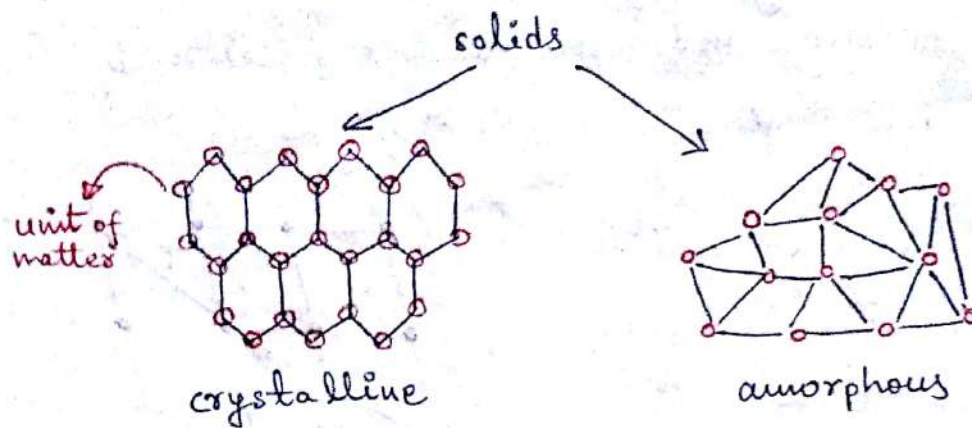


SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holly grain



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

what's "solid"? \rightarrow elasticity

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

x = displacement

l = length of lattice

$$\text{But } \frac{1}{2} K \bar{x}^2 = \frac{1}{2} K_B T$$

(equipartition theorem)

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

$$\therefore \bar{x}^2 = \frac{K_B T}{K} = \frac{K_B T}{K l}$$

So if $K \rightarrow 0$, $\bar{x}^2 \rightarrow \infty \rightarrow$ "rigidity"

amorphous solids \longleftrightarrow highly viscous, supercooled liquids.

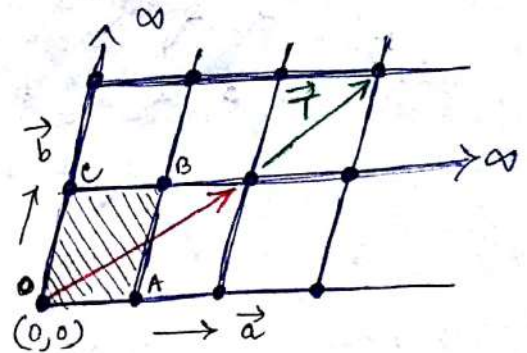
Example pitch, plastic, silicate glass.

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



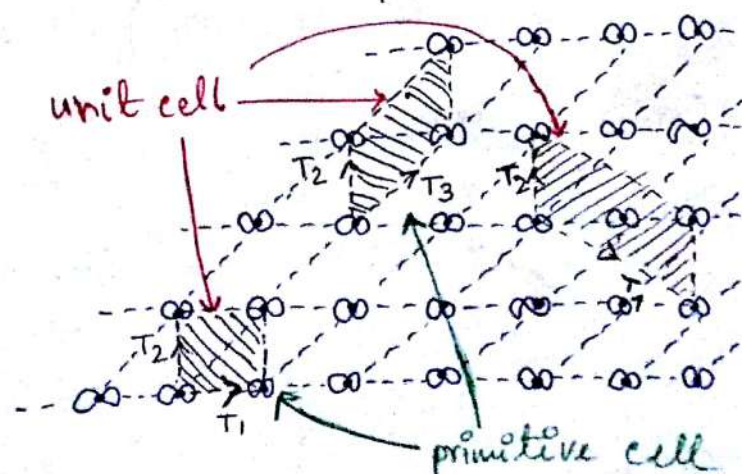
Atomic position vector $\vec{r}' = \vec{r} + \vec{r}$
 $= \vec{r} + n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

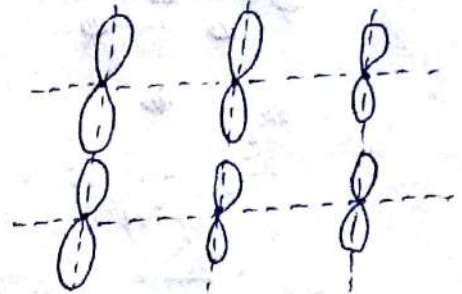
Unit cell is volume from which entire crystal can be constructed by translational repetition. (OABC parallelogram)

primitive cell is a type of unit cell that contain 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
(point mass atom)

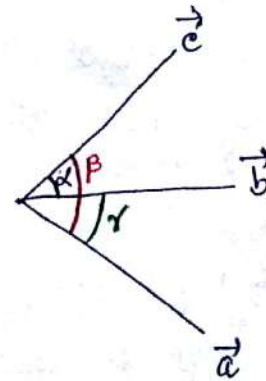
$$n(\vec{r}) = \sum_{\vec{T}} \delta(\vec{r} - \vec{T})$$

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} .

