all symmetry elements is space group.

In 2D: 17, 3D: 230.

Bravais lattice: $|\vec{a}|, |\vec{b}|, \phi$ 5 combination : symmetry operations are maintained.



3D lattice types

14 Bravais lattices

<u>Class</u>	Type & number	Angle	Length of primitive unit cell
Cubic	P, F, I	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$
Tetragonal	P, I	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$
Hexagonal	P	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b \neq c$
Rhombohedral/ Trigonal	R	$\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$	$a = b = c$
Orthorhombic	P, F, I, C	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$
Monoclinic	P, C	$\alpha = \gamma = 90^\circ \neq \beta$	$a \neq b \neq c$
Triclinic	P	$\alpha \neq \beta \neq \gamma$	$a \neq b \neq c$

Atoms per unit cell

- (i) Eight corner atoms in cubic unit cell $\frac{1}{8}$ th atom
- (ii) Six face atoms in unit cell $\frac{1}{2}$ th atom.
- (iii) If on edge then shared between 4 unit, $\frac{1}{4}$ th atom
- (iv) If inside cell, then (of course) 1 atom as whole.

Simple cubic cell (sc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} = 1.$$

Body centered cubic cell (bcc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} + 1 = 2$$

Face centered cubic cell (fcc)

$$\# \text{ of atoms / unit cell} = \frac{8}{8} + \frac{6}{2} = 4$$

Coordination Number In crystal lattice, the number of nearest neighbours of an atom is called coordination no.

sc cell, coord. no. = 6.

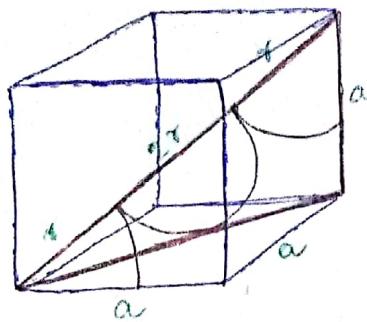
bcc cell, coord no. = 8

fcc cell, coord no. = $4 \times 3 = 12$

1 plane in XY, YZ, XZ plane

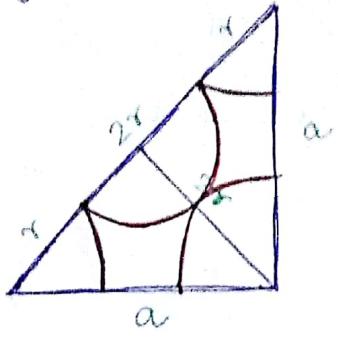
Atomic radius

Distance between centre of two touching atoms.



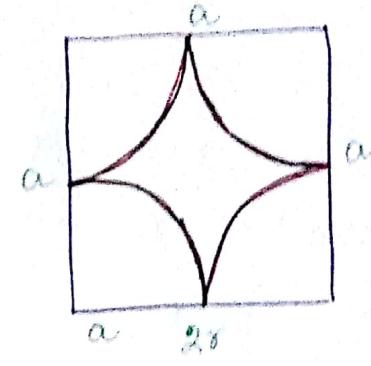
[bcc]

$$(4r)^2 = (\sqrt{2}a)^2 + a^2 \\ \text{or } r = \frac{\sqrt{3}}{4}a$$



[fcc]

$$(4r)^2 = 2a^2 \\ \text{or } r = \frac{a}{2\sqrt{2}}$$



[sc]

$$2r = a \\ \text{or } r = \frac{a}{2}$$

Atomic packing fraction/factor / relative packing density

$$\text{P.F. (f)} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$$

[bcc] 2 atoms / unit cell, $r = \frac{\sqrt{3}}{4}a$

$$\therefore \text{vol. of atoms} = 2 \times \frac{1}{3}\pi r^3, \text{ vol. of unit cell} = a^3.$$

$$\therefore f = \frac{2 \times \frac{4}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 68\%.$$

Example :- Barium, chromium, sodium, iron, caesium chloride

[fcc] 4 atoms / unit cell, $r = \frac{a}{2\sqrt{2}}$.

$$\therefore f = \frac{4 \times \frac{4}{3}\pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 74\%. \quad \begin{array}{l} \text{nickel} \\ \text{example: barium,} \\ \text{copper, aluminium, lithium,} \\ \text{chromium, sodium, etc.} \end{array}$$

[sc] 1 atom / unit cell, $r = \frac{a}{2}$.

$$\therefore f = \frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 52\%$$

Example :- polonium, potassium chloride

- HW 1. Primitive translation vector of hcp lattice $\vec{a} = \frac{\sqrt{3}}{2}a\hat{i} + \frac{a}{2}\hat{j}$, $\vec{b} = -\frac{\sqrt{3}}{2}a\hat{i} + \frac{a}{2}\hat{j}$, $\vec{c} = \hat{c}\hat{k}$. Compute the volume of the primitive cell.

2. Show that for a fcc crystal structure, lattice constant is $a = \left(\frac{4M}{\rho N}\right)^{\frac{1}{3}}$ where M is the gram molecular weight of molecules at lattice points, ρ is the density & N is Avogadro's number.

NaCl structure

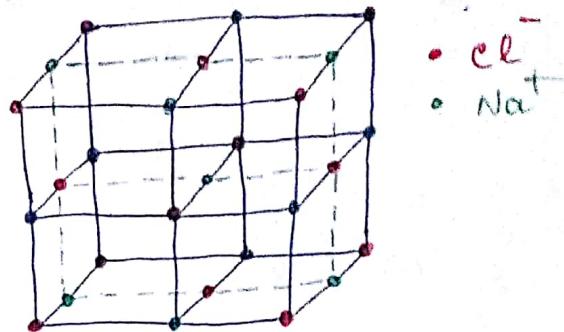
ionic crystal Na^+ & Cl^- , fcc Bravais lattice

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

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

1 NaCl molecule in unit cube.

$\text{Na}^+(0,0,0)$ & $\text{Cl}^-(\frac{1}{2}, 0, 0) \rightarrow$ 6 nearest neighbour (coordination number)

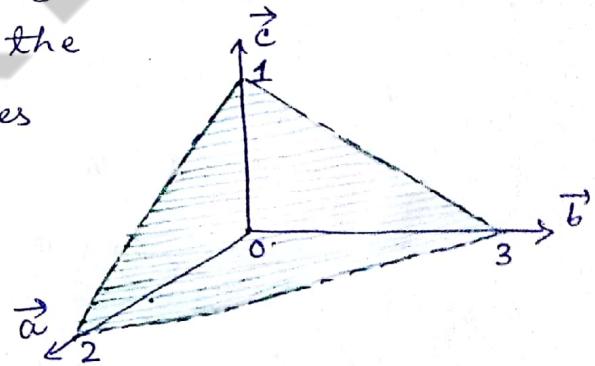


Miller indices To designate the position & orientation of a crystal plane according to following rule:

(a) In terms of lattice constant, find the intercepts of the plane on crystal axes

$\vec{a}, \vec{b}, \vec{c}$ (primitive or nonprimitive)

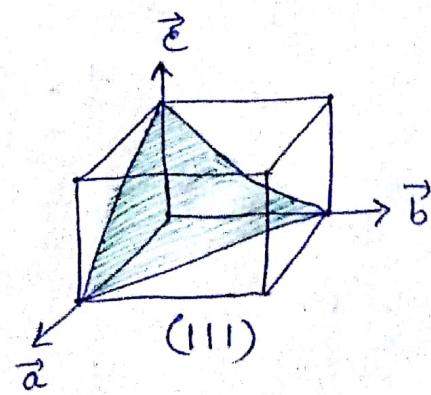
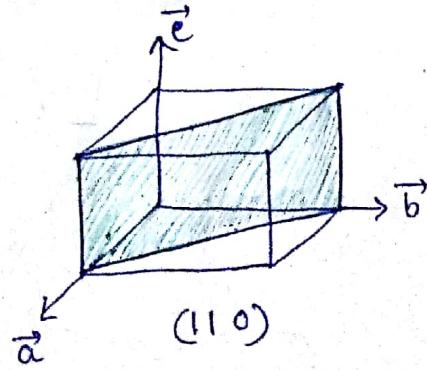
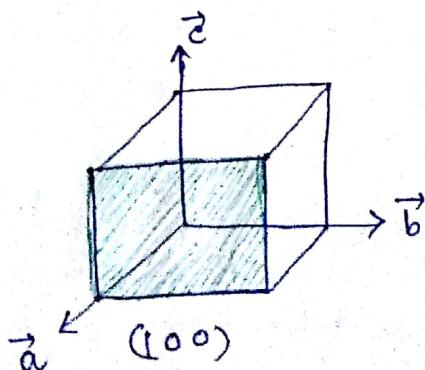
$(2,0,0), (0,3,0), (0,0,1) \rightarrow 2a, 3b, c.$



(b) Take reciprocals of them & reduce to smallest 3 integers, Denote with (h, k, l)

So $2a, 3b, c \xrightarrow{\text{reciprocal}} \frac{1}{2}, \frac{1}{3}, 1 \xrightarrow{\text{smallest}} 3, 2, 6.$

Miller index is $(3, 2, 6)$ plane.



If plane cuts negative side of axis, Miller index (h, \bar{k}, l)
(say $-\vec{b}$)

6-faces of cubic crystal, Miller index $(1, 0, 0), (0, 1, 0), (0, 0, 1)$ $\equiv \{1, 0, 0\}$
because through rotation, all faces $(\bar{1}, 0, 0), (0, \bar{1}, 0), (0, 0, \bar{1})$
are equivalent & written in $\{1, 0, 0\}$.

So $(2, 0, 0)$ plane intercepts on $\vec{a}, \vec{b}, \vec{c}$ are $\frac{1}{2}a, \infty, \infty$. & parallel
(Miller index) to $(1, 0, 0)$ & $(\bar{1}, 0, 0)$ plane.

Indices of a direction $[h, k, l]$ & direction \vec{b} perpendicular to
plane (h, k, l) . \vec{a} axis = $[1, 0, 0]$, $-\vec{b}$ axis = $[0, \bar{1}, 0]$
body diagonal = $[1, 1, 1]$

*

Spacing of planes in sc lattice

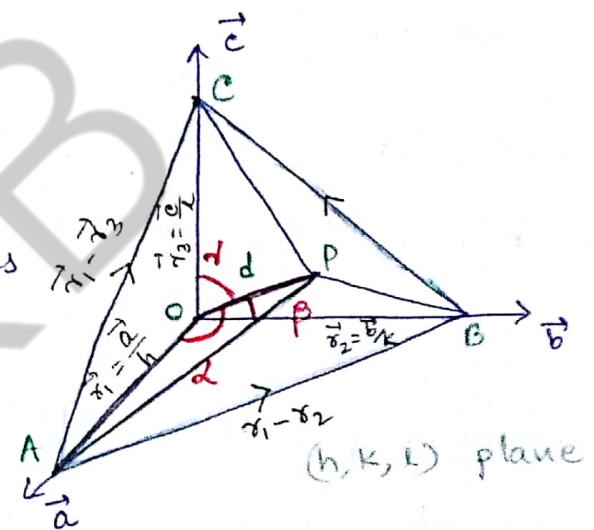
simple unit cell $\vec{a} \perp \vec{b} \perp \vec{c}$ &
a plane (h, k, l) (Miller index).

Intercepts $a/h, b/k, c/l$ on $\vec{a}, \vec{b}, \vec{c}$ axes

$OP \perp (h, k, l)$ plane & $OP = d$.

& $\angle AOP = \alpha, \angle BOP = \beta, \angle COP = \gamma$.

& $\angle APO = \angle BPO = \angle CPO = 90^\circ$.



$$\frac{OP}{OA} = \cos \alpha \quad \text{or} \quad OP = OA \cos \alpha \quad \text{or} \quad d = \frac{a}{h} \cos \alpha \quad \text{or} \quad \cos \alpha = \frac{d h}{a}$$

$$\text{Similarly } \cos \beta = \frac{d k}{b}, \quad \cos \gamma = \frac{d l}{c}.$$

Law of direction cosines, $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$

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

$$\therefore d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

If cubic lattice, $a = b = c$, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$d_{100} = \frac{a}{\sqrt{1+0+0}} = a, \quad d_{110} = \frac{a}{\sqrt{1+1+0}} = \frac{a}{\sqrt{2}}, \quad d_{111} = \frac{a}{\sqrt{1+1+1}} = \frac{a}{\sqrt{3}}$$

Spacing of planes in bcc lattice

One atom at each corner + one atom at cube centre.
(portion) (whole)

$\therefore d_{100} = \frac{a}{2}$ as additional $(1,0,0)$ is there halfway between (100) plane of sc.

$d_{110} = d_{1\bar{1}0}^{\text{sc}} = \frac{a}{\sqrt{2}}$. but $d_{111} = \frac{1}{2} \frac{a}{\sqrt{3}}$ as $(1,1,1)$ plane lies midway of (111) plane of sc.

Spacing of planes in fcc lattice

One atom at each corner + one atom at each face.
(portion) (portion)

$\therefore d_{100} = \frac{a}{2}$ as additional $(1,0,0)$ is there halfway between $(1,00)$ plane of sc.

But $d_{110} = \frac{1}{2} \frac{a}{\sqrt{2}}$ as additional set of (110) is there halfway between $(1,1,0)$ plane.

$d_{111} = \frac{a}{\sqrt{3}}$ as centre of all face plane without new plane.

$$\textcircled{*} \quad \vec{r}_1 = \vec{a}/h, \vec{r}_2 = \vec{b}/k, \vec{r}_3 = \vec{c}/l.$$

$h\vec{a} + k\vec{b} + l\vec{c}$ represents $[h, k, l]$

$$\text{Now } (\vec{r}_1 - \vec{r}_2) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) = \left(\frac{\vec{a}}{h} - \frac{\vec{b}}{k}\right) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) \\ = \vec{a} \cdot \vec{a} - \vec{b} \cdot \vec{b} = 0. \quad (\text{as } |a| = |b|)$$

$$\text{Similarly } (\vec{r}_1 - \vec{r}_3) \cdot (h\vec{a} + k\vec{b} + l\vec{c}) = 0 \quad (\text{as } |a| = |c|)$$

As vectors $\vec{r}_1 - \vec{r}_2$ & $\vec{r}_1 - \vec{r}_3$ lie in (h, k, l) plane, so $[h, k, l]$ is perpendicular to plane (h, k, l) .

Reciprocal lattice To represent slope λ , interplanar spacing of crystal plane, each set of parallel plane in a space lattice is represented by normals of planes with length = $\frac{1}{\text{interplanar spacing}}$ points marked at ends.

points form regular arrangement \rightarrow reciprocal lattice

for $\vec{a}, \vec{b}, \vec{c}$, we describe reciprocal basis vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$

(primitive) such that $\vec{a} \cdot \vec{a}^* = 2\pi, \vec{b} \cdot \vec{a}^* = 0, \vec{c} \cdot \vec{a}^* = 0$
 $\vec{a} \cdot \vec{b}^* = 0, \vec{b} \cdot \vec{b}^* = 2\pi, \vec{c} \cdot \vec{b}^* = 0$
 $\vec{a} \cdot \vec{c}^* = 0, \vec{b} \cdot \vec{c}^* = 0, \vec{c} \cdot \vec{c}^* = 2\pi$.

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

reciprocal lattice vector $\vec{r}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

properly (i) reciprocal lattice is normal to lattice plane of direct crystal lattice-

$$\vec{r}^* \cdot (\vec{r}_1 - \vec{r}_2) = (h\vec{a}^* + k\vec{b}^* + l\vec{c}^*) \cdot \left(\frac{\vec{a}}{h} - \frac{\vec{b}}{k} \right) = 0.$$

Similarly $\vec{r}^* \cdot (\vec{r}_1 - \vec{r}_3) = 0$.