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

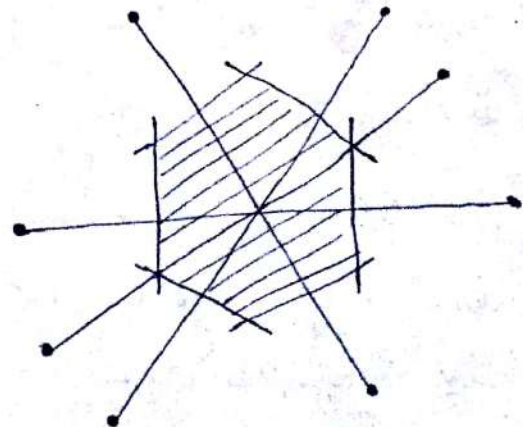
For cubic structure $|\vec{a}| = |\vec{b}| = |\vec{c}|$
 $\alpha = \beta = \gamma = \frac{\pi}{2}$

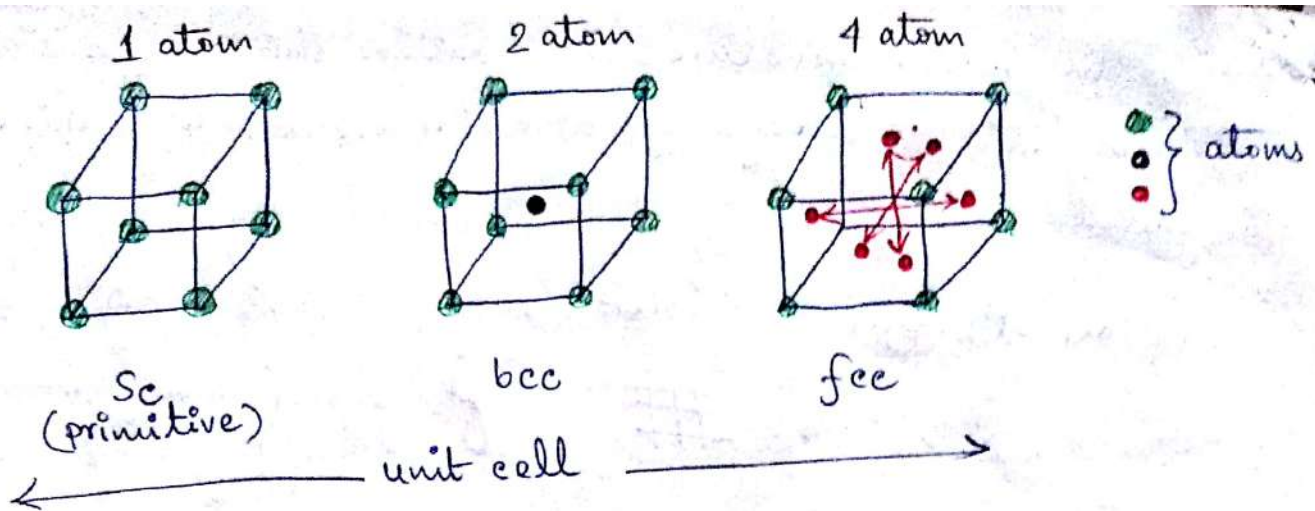


Wigner-Sitz primitive cell

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

This is WS primitive cell.

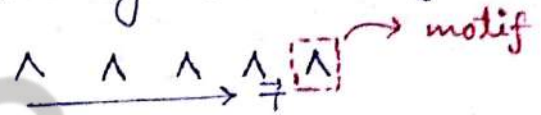




Elements of symmetry

A symmetry operation transforms the crystal to itself.

(i) Translation $\vec{r}' = \vec{r} + \vec{T}$



(ii) Rotation $n\phi = 2\pi$

n = multiplicity of rotation axis.

= 1, 2, 3, 4, ~~5~~, 6.

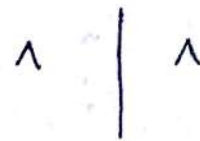


$$\phi = 60^\circ = \frac{2\pi}{6}$$

A 2D square lattice has 4-fold rotational symmetry.

(iii) Reflection

mirror image



(iv) Inversion

(only for 3D lattice)



Symmetry operation performed about a point/line are called point group symmetry. 3 type 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?

$$AB = a = |\vec{a}| = |\vec{r}_1 - \vec{r}_2|$$

$$= AA' = BB'$$

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

$$\angle A'AC' = \angle D'BB' = \theta - \frac{\pi}{2}$$

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

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

$$q|\vec{a}| = |\vec{a}| + 2|\vec{a}| \cos \theta$$

$$\cos \theta = \frac{q-1}{2}$$

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

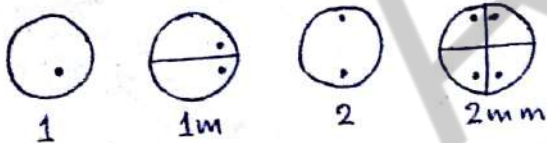
$$\{q = -1, \theta = \frac{2\pi}{2}\}, \{q = 0, \theta = \frac{2\pi}{3}\}, \{q = 1, \theta = \frac{2\pi}{4}\}$$