(ii) direct lattice is reciprocal of reciprocal lattice.

SC = self-reciprocal.

BCC \leftrightarrow FCC reciprocal of each other.

Definition of R.L. $\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$ direct lattice vector &

say \vec{K} constitutes a plane wave $e^{i\vec{K} \cdot \vec{r}}$ which may not have the periodicity of Bravais lattice but \vec{R} has that periodicity.

$$e^{i\vec{K} \cdot (\vec{r} + \vec{T})} = e^{i\vec{K} \cdot \vec{r}} \quad \text{or} \quad e^{i\vec{K} \cdot \vec{T}} = 1$$

$$\vec{K} = k_1 \vec{a}^* + k_2 \vec{b}^* + k_3 \vec{c}^* =$$

$$\therefore \vec{K} \cdot \vec{T} = 2\pi(k_1 n_1 + k_2 n_2 + k_3 n_3)$$

If $e^{i\vec{K} \cdot \vec{T}} = 1$, then $\vec{K} \cdot \vec{T}$ must be $2\pi \times \text{integer} \Rightarrow k_1, k_2, k_3$ integers

So from \vec{K} only \vec{R} which is linear combination of $\vec{a}^*, \vec{b}^*, \vec{c}^*$ with integral coefficient makes \vec{R} a reciprocal lattice vector.

Reciprocal of reciprocal lattice

As by construction, reciprocal lattice is a "Braais lattice", reciprocal gives back the direct lattice.

HW Define $\vec{a}^{**} = 2\pi \frac{\vec{b}^* \times \vec{c}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$, ~~$\vec{b}^{**} = 2\pi \frac{\vec{c}^* \times \vec{a}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$, $\vec{c}^{**} = 2\pi \frac{\vec{a}^* \times \vec{b}^*}{\vec{a}^* \cdot \vec{b}^* \times \vec{c}^*}$~~ as three vectors generated by primitive vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$. Check first, $\vec{a}^* \cdot \vec{b}^* \times \vec{c}^* = \frac{(2\pi)^3}{\vec{a} \cdot \vec{b} \times \vec{c}}$ & then show that $\vec{a}^{**} = \vec{a}$, $\vec{b}^{**} = \vec{b}$, $\vec{c}^{**} = \vec{c}$.

Reciprocal of sc lattice

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

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

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

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

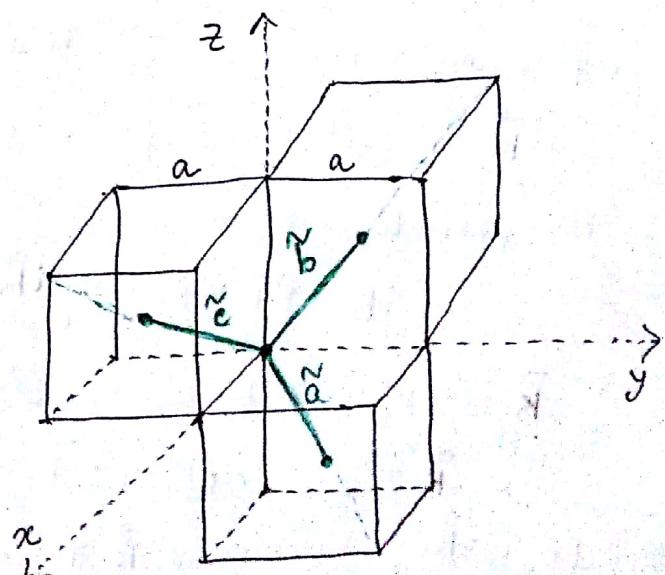
Lattice constant = $2\pi/a$.

Reciprocal of bcc lattice

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

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

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



volume of primitive cell = $\vec{a} \cdot \vec{b} \times \vec{c} = a^3/2$.

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

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

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

Reciprocal of fcc lattice

volume of primitive cell = $\vec{a} \cdot \vec{b} \times \vec{c} = a^3/4$.

$$\text{and } \vec{a}^* = \frac{2\pi}{a} (\hat{i} + \hat{j} - \hat{k}), \quad \vec{b}^* = \frac{2\pi}{a} (-\hat{i} + \hat{j} + \hat{k}), \quad \vec{c}^* = \frac{2\pi}{a} (\hat{i} - \hat{j} + \hat{k})$$

\therefore Reciprocal bcc lattice vectors = primitive fcc lattice vectors
 Reciprocal fcc lattice vectors = primitive bcc lattice vectors

$$\text{volume of primitive cell} = \vec{a} \cdot \vec{b} \times \vec{c} = a^3/2$$

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

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

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

Reciprocal of fcc lattice

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

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

$$\text{volume of primitive cell} = \vec{a} \cdot \vec{b} \times \vec{c} = a^3/4.$$

$$\text{and } \vec{a}^* = \frac{2\pi}{a} (\hat{i} + \hat{j} - \hat{k}), \quad \vec{b}^* = \frac{2\pi}{a} (-\hat{i} + \hat{j} + \hat{k}), \quad \vec{c}^* = \frac{2\pi}{a} (\hat{i} - \hat{j} + \hat{k})$$

\therefore Reciprocal bcc lattice vectors = primitive fcc lattice vectors
 Reciprocal fcc lattice vectors = primitive bcc lattice vectors

Crystal diffraction

Why use x-ray for crystallography?

Atomic spacing (say for NaCl) is 2.8 \AA . When X-ray is produced by accelerating electrons through a potential difference V ,

$$eV = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{eV} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-19} \times 10^4} \text{ (say } V=10 \text{ kV)} \\ = 1.24 \text{ \AA.}$$

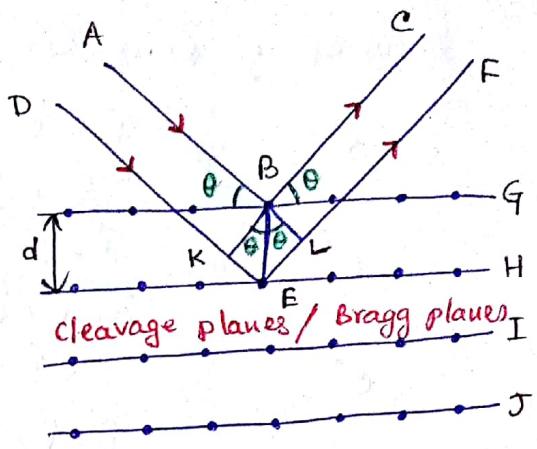
$\lambda_{x\text{-ray}} \approx a$ (elastic scattering without change in λ)

$\lambda_{\text{visible/UV}} \gg a$ (reflection or refraction)

$\lambda_{x\text{-ray}} \ll a$ (small angle diffraction)

Bragg's law for crystal diffraction

Maximum intensity from reflected beam (waves) from two different atomic planes (cleavage planes) with path difference equal to integral multiple of $\lambda_{\text{x-ray}}$.



Path difference between ray $[AB, BC]$ & $[DE, EF]$ is $KE + EL$

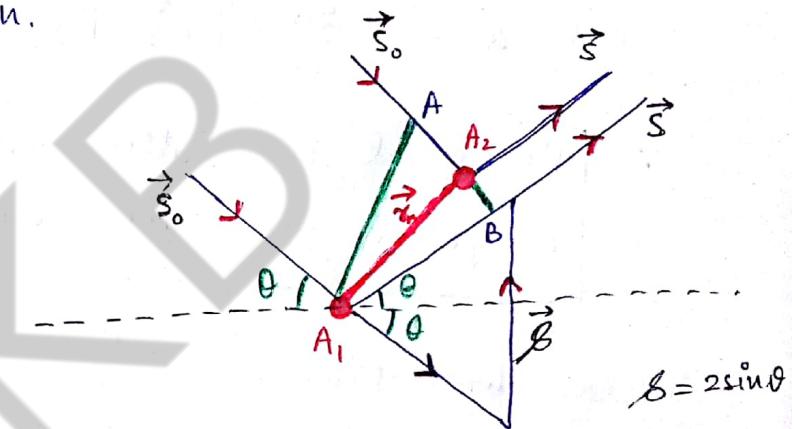
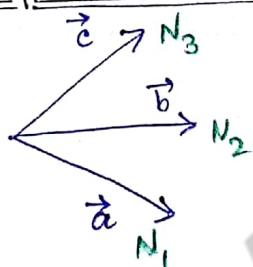
$$= d \sin \theta + d \sin \theta = 2d \sin \theta.$$

So for constructive interference,

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots \Rightarrow \text{Bragg's law.}$$

λ, θ = known, d = unknown.