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

So, $n = 1, 2, 3, 4, 6 \rightarrow$ hexad.
 \downarrow
 diad \rightarrow triad \rightarrow 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 lattices: $|\vec{a}|, |\vec{b}|, \phi$ combination : symmetry operations are maintained.

oblique
 $|\vec{a}| \neq |\vec{b}|, \phi \neq \frac{\pi}{2}$
 $\{\frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}\}$
 rotation

square
 $|\vec{a}| = |\vec{b}|, \phi = \frac{\pi}{2}$
 $\{\frac{2\pi}{4}\}$
 rotation

hexagonal
 $|\vec{a}| = |\vec{b}|, \phi = \frac{2\pi}{3}$
 $\{\frac{2\pi}{6}\}$
 rotation

primitive rectangular
 $|\vec{a}| \neq |\vec{b}|, \phi = \frac{\pi}{2}$
 $\{\frac{2\pi}{2}\}$
 reflection

centered rectangular
 $|\vec{a}| \neq |\vec{b}|, \phi = \frac{\pi}{2}$
 $\{\frac{2\pi}{2}\}$
 inversion

3D lattice types

14 Bravais lattices

Class	Type & number	Angle	length of primitive	
Cubic	P, F, I	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$	isotropic cubic crystal
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	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$	biaxial crystal
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 (off course) 1 atom as whole.

Simple cubic cell (sc)

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

Body centered cubic cell (bcc)

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

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.

$$\text{sc cell, coord no.} = 6.$$

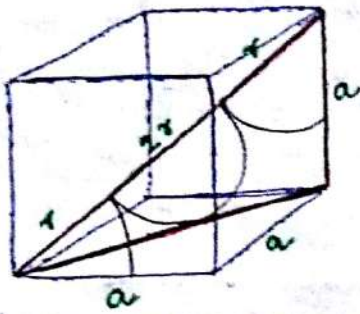
$$\text{bcc cell, coord no.} = 8$$

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

1 plane
6 XY, YZ, XZ plane

Atomic radius

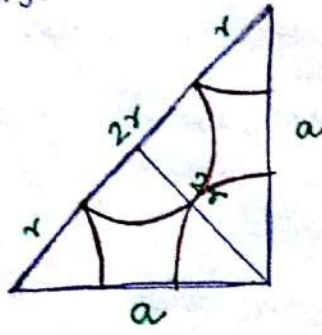
Distance between centre of two touching atoms.



[bcc]

$$(4r)^2 = (\sqrt{2}a)^2 + a^2$$

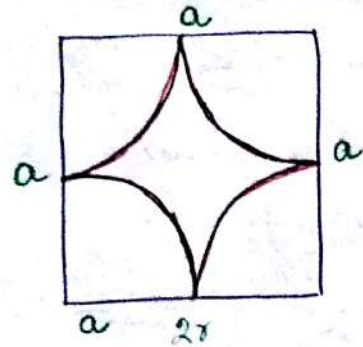
$$\text{or } r = \frac{\sqrt{3}}{4}a$$



[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

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

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

$$\therefore \text{vol. of atoms} = 2 \times \frac{4}{3} \pi r^3, \text{ vol. of unit cell} = a^3$$

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

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

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

$$\therefore f = \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = \underline{74\%}$$

example: ^{nickel} barium, copper, aluminium, lithium, chromium, sodium, iron

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

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

example: polonium, potassium chloride

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

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

NaCl structure

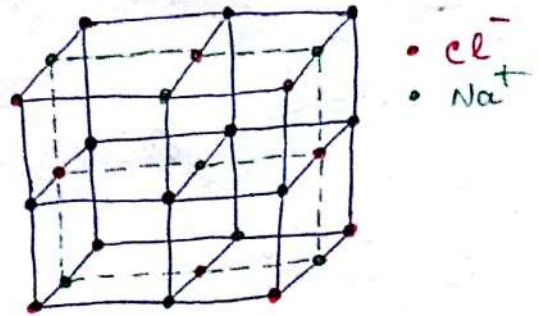
ionic crystal Na^+ & Cl^- , fcc Bravais lattice

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

4 NaCl molecule in unit cube.

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



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

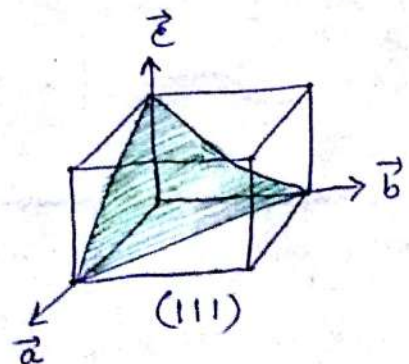
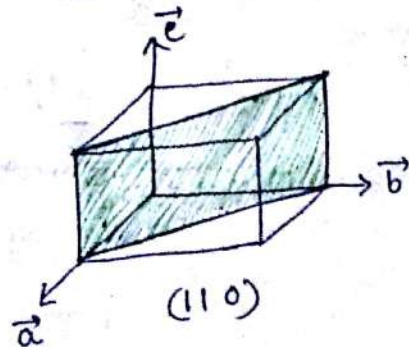
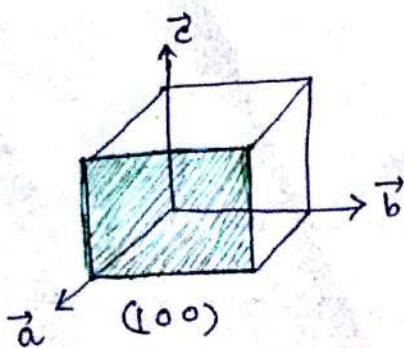
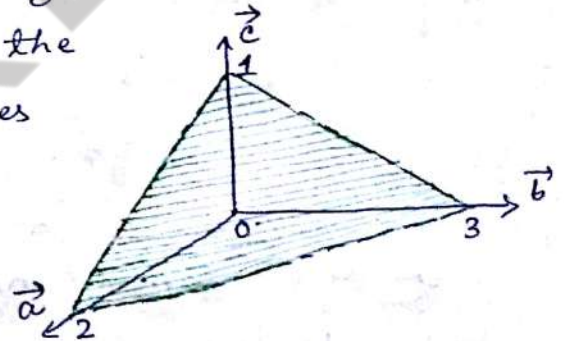
- (a) In terms of lattice constant, find the intercept of the plane on crystal axes $\vec{a}, \vec{b}, \vec{c}$ (primitive or nonprimitive)

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

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

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

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



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

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

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

Indices of a direction $[h, k, l]$ & direction is 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

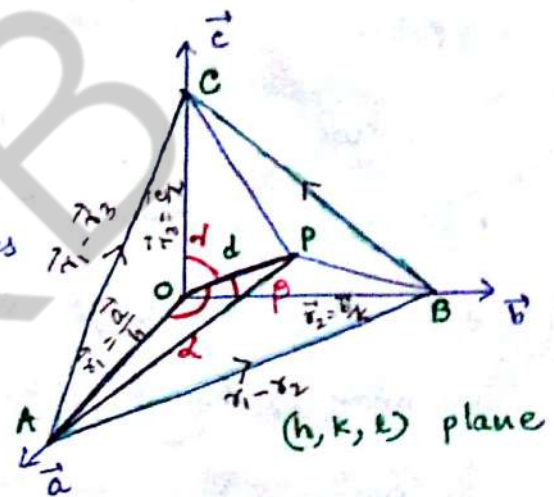
simple unit cell $\vec{a} \perp \vec{b} \perp \vec{c}$ & a plane (h, k, l) (Miller index).

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

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

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

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



$$\frac{OP}{OA} = \cos \alpha \quad \Rightarrow \quad OP = OA \cos \alpha \quad \Rightarrow \quad d = \frac{a}{h} \cos \alpha \quad \Rightarrow \quad \cos \alpha = \frac{dh}{a}$$

$$\text{Similarly } \cos \beta = \frac{dk}{b}, \quad \cos \gamma = \frac{dl}{c}.$$

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

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

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

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

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

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.

$d_{110} = d_{110}^{sc} = \frac{a}{\sqrt{2}}$ 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 $(1,0,0)$ 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.

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

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

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

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

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 & interplanar spacing⁵ 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

$$\begin{aligned} \vec{a} \cdot \vec{a}^* &= 2\pi, & \vec{b} \cdot \vec{a}^* &= 0, & \vec{c} \cdot \vec{a}^* &= 0 \\ \vec{a} \cdot \vec{b}^* &= 0, & \vec{b} \cdot \vec{b}^* &= 2\pi, & \vec{c} \cdot \vec{b}^* &= 0 \\ \vec{a} \cdot \vec{c}^* &= 0, & \vec{b} \cdot \vec{c}^* &= 0, & \vec{c} \cdot \vec{c}^* &= 2\pi. \end{aligned}$$

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

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

property (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. $\vec{T} = u_1\vec{a} + u_2\vec{b} + u_3\vec{c}$ 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{k} has that periodicity.

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

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

$$\therefore \vec{k} \cdot \vec{T} = 2\pi(k_1u_1 + k_2u_2 + k_3u_3)$$

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

Reciprocal of reciprocal lattice

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

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

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

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

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

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

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

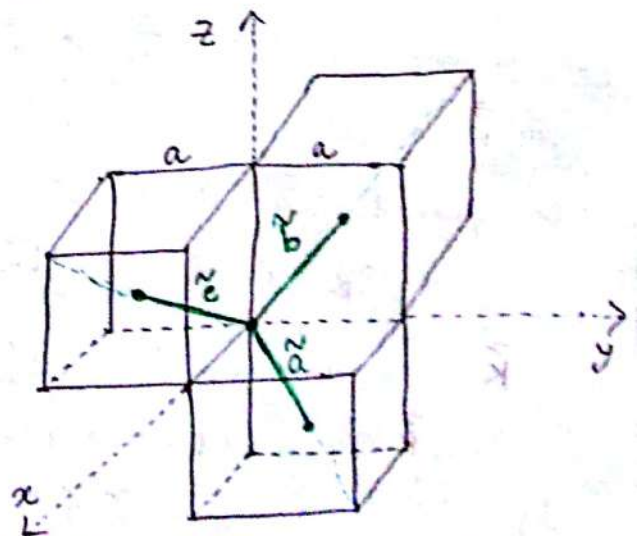
lattice constant = $2\pi/a$.