Lau's equation of XRD



Assumptions: (a) The primary X-ray beam travels within the crystal at the speed of light. (b) Each scattered wavelet travels through the crystal without getting rescattered.

Say N_1 number of points along direction \vec{a}

N_2 number of points along direction \vec{b}

N_3 number of points along direction \vec{c}

Total $N = N_1 N_2 N_3$ points in the crystal lattice.

Path difference between two X-rays is $d = \vec{r}_n \cdot \vec{s} - \vec{r}_n \cdot \vec{s}_0 = \vec{r}_n \cdot \vec{\delta}$

\therefore Phase difference is $\frac{2\pi}{\lambda} d = \frac{2\pi}{\lambda} \vec{r}_n \cdot \vec{\delta} = k \vec{r}_n \cdot \vec{\delta}$

remember: \vec{s}, \vec{s}_0 unit vector, $|\vec{\delta}| = \delta = a \sin \theta$, $\vec{r}_n = n^{\text{th}}$ lattice point from origin = $\vec{r} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$.

If y is the displacement of the scattered wave from origin at a distance R at time t with amplitude A_0 , then

$$y_0 = \frac{A_0}{R} e^{i\omega t}. \quad \therefore \text{displacement from } \vec{r}_n \text{ is}$$

$$y = \frac{A_0}{R} e^{i\omega t} e^{iK \vec{r}_n \cdot \vec{s}}$$

\therefore Total displacement due to the whole Bravais lattice is

$$\begin{aligned} Y &= \sum \frac{A_0}{R} e^{i\omega t} e^{iK \vec{r}_n \cdot \vec{s}} \\ &= \sum_{\substack{\text{all points} \\ n_1=0 \\ n_2=0 \\ n_3=0}} \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} e^{iK[(n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}) \cdot \vec{s}]} \frac{A_0}{R} e^{i\omega t} \\ &= \frac{A_0}{R} e^{i\omega t} \sum_{n_1=0}^{N_1-1} e^{iK n_1 \vec{a} \cdot \vec{s}} \sum_{n_2=0}^{N_2-1} e^{iK n_2 \vec{b} \cdot \vec{s}} \sum_{n_3=0}^{N_3-1} e^{iK n_3 \vec{c} \cdot \vec{s}} \end{aligned}$$

$$\begin{aligned} \text{Now } \sum_{n_1=0}^{N_1-1} e^{iK n_1 \vec{a} \cdot \vec{s}} &= 1 + e^{iK \vec{a} \cdot \vec{s}} + e^{i2K \vec{a} \cdot \vec{s}} + \dots + e^{i(N_1-1)K \vec{a} \cdot \vec{s}} \\ &= \frac{1 - e^{iN_1(\vec{a} \cdot \vec{s})K}}{1 - e^{i(\vec{a} \cdot \vec{s})K}} \end{aligned}$$

$$\begin{aligned} \therefore \left(\sum_{n_1=0}^{N_1-1} e^{iK n_1 \vec{a} \cdot \vec{s}} \right) \left(\sum_{n_1=0}^{N_1-1} e^{iK n_1 \vec{a} \cdot \vec{s}} \right)^* &= \frac{1 - e^{-iN_1(\vec{a} \cdot \vec{s})K}}{1 - e^{-i(\vec{a} \cdot \vec{s})K}} \\ &= \frac{1 - e^{iN_1(\vec{a} \cdot \vec{s})K}}{1 - e^{i(\vec{a} \cdot \vec{s})K}} \times \frac{1 - e^{-iN_1(\vec{a} \cdot \vec{s})K}}{1 - e^{-i(\vec{a} \cdot \vec{s})K}} \\ &= \frac{1 - \cos \{ N_1(\vec{a} \cdot \vec{s})K \} + i \sin \{ N_1(\vec{a} \cdot \vec{s})K \}}{1 - \cos \{ (\vec{a} \cdot \vec{s})K \} - i \sin \{ (\vec{a} \cdot \vec{s})K \}} \times \\ &\quad \frac{1 - \cos \{ N_1(\vec{a} \cdot \vec{s})K \} + i \sin \{ N_1(\vec{a} \cdot \vec{s})K \}}{1 - \cos \{ (\vec{a} \cdot \vec{s})K \} + i \sin \{ (\vec{a} \cdot \vec{s})K \}} \\ &= \frac{(1 - \cos \{ N_1(\vec{a} \cdot \vec{s})K \})^2 + (\sin \{ N_1(\vec{a} \cdot \vec{s})K \})^2}{(1 - \cos \{ (\vec{a} \cdot \vec{s})K \})^2 + (\sin \{ (\vec{a} \cdot \vec{s})K \})^2} \\ &= \frac{1 - \cos \{ N_1(\vec{a} \cdot \vec{s})K \}}{1 - \cos \{ (\vec{a} \cdot \vec{s})K \}} = \frac{\sin^2 \frac{N_1(\vec{a} \cdot \vec{s})K}{2}}{\sin^2 \frac{(\vec{a} \cdot \vec{s})K}{2}} = \frac{\sin^2 (N_1 \psi_1)}{\sin^2 (\psi_1)} \end{aligned}$$

where $\Psi_1 = \frac{1}{2} K \vec{a} \cdot \vec{s}$.

$$\therefore \text{Total intensity } I = YY^* = \left(\frac{|A_0|}{R}\right)^2 \frac{\sin^2(N_1 \psi_1)}{\sin^2 \psi_1} \frac{\sin^2(N_2 \psi_2)}{\sin^2 \psi_2} \frac{\sin^2(N_3 \psi_3)}{\sin^2 \psi_3}$$

$$\psi_1 = \frac{1}{2} K \vec{a} \cdot \vec{s} = \frac{1}{2} K |\vec{a}| |\vec{s}| \cos \alpha = \frac{1}{2} \frac{2\pi}{\lambda} a 2 \sin \theta \cos \delta = \frac{2\pi a \sin \theta \cos \delta}{\lambda}$$

$$\text{Similarly } \psi_2 = \frac{1}{2} K \vec{b} \cdot \vec{s} = \frac{2\pi b \sin \theta \cos \beta}{\lambda},$$

$$\psi_3 = \frac{1}{2} K \vec{c} \cdot \vec{s} = \frac{2\pi c \sin \theta \cos \gamma}{\lambda}$$

[Notice the analogy of \vec{s} with $[h, k, l]$ plane with angles α, β, γ]

$$\text{In } \lim_{\psi_1 \rightarrow h\pi}, \frac{\sin^2(N_1 \psi_1)}{\sin^2 \psi_1} \text{ is maximum} = N_1^2$$

$$\text{Similarly } \lim_{\psi_2 \rightarrow k\pi} \frac{\sin^2(N_2 \psi_2)}{\sin^2 \psi_2} = N_2^2, \quad \lim_{\psi_3 \rightarrow l\pi} \frac{\sin^2(N_3 \psi_3)}{\sin^2 \psi_3} = N_3^2$$

$$\text{Then } I_{\max} = \left(\frac{|A_0|}{R}\right)^2 N_1^2 N_2^2 N_3^2 = \frac{|A_0|^2}{R^2} N^2$$

$$\therefore \frac{2\pi a \sin \theta \cos \delta}{\lambda} = h\pi,$$

$$\frac{2\pi b \sin \theta \cos \beta}{\lambda} = k\pi,$$

$$\frac{2\pi c \sin \theta \cos \gamma}{\lambda} = l\pi,$$

$$2a \sin \theta \cos \delta = h\lambda,$$

$$2b \sin \theta \cos \beta = k\lambda$$

$$2c \sin \theta \cos \gamma = l\lambda$$

"Lau equations".

Bragg's law from Lau equations

from Lau equation, direction

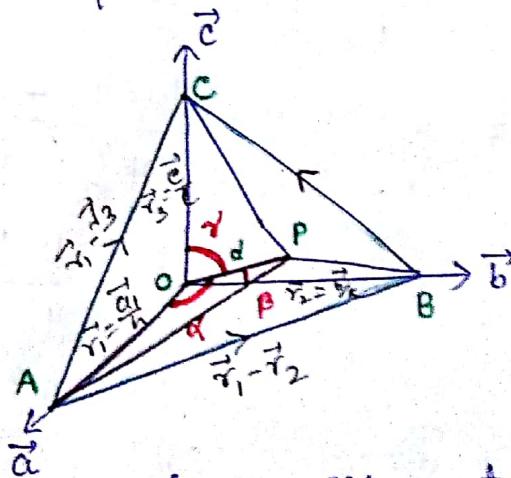
cosines of \vec{s} are

$$\cos \alpha = \frac{h\lambda}{2a \sin \theta}, \quad \cos \beta = \frac{k\lambda}{2b \sin \theta},$$

$$\cos \gamma = \frac{l\lambda}{2c \sin \theta}.$$

But also see that if (h, k, l) is a miller plane with equation

$$\frac{x}{a/h} + \frac{y}{b/k} + \frac{z}{c/l} = 1 \quad \text{then} \quad \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma = d.$$



The direction cosines of \vec{r} are also proportional to n_x, n_y, n_z , so the X-ray is diffracted from \vec{r}_0 to \vec{r} by the Miller plane (h, k, l).

$$\begin{aligned}\therefore d &= \frac{a}{n} \cos\alpha = \frac{a}{n} \frac{n\lambda}{2ds\sin\theta} = \frac{\lambda}{2s\sin\theta} \\ &= \frac{b}{k} \cos\beta = \frac{b}{k} \frac{k\lambda}{2ds\sin\theta} = \frac{\lambda}{2s\sin\theta} \\ &= \frac{c}{l} \cos\gamma = \frac{c}{l} \frac{l\lambda}{2ds\sin\theta} = \frac{\lambda}{2s\sin\theta}\end{aligned}$$

Note that h, k, l of Laue equation aren't necessarily identical with Miller indices but may contain a common factor n .

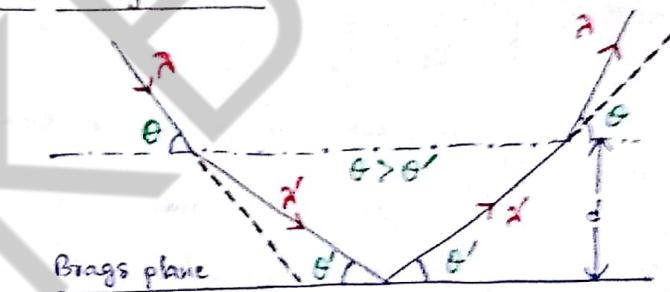
$$\therefore 2ds\sin\theta = n\lambda$$

with $d = \text{adjacent interplanar spacing with Miller indices}$

$$\frac{h}{n}, \frac{k}{n} \text{ & } \frac{l}{n}.$$

Modification of Bragg's law due to refraction

Refraction of X-rays due to change in wavelength & angle of incidence because of the refractive index of the crystal.



$$\text{Bragg's equation } n\lambda = 2ds\sin\theta'$$

$$\text{Using Snell's law, refractive index } \mu = \frac{\lambda}{\lambda'} = \frac{\cos\theta}{\cos\theta'}$$

$$\therefore n\frac{\lambda}{\mu} = 2d \sqrt{1 - \frac{\cos^2\theta}{\mu^2}}$$

$$n\lambda = 2d \sqrt{\mu^2 - \cos^2\theta} = 2d \sqrt{\sin^2\theta - (1 - \mu^2)} = 2ds\sin\theta \sqrt{1 - \frac{1 - \mu^2}{\sin^2\theta}}$$

$$\approx 2ds\sin\theta \left(1 - \frac{1 - \mu^2}{2\sin^2\theta}\right)$$

$$\approx 2ds\sin\theta \left(1 - \frac{2(1 - \mu)}{2\sin^2\theta}\right)$$

$$\approx 2ds\sin\theta \left(1 - (1 - \mu) \frac{4\theta^2}{n^2\lambda^2}\right)$$

$$[1 - \mu^2 = (1 + \mu)(1 - \mu)]$$

$$\approx 2(1 - \mu) \text{ as } \mu \approx 1$$

$$\boxed{2ds\sin\theta = n\lambda}$$

$$\text{or } \frac{1}{\sin^2\theta} = \frac{4d^2}{n^2\lambda^2}$$

$$\boxed{n\lambda = 2ds\sin\theta \left[1 - \frac{4d^2(1 - \mu)}{n^2\lambda^2}\right]}$$

Point: The correction term $\frac{4d^2(1 - \mu)}{n^2\lambda^2}$ is small & becomes more small as "n" increases.

∴ The direction cosines of \vec{s} are also proportional to h, k, l , so the X-ray is diffracted from \vec{s}_0 to \vec{s} by the miller plane (h, k, l) .

$$\begin{aligned} \therefore d &= \frac{a}{h} \cos\alpha = \frac{a}{h} \frac{h\lambda}{2as \sin\theta} = \frac{\lambda}{2s \sin\theta} \\ &= \frac{b}{k} \cos\beta = \frac{b}{k} \frac{k\lambda}{2bs \sin\theta} = \frac{\lambda}{2s \sin\theta} \\ &= \frac{c}{l} \cos\gamma = \frac{c}{l} \frac{l\lambda}{2cs \sin\theta} = \frac{\lambda}{2s \sin\theta}. \end{aligned}$$

Note that h, k, l of Laue equation aren't necessarily identical with Miller indices but may contain a common factor n .

$$\therefore 2ds \sin\theta = n\lambda$$

with d = adjacent interplanar spacing with Miller indices

$$\frac{h}{n}, \frac{k}{n} \text{ & } \frac{l}{n}.$$

Interpretation of Laue's equation in reciprocal lattice

Reciprocal lattice vector $\vec{q}^* = \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$

magnitude = reciprocal of spacing of (h, k, l) planes of direct lattice.

direction = perpendicular to (h, k, l) plane.

$$\begin{aligned} \vec{G} \cdot \vec{a} &= \vec{q}^* \cdot \vec{a} = 2\pi h. \\ \vec{G} \cdot \vec{b} &= \vec{q}^* \cdot \vec{b} = 2\pi k \\ \vec{G} \cdot \vec{c} &= \vec{q}^* \cdot \vec{c} = 2\pi l \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\}$$

$$\text{From Laue equation, } \Psi_1 = \frac{1}{2} K \vec{a} \cdot \vec{s} = h\pi \quad \text{or} \quad \frac{1}{2} \frac{2\pi}{\lambda} \vec{s} \cdot \vec{a} = h\pi$$

$$\therefore \frac{2\pi \vec{s}}{\lambda} \cdot \vec{a} = 2\pi h.$$

$$\text{Similarly from } \Psi_2 \text{ & } \Psi_3, \quad \frac{2\pi \vec{s}}{\lambda} \cdot \vec{b} = 2\pi k, \quad \frac{2\pi \vec{s}}{\lambda} \cdot \vec{c} = 2\pi l. \quad \left. \begin{array}{l} \\ \\ \end{array} \right\}$$

Comparing,

$$\boxed{\vec{q}^* = \vec{G} = \frac{2\pi \vec{s}}{\lambda}}$$

Ewald's construction

Geometrical construction to obtain a relation between wave vector \vec{K} & the direction of incident X-ray using the reciprocal lattice & deducing Bragg's law in vectorial form.