Reciprocal of bcc lattice

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

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

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



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

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

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

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

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 ,

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

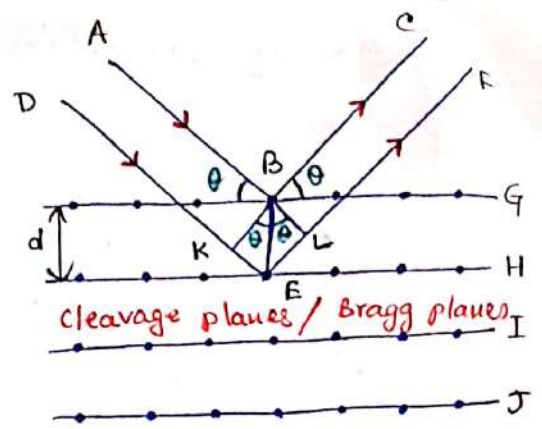
$\lambda_{\text{X-ray}} \approx a$ (elastic scattering without change in λ)

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

$\lambda_{\text{X-ray}} \ll a$ (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 λ x-ray.



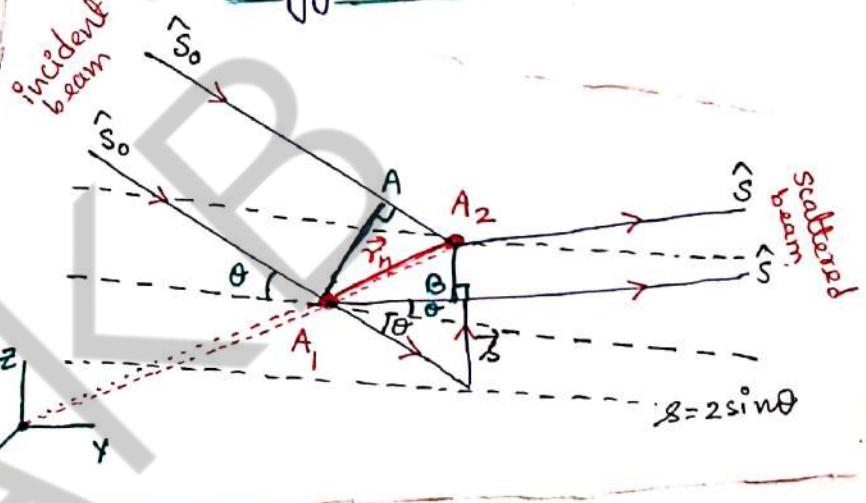
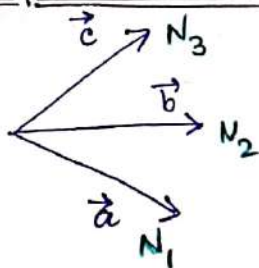
Path difference between ray [AB, BC] & [DE, EF] is $KE + EL$

$$= d \sin \theta + d \sin \theta = 2d \sin \theta. \quad \text{So for constructive interference,}$$

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

$\lambda, \theta = \text{Known}, \quad d = \text{unknown}$

Laue'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 $d = \vec{r}_n \cdot \vec{S} - \vec{r}_n \cdot \vec{S}_0 = \vec{r}_n \cdot \vec{S}$

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

remember: \vec{S}, \vec{S}_0 unit vector, $|\vec{S}| = |\vec{S}_0| = 1$, $\vec{r}_n = n^{\text{th}}$ lattice point from origin

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

$$\vec{r}_n = \vec{r}$$

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

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

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

\therefore Total displacement due to the whole Bravais lattice is

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

$$\begin{aligned} \text{Now } \sum_{n_1=0}^{N_1-1} e^{i\vec{k} n_1 \vec{a} \cdot \vec{r}_n} &= 1 + e^{i\vec{k} \vec{a} \cdot \vec{r}_n} + e^{i2\vec{k} \vec{a} \cdot \vec{r}_n} + \dots + e^{i(N_1-1)\vec{k} \vec{a} \cdot \vec{r}_n} \\ &= \frac{1 - e^{iN_1(\vec{a} \cdot \vec{r}_n)K}}{1 - e^{i(\vec{a} \cdot \vec{r}_n)K}} \end{aligned}$$

$$\begin{aligned} \therefore \left(\sum_{n_1=0}^{N_1-1} e^{i\vec{k} n_1 \vec{a} \cdot \vec{r}_n} \right) \left(\sum_{n_1=0}^{N_1-1} e^{i\vec{k} n_1 \vec{a} \cdot \vec{r}_n} \right)^* &= \frac{1 - e^{iN_1(\vec{a} \cdot \vec{r}_n)K}}{1 - e^{i(\vec{a} \cdot \vec{r}_n)K}} \times \frac{1 - e^{-iN_1(\vec{a} \cdot \vec{r}_n)K}}{1 - e^{-i(\vec{a} \cdot \vec{r}_n)K}} \\ &= \frac{1 - e^{iN_1(\vec{a} \cdot \vec{r}_n)K}}{1 - e^{i(\vec{a} \cdot \vec{r}_n)K}} \times \frac{1 - e^{-iN_1(\vec{a} \cdot \vec{r}_n)K}}{1 - e^{-i(\vec{a} \cdot \vec{r}_n)K}} \end{aligned}$$