$\vec{K} = \frac{2\pi}{\lambda}$ (magnitude), direction along X-ray beam from O & terminating at point A.

From O with radius $K = \frac{2\pi}{\lambda}$, draw a sphere (reflex sphere).

Suppose it intersects B, then \vec{AB} represents reciprocal vector \vec{G} & $G \perp OC$ (direct lattice plane)

$$G = \frac{2\pi n}{d}$$

\vec{K}' = diffracted (reflected) wave vector, with $|\vec{K}| = |\vec{K}'|$
So magnitude is same, only direction changes.

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

$$\cancel{|\vec{K}'|^2} = (\vec{K} + \vec{G}) \cdot (\vec{K} + \vec{G}) = \cancel{|\vec{K}|^2} + 2\vec{K} \cdot \vec{G} + \vec{G} \cdot \vec{G}$$

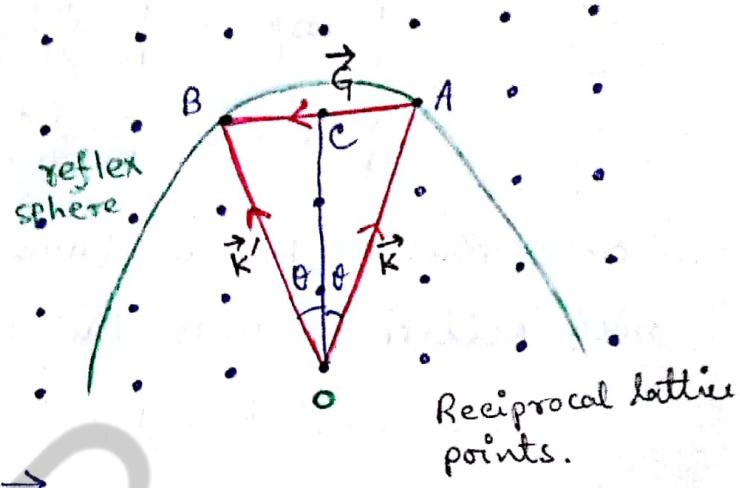
$$\therefore (\vec{K} + \frac{\vec{G}}{2}) \cdot \vec{G} = 0 \Rightarrow \text{Bragg's law (vectorial form)} \\ \text{in reciprocal lattice.}$$

Notice that $AC = OA \sin\theta = CB$.

$$\therefore AB = 2OA \sin\theta = 2K \sin\theta = 2 \frac{2\pi}{\lambda} \sin\theta$$

$$\therefore G = \frac{4\pi}{\lambda} \sin\theta \quad \therefore \frac{2\pi n}{d} = \frac{4\pi}{\lambda} \sin\theta$$

$$\therefore 2ds \sin\theta = n\lambda$$



CW 1. Calculate wavelength & speed of neutron beam, where spacing between successive (100) planes is 3.84 \AA , grazing angle is 30° & order of Bragg reflection = 1.

Bragg's Law $2d \sin \theta = n\lambda$,

$$d = 3.84 \times 10^{-10} \text{ m}, \theta = 30^\circ, n=1 \quad \therefore 2 \times 3.84 \times 10^{-10} \times \frac{1}{2} = \lambda$$

$$\therefore \lambda = 3.84 \text{ \AA}.$$

Using de-Broglie relation $\lambda = \frac{h}{p} = \frac{h}{mv}$

$$v = \frac{n}{m\lambda} = \frac{6.62 \times 10^{-34} \text{ Js}}{1.67 \times 10^{-27} \text{ kg} \times 3.84 \times 10^{-10} \text{ m}} = 1.03 \times 10^3 \text{ m/s}$$

$$= 1.03 \text{ km/s.}$$

2. X-ray of wavelength 1.24 \AA is reflected by cubic crystal KCl.

Calculate the interplanar distance for (100), (110) & (111) planes. Given density of KCl = $1.98 \times 10^3 \text{ kg/m}^3$, molecular weight 74.5 kg .

Avogadro's no. $N = 6.023 \times 10^{26} \text{ kg/mole.}$

for cubic crystal, $a = \left(\frac{nM}{\rho N}\right)^{\frac{1}{3}}$.

$$\text{for KCl, } n=1, \quad a = \left(\frac{4 \times 74.5}{1.98 \times 10^3 \times 6.023 \times 10^{26}}\right)^{\frac{1}{3}} = 6.3 \times 10^{-10} \text{ m} = 6.3 \text{ \AA}$$

$$\therefore d_{100} = \frac{a}{\sqrt{1^2+0^2}} = \frac{6.3 \text{ \AA}}{2} \quad d_{110} = \frac{a}{\sqrt{1^2+1^2}} = \frac{1}{2}\sqrt{2}a = \frac{1}{2}\sqrt{2} \times \frac{6.3 \text{ \AA}}{2} = \frac{4.45 \text{ \AA}}{2}$$

$$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}} = 3.63 \text{ \AA}.$$

(remember KCl is fcc).

3.(a) Calculate the Bragg angle for x-rays with $\lambda = 1.54 \text{ \AA}$ in different orders 1, 2, 3 if interplanar spacing is 2.67 \AA . (b) If Bragg glancing angle is 15° for 1st order, then calculate glancing angles for 2nd & 3rd order spectrum?

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

$$\lambda = 1.54 \times 10^{-10} \text{ m}, \quad d = 2.67 \times 10^{-10} \text{ m},$$

$$n=1 \text{ (1st order)} \quad 2d \sin \theta_1 = \lambda$$

$$\theta_1 = \sin^{-1} \left[\frac{\lambda}{2d} \right] = \sin^{-1} \left[\frac{1.54 \times 10^{-10}}{2 \times 2.69 \times 10^{-10}} \right] \approx 16.76^\circ$$

$$n=2 \text{ (2nd order)} \quad \theta_2 = \sin^{-1} \left[\frac{2\lambda}{2d} \right] = 35.22^\circ$$

$$n=3 \text{ (3rd order)} \quad \theta_3 = \sin^{-1} \left[\frac{3\lambda}{2d} \right] = 59.9^\circ$$

$$(b) \quad 2d \sin \theta_1 = \lambda, \quad \theta_1 = 15^\circ \quad \therefore \cancel{2d} \frac{\lambda}{2d} = \sin 15^\circ = 0.2588.$$

$$\text{So for 2nd order, } \sin \theta_2 = 2 \frac{\lambda}{2d} = 2 \times 0.2588 = 0.5176$$

$$\theta_2 = 31.17^\circ$$

$$\text{for 3rd order, } \sin \theta_3 = 3 \frac{\lambda}{2d} = 3 \times 0.2588 = 0.7764$$

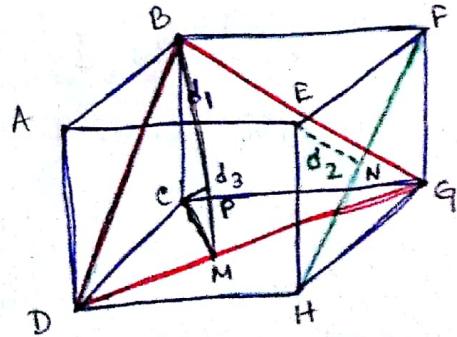
$$\theta_3 = 50.93^\circ$$

HW 1. Molecular weight of rock salt (NaCl) crystal is 58.5 Kg/kilomole & density $2.16 \times 10^3 \text{ kg/m}^3$. Calculate grating spacing d_{100} of rock salt. Using that, calculate λ of X-rays in 2nd order if angle of diffraction is 26° .

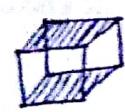
2. If X-rays with $\lambda = 0.5 \text{ \AA}$ is diffracted at 5° in 1st order, what is the spacing between adjacent planes of a crystal? At ~~what~~ what angle will 2nd maximum occur?

3. Bragg angle for 1st order reflection from (111) plane of a crystal is 60° , when $\lambda = 1.8 \text{ \AA}$. Calculate interatomic spacing.

Determination of crystal structure

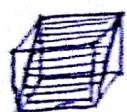


d is to be calculated for given X-ray (λ) by using different plane.



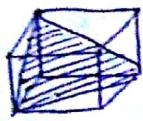
$ABFE \perp CGHD$.

d_1 distance apart. \rightarrow Total 6 faces (100) plane.



Diagonal plane BFHD inclined at 75° to (100) planes

d_2 is interplanar spacing $\frac{d_2}{d_1} = \sin 45^\circ = \frac{1}{\sqrt{2}}$ $\therefore d_2 = \frac{d_1}{\sqrt{2}}$.
 (110) plane.

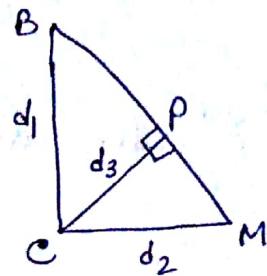


BGD plane. Here $CM \perp DG$ & BM joined to obtain right-angle triangle BCM. $CM = d_2$

$$BM = \sqrt{d_1^2 + d_2^2} \quad CP = d_3,$$

$$\sin B = \frac{d_3}{d_1} = \frac{d_2}{\sqrt{d_1^2 + d_2^2}}$$

$$\therefore d_3 = \frac{d_1 d_2}{\sqrt{d_1^2 + d_2^2}} = \frac{d_1}{\sqrt{3}} \quad (\text{substitute } d_2 = \frac{d_1}{\sqrt{2}}).$$



These are (111) planes.

$$\therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = 1 : \sqrt{2} : \sqrt{3}$$

Bragg found for KCl crystal for 1st order reflection

$$\theta_1 \text{ (from (100) plane)} = 5.22^\circ \quad \theta_3 \text{ (from (111) plane)} = 9.05^\circ.$$

$$\theta_2 \text{ (from (110) plane)} = 7.30^\circ$$

$$\text{as } \frac{1}{d} = \frac{2 \sin \theta}{\lambda} \quad \therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = \sin 5.22 : \sin 7.30 : \sin 9.05 \\ = 0.0910 : 0.1272 : 0.1570 \\ = 1 : 1.40 : 1.73 = 1 : \sqrt{2} : \sqrt{3}.$$

So KCl has cubic crystal symmetry.

NaCl crystal

8 ions at corner $\rightarrow 4 \text{ Na}^+, 4 \text{ Cl}^-$

\therefore Each ion of NaCl is shared between

two adjacent cube of unit cell contain half a molecule of NaCl.

$$\text{mass of unit cell} = \frac{M}{2N} = \frac{23 + 35.5}{2 \times 6.023 \times 10^{26}} \text{ kg.}$$

$$\text{density of NaCl} = 2.17 \times 10^3 \text{ kg/m}^3.$$

$$\therefore \text{volume } d^3 = \frac{58.5}{2 \times 6.023 \times 10^{26} \times 2.17 \times 10^3} \quad \therefore d = 2.814 \text{ \AA.}$$

Now verify Bragg's law for different order of diffraction.

$$1^{\text{st}} \text{ order}, n=1, \theta = 11.8^\circ, \lambda = 2ds\sin\theta = 2 \times 2.814 \times 10^{-10} \times \sin 11.8^\circ = 1.12 \text{ \AA}.$$

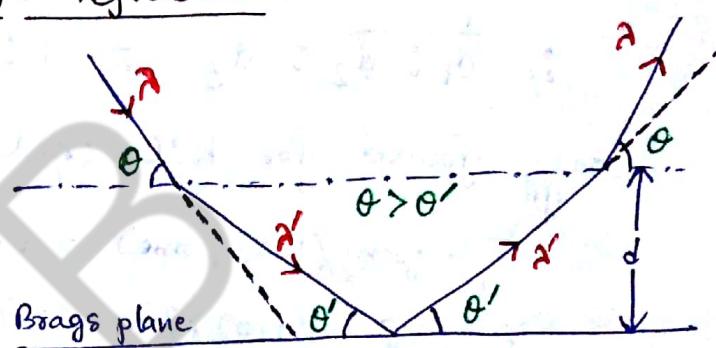
$$2^{\text{nd}} \text{ order}, n=2, \theta = 23.5^\circ, \lambda = \frac{2ds\sin\theta}{2} = 2.814 \times 10^{-10} \times \sin 23.5^\circ = 1.12 \text{ \AA}.$$

$$3^{\text{rd}} \text{ order}, n=3, \theta = 36^\circ, \lambda = \frac{2ds\sin\theta}{3} = \frac{2}{3} \times 2.814 \times 10^{-10} \times \sin 36^\circ = 1.12 \text{ \AA}.$$

\therefore Diffraction from NaCl crystal verified Bragg's law.

Modification of Bragg's law due to refraction

Refraction of X-rays due to change in wavelength & angle of incidence because of the refractive index of the crystal.



$$\text{Bragg's equation } n\lambda' = 2d\sin\theta'$$

$$\text{Using Snell's law, refractive index is } \mu = \frac{\lambda}{\lambda'} = \frac{\cos\theta}{\cos\theta'}$$

$$\therefore n \frac{\lambda}{\mu} = 2d \sqrt{1 - \frac{\cos^2\theta}{\mu^2}}$$

$$\Rightarrow n\lambda = 2d \sqrt{\mu^2 - \cos^2\theta} = 2d \sqrt{\sin^2\theta - (1 - \mu^2)} = 2d\sin\theta \sqrt{1 - \frac{1 - \mu^2}{\sin^2\theta}}$$

$$\approx 2d\sin\theta \left(1 - \frac{1 - \mu^2}{2\sin^2\theta}\right)$$

$$[1 - \mu^2 = (1 + \mu)(1 - \mu)]$$

$$\approx 2d\sin\theta \left(1 - \frac{2(1 - \mu)}{2\sin^2\theta}\right)$$

$$\approx 2(1 - \mu) \text{ as } \mu \approx 1$$

$$\approx 2d\sin\theta \left(1 - (1 - \mu) \frac{4d^2}{n^2\lambda^2}\right)$$

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

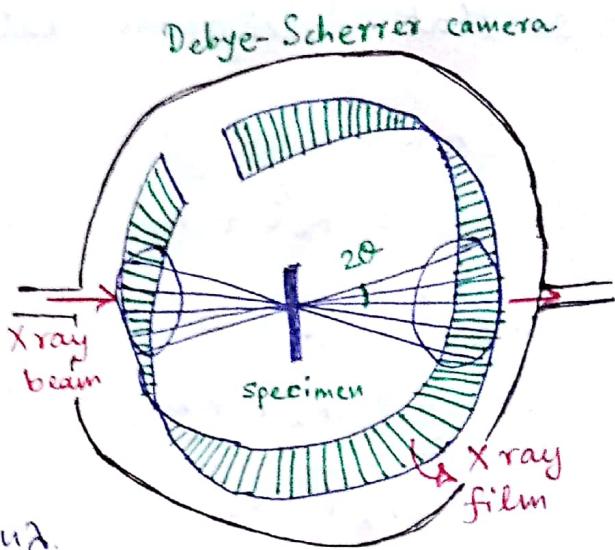
$$\text{or } \frac{1}{\sin^2\theta} = \frac{4d^2}{n^2\lambda^2}$$

$$n\lambda = 2d\sin\theta \left[1 - \frac{4d^2(1 - \mu)}{n^2\lambda^2}\right]$$

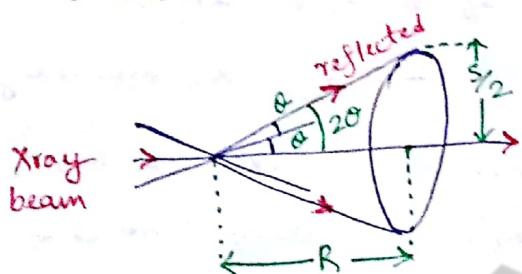
Forgot! The correction term $\frac{4d^2(1 - \mu)}{n^2\lambda^2}$ is small & becomes more small as "n" increases.