$$\begin{aligned} &= \frac{1 - \cos\{N_1(\vec{a} \cdot \vec{r}_n)K\} + i\sin\{N_1(\vec{a} \cdot \vec{r}_n)K\}}{1 - \cos\{(\vec{a} \cdot \vec{r}_n)K\} - i\sin\{(\vec{a} \cdot \vec{r}_n)K\}} \times \frac{1 - \cos\{N_1(\vec{a} \cdot \vec{r}_n)K\} + i\sin\{N_1(\vec{a} \cdot \vec{r}_n)K\}}{1 - \cos\{(\vec{a} \cdot \vec{r}_n)K\} + i\sin\{(\vec{a} \cdot \vec{r}_n)K\}} \end{aligned}$$

$$= \frac{(1 - \cos\{N_1(\vec{a} \cdot \vec{r}_n)K\})^2 + (\sin\{N_1(\vec{a} \cdot \vec{r}_n)K\})^2}{(1 - \cos\{(\vec{a} \cdot \vec{r}_n)K\})^2 + (\sin\{(\vec{a} \cdot \vec{r}_n)K\})^2}$$

$$= \frac{1 - \cos\{N_1(\vec{a} \cdot \vec{r}_n)K\}}{1 - \cos\{(\vec{a} \cdot \vec{r}_n)K\}} = \frac{\sin^2\left\{\frac{N_1(\vec{a} \cdot \vec{r}_n)K}{2}\right\}}{\sin^2\left\{\frac{(\vec{a} \cdot \vec{r}_n)K}{2}\right\}} = \frac{\sin^2(N_1\psi_1)}{\sin^2(\psi_1)}$$

where $\psi_1 = \frac{1}{2} \mathbf{k} \cdot \vec{a}$.

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

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

Similarly $\psi_2 = \frac{1}{2} \mathbf{k} \cdot \vec{b} = \frac{2\pi b \sin \theta \cos \beta}{\lambda}$,
 $\psi_3 = \frac{1}{2} \mathbf{k} \cdot \vec{c} = \frac{2\pi c \sin \theta \cos \gamma}{\lambda}$

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

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

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

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

$\therefore \frac{2\pi a \sin \theta \cos \alpha}{\lambda} = h\pi$,
 $\frac{2\pi b \sin \theta \cos \beta}{\lambda} = k\pi$,
 $\frac{2\pi c \sin \theta \cos \gamma}{\lambda} = l\pi$,

$2a \sin \theta \cos \alpha = h\lambda$

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

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

"Laue equations".

Bragg's law from Laue equations

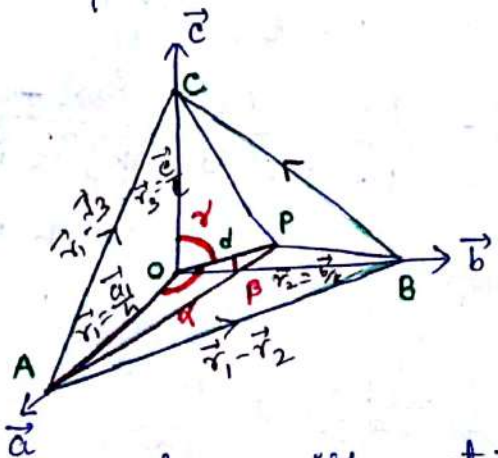
from Laue equation, direction cosines of \vec{s} are

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

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

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

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



∴ The direction cosines of \vec{S} are also proportional to $1/a, 1/b, 1/c$, so the X-ray is diffracted from \vec{S}_0 to \vec{S} by the miller plane (h, k, l) .

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

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

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

with d = adjacent interplanar spacing with Miller indices

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

Interpretation of Laue's equation in reciprocal lattice

Reciprocal lattice vector $\vec{r}^* = \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$
 magnitude = reciprocal of spacing of (h, k, l) planes of direct lattice.
 direction = perpendicular to (h, k, l) plane.

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

From Laue equation, $\psi_1 = \frac{1}{2}k \vec{a} \cdot \vec{S} = h\pi$ or $\frac{1}{2} \frac{2\pi}{\lambda} \vec{S} \cdot \vec{a} = h\pi$

$$\Rightarrow \frac{2\pi \vec{S}}{\lambda} \cdot \vec{a} = 2\pi h.$$

Similarly from ψ_2 & ψ_3 , $\frac{2\pi \vec{S}}{\lambda} \cdot \vec{b} = 2\pi k$, $\frac{2\pi \vec{S}}{\lambda} \cdot \vec{c} = 2\pi l$.

Comparing,

$$\boxed{\vec{r}^* = \vec{G} = \frac{2\pi \vec{S}}{\lambda}}$$

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} & $\vec{G} \perp OC$ (direct lattice plane)

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

\vec{k}' = diffracted (reflected) wave vector, with $|\vec{k}| = |\vec{k}'|$

So magnitude is same, only direction changes.

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

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

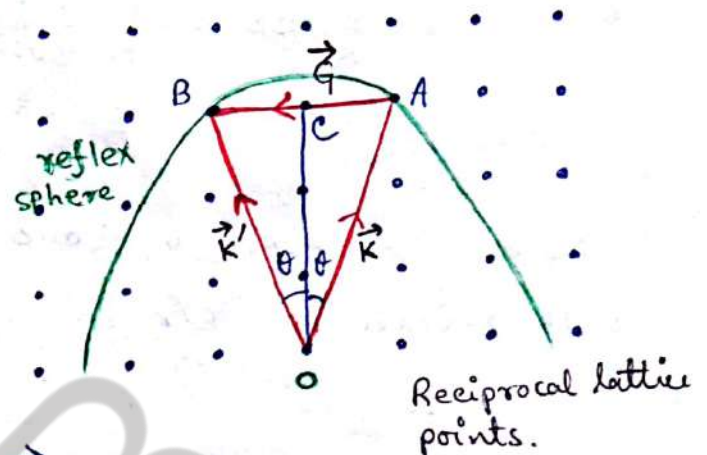
$$\therefore (\vec{k} + \frac{\vec{G}}{2}) \cdot \vec{G} = 0 \quad \Rightarrow \text{Bragg's law (vectorial form) in reciprocal lattice.}$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

(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?

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

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

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

$$\theta_1 = \sin^{-1} \left[\frac{\lambda}{2d} \right] = \sin^{-1} \left[\frac{1.54 \times 10^{-10}}{2 \times 2.67 \times 10^{-10}} \right] = 16.76^\circ$$

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

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

$$(b) \quad 2d \sin \theta_1 = \lambda, \quad \theta_1 = 15^\circ \quad \therefore \lambda = 2d \sin 15^\circ = 0.2588$$

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

$$\theta_2 = 31.17^\circ$$

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

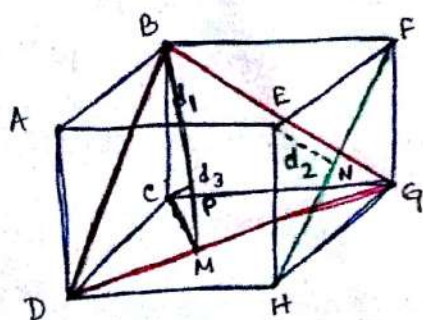
$$\theta_3 = 50.93^\circ$$

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° .

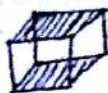
2. If X-rays with $\lambda = 0.5 \text{ \AA}$ is diffracted at 5° in 1st order, what is the spacing between adjacent planes of a crystal? At what angle will 2nd maximum occur?

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.

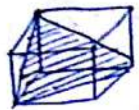


ABFE & CGHD.
 d_1 distance apart. \rightarrow Total 6 faces (100) plane.



Diagonal plane BFHD inclined at $\pi/4$ to (100) planes

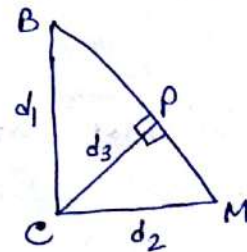
d_2 is interplanar spacing $\frac{d_2}{d_1} = \sin 45^\circ = \frac{1}{\sqrt{2}} \therefore d_2 = \frac{d_1}{\sqrt{2}}$.
 (110) plane.



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

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

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

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

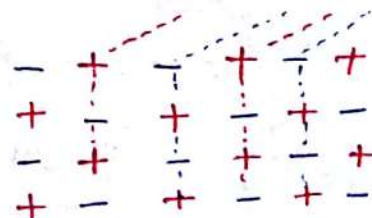
So KCl has cubic crystal symmetry.

NaCl crystal

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

\therefore Each ion of NaCl is shared between

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



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

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

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

$$\therefore d = 2.814 \text{ \AA}$$

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

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

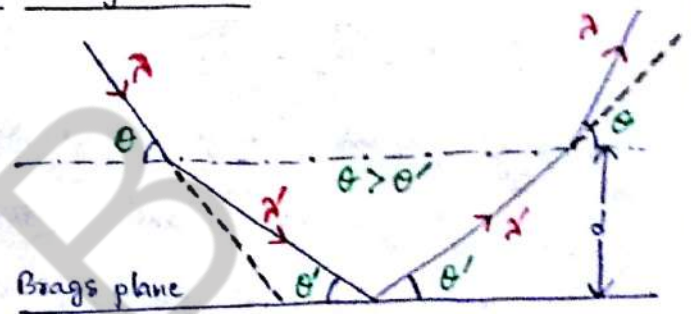
$$2^{\text{nd}} \text{ order, } n=2, \theta = 23.5^\circ \quad \lambda = \frac{2d \sin \theta}{2} = 2.814 \times 10^{-10} \times \sin 23.5^\circ = 1.12 \text{ \AA}$$

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

∴ 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.