Focussed Method of XRD

$2ds\sin\theta = n\lambda$, $d \& \theta$ varies for fixed λ . Powdered specimen is kept in a thin capillary tube on a movable mount at the centre of a cylindrical camera.



For arbitrary orientation, some planes satisfy Bragg reflection $2ds\sin\theta = n\lambda$. They lie on a conical section with semi-vertical angle 2θ . Other cones arise due to other set of planes. Cones intersect X-ray film in concentric rings with sharp centre. Specimen is rotated to ensure all possible planes to face the X-rays.



S = distance between diffracted lines

R = radius of the film

$$\frac{S}{2R} = 2\theta \quad \text{or} \quad \theta = \frac{S}{4R} \quad \text{and} \quad \sin\theta \approx \theta$$

$$\text{so that } 2ds\sin\theta = \lambda \quad (\text{for } n=1)$$

$$\approx 2d\theta = \lambda$$

$$\approx 2d \frac{S}{4R} = \lambda \quad \Rightarrow \quad d = \frac{2R\lambda}{S}$$

from known (measured) R, S, λ , interplanar spacing d is calculated.

Brillouin Zones

We have learned that all \mathbf{k} values for which the reciprocal lattice points intersect the Ewald sphere are Bragg reflected. Brillouin zone is the locus of all these \mathbf{k} values in the reciprocal lattice which are Bragg reflected.

Brillouin zones for sc lattice in 2D

primitive translation vectors $\vec{a} = \hat{a}\mathbf{i}$, $\vec{b} = \hat{a}\mathbf{j}$, $\vec{c} = \hat{a}\mathbf{l}$
corresponding translation vector in reciprocal lattice $\vec{a}^* = \frac{2\pi}{a}\hat{\mathbf{i}}$, $\vec{b}^* = \frac{2\pi}{a}\hat{\mathbf{j}}$

so that reciprocal lattice vector $\vec{G} = h\hat{a}^* + k\hat{b}^*$
 $= \frac{2\pi}{a}(h\hat{i} + k\hat{j})$.

(h, k are integers)

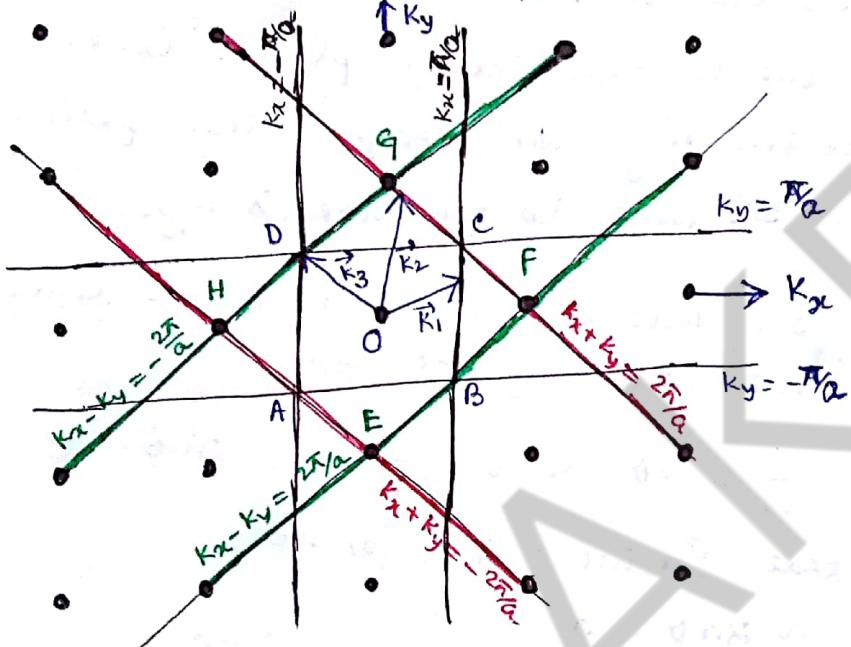
$\vec{R} = k_x\hat{i} + k_y\hat{j}$. so from Bragg's vectorial condition

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

$$\text{or } \frac{4\pi}{a}(hK_x + kK_y) + \frac{4\pi^2}{a^2}(h^2 + k^2) = 0$$

$$\text{or } hK_x + kK_y = -\frac{\pi}{a}(h^2 + k^2)$$

For all h, k values, we can obtain \vec{R} .



If $h = \pm 1, k = 0$ then

$$K_x = \pm \frac{\pi}{a} \quad (K_y \text{ arbitrary})$$

If $h = 0, k = \pm 1$, then

$$K_y = \pm \frac{\pi}{a} \quad (K_x \text{ arbitrary})$$

All \vec{R} (for example $\vec{R}_1, \vec{R}_2, \vec{R}_3$) originating from O &

terminating on these parallel lines are Bragg reflected.

If $h = \pm 1, k = \pm 1$ then $\pm K_x \pm K_y = \frac{2\pi}{a}$.

Region enclosed by such lines are the Brillouin zones.

ABCD is the first Brillouin zone & EFGH is the second Brillouin zone.

Brillouin zone boundary represent loci of \vec{R} that obey Bragg's law, meaning they're the reflecting planes. $ABCD \Rightarrow 2dsin\theta = \lambda$. $EFGH \Rightarrow 2dsin\theta = 2\lambda$ & so on.

$$\text{In 3D, } hK_x + kK_y + lK_z = -\frac{\pi}{a}(h^2 + k^2 + l^2)$$

with cubes represent Brillouin zone.

Brillouin zones of the fcc lattice

primitive translation vectors of fcc lattice are

$\vec{a} = \frac{a}{2}(\hat{i} + \hat{j})$, $\vec{b} = \frac{a}{2}(\hat{j} + \hat{k})$, $\vec{c} = \frac{a}{2}(\hat{k} + \hat{i})$. & primitive translation vectors in reciprocal space are

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

$$\begin{aligned}\therefore \vec{q} &= h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \\ &= \frac{2\pi}{a}[(h-k+l)\hat{i} + (h+k-l)\hat{j} + (-h+k+l)\hat{k}]\end{aligned}$$

To make shortest \vec{q} , we can use 8 combinations

$$\vec{q} = \frac{2\pi}{a}(\pm\hat{i} \pm \hat{j} \pm \hat{k})$$

first zone boundary is determined by the 8 planes $\perp q$ at their midpoint. But the corners of the octahedron are truncated by planes which are perpendicular bisector of 6 reciprocal lattice vector $\frac{2\pi}{a}(\pm 2\hat{i})$, $\frac{2\pi}{a}(\pm 2\hat{j})$, $\frac{2\pi}{a}(\pm 2\hat{k})$. So first Brillouin zone is truncated octahedron, which is also the primitive unit cell of bcc lattice.

Brillouin zones of bcc lattice

primitive translation vectors of bcc lattice are

$$\vec{a} = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k}), \vec{b} = \frac{a}{2}(-\hat{i} + \hat{j} + \hat{k}), \vec{c} = \frac{a}{2}(\hat{i} - \hat{j} + \hat{k}) \text{ &}$$

primitive translation vectors of reciprocal lattice are

$$\vec{a}^* = \frac{2\pi}{a}(\hat{i} + \hat{j}), \vec{b}^* = \frac{2\pi}{a}(\hat{j} + \hat{k}), \vec{c}^* = \frac{2\pi}{a}(\hat{k} + \hat{i}).$$

$\vec{q} = \frac{2\pi}{a}[(h+k)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}]$ & shortest \vec{q} are the 12 vectors, $\vec{q} = \frac{2\pi}{a}(\pm\hat{i} \pm \hat{j})$

$$= \frac{2\pi}{a}(\pm\hat{j} \pm \hat{k})$$

$$= \frac{2\pi}{a}(\pm\hat{k} \pm \hat{i})$$

first Brillouin zone is volume by normal bisector of 12 vectors
 \Rightarrow rhombic dodecahedron.