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

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

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

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

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

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

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

$$\begin{aligned} [1 - \mu^2 &= (1 + \mu)(1 - \mu) \\ &\approx 2(1 - \mu) \text{ as } \mu \approx 1] \end{aligned}$$

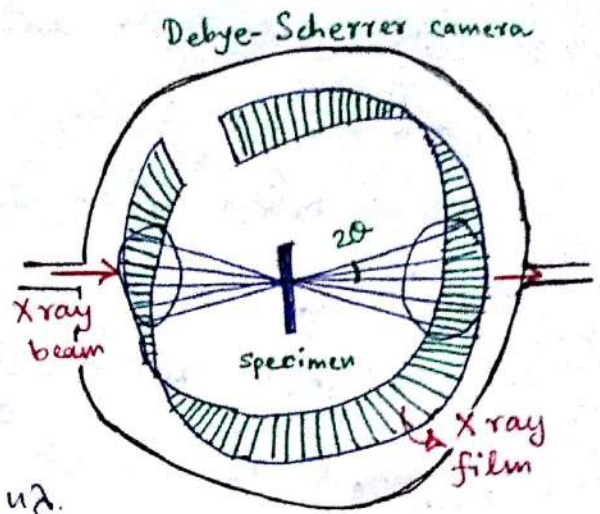
$$\begin{aligned} [2d \sin \theta &= n\lambda \\ \text{or } \frac{1}{\sin^2 \theta} &= \frac{4d^2}{n^2 \lambda^2}] \end{aligned}$$

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

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

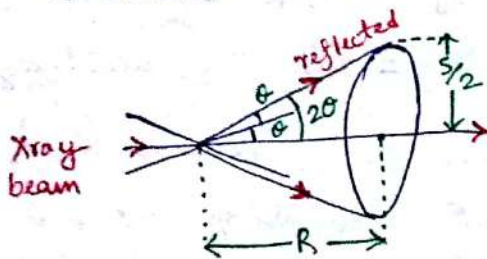
Powder Method of XRD

$2d \sin \theta = n\lambda$, d & θ 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 plane satisfy Bragg reflection $2d \sin \theta = n\lambda$.

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

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

so that $2d \sin \theta = \lambda$ (for $n=1$)

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

$$\text{or } 2d \frac{S}{4R} = \lambda \Rightarrow d = \frac{2R\lambda}{S}$$

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

Brillouin Zones

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

Brillouin zones for sc lattice in 2D

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

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

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

(h, k are integers)

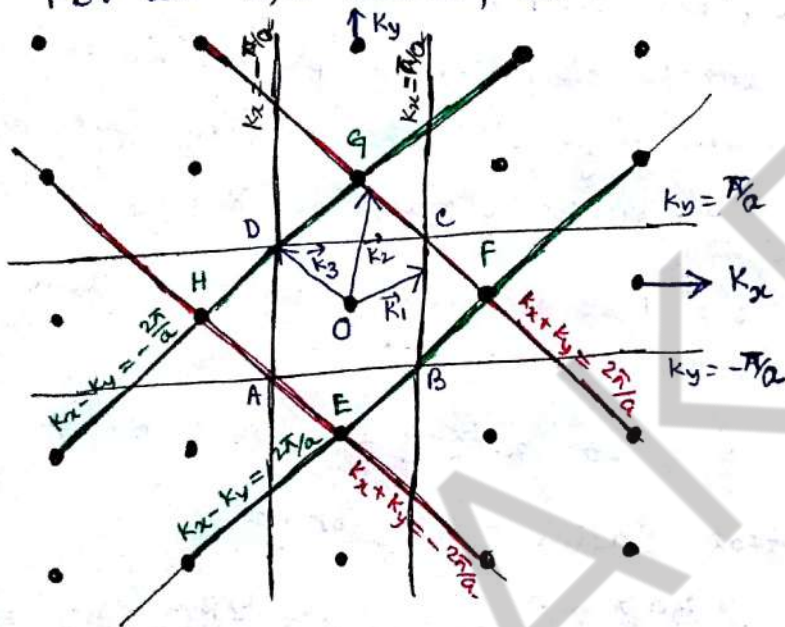
$\vec{K} = K_x\hat{i} + K_y\hat{j}$. \therefore from Bragg's vectorial condition

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

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

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

For all h, k values, we can obtain k.



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{K} (for example \vec{K}_1, \vec{K}_2 or \vec{K}_3) originating from O & terminating on these parallel lines are Bragg reflected.

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

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{K} that obey Bragg's law, meaning they're the reflecting planes. $ABCD \Rightarrow 2d \sin \theta = \lambda$.

$EFGH \Rightarrow 2d \sin \theta = 2\lambda$ & so on.

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

with cubes represent Brillouin zone.

Brillouin zones of the fcc lattice

primitive translation vectors of fcc lattice are

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

translation vectors in reciprocal space are

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

$$\therefore \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

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

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

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

First zone boundary is determined by the 8 planes $\perp \vec{G}$ 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

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

$$\vec{G} = \frac{2\pi}{a}[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}] \text{ \& shortest } \vec{G} \text{ are}$$

$$\text{the 12 vectors, } \vec{G} = \frac{2\pi}{a}(\pm\hat{i} \pm \hat{j})$$

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

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

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