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

$$\therefore d = \frac{a}{h}\cos\alpha = \frac{a}{h}\frac{h\lambda}{2a\sin\theta} = \frac{\lambda}{2\sin\theta}$$

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

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

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 $\frac{1}{\cancel{2}}\frac{\cancel{2}\pi}{\lambda}\vec{s}\cdot\vec{a} = h\cancel{\pi}$

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

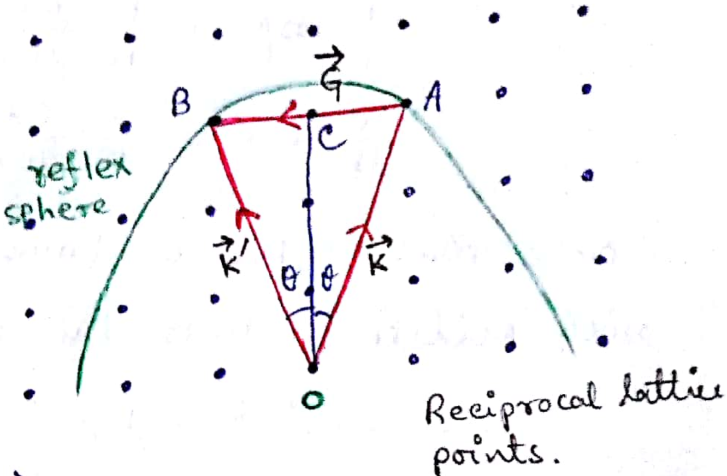
Similarly from ψ_2 & ψ_3, $\frac{2\pi\vec{s}}{\lambda}\cdot\vec{b} = 2\pi k$, $\frac{2\pi\vec{s}}{\lambda}\cdot\vec{c} = 2\pi l.$

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 $\vec{G}$ & $G \perp OC$ (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.

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

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

$$\therefore \left(\vec{K} + \frac{\vec{G}}{2}\right)\cdot\vec{G} = 0$$

$\Rightarrow$ Bragg's law (vectorial form) in reciprocal lattice.

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

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

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

$$\text{or } 2d\sin\theta = n\lambda$$

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

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

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

$\therefore \lambda = 3.84$ Å.

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

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

$= 1.03$ Km/s.

2. X-ray of wavelength 1.24 Å is reflected by cubic crystal KCl. Calculate the interplanar distance for (100), (110) & (111) planes. Given density of KCl = 1.98×10^{3} kg/m³, molecular weight 74.5 kg. Avogadro's no. $N = 6.023 \times 10^{26}$ kg/mole.

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

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

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

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

(remember KCl is fcc).

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

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

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

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

$$\theta_1 = \sin^{-1}\left[\frac{\lambda}{2d}\right] = \sin^{-1}\left[\frac{1.54\times10^{-10}}{2\times2.67\times10^{-10}}\right] = 16.76^\circ.$$

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

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

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

So for 2^{nd} order $\quad \sin\theta_2 = 2\frac{\lambda}{2d} = 2\times0.2588 = 0.5176$

$$\theta_2 = 31.17^\circ$$

for 3^{rd} order, $\quad \sin\theta_3 = 3\frac{\lambda}{2d} = 3\times0.2588 = 0.7764$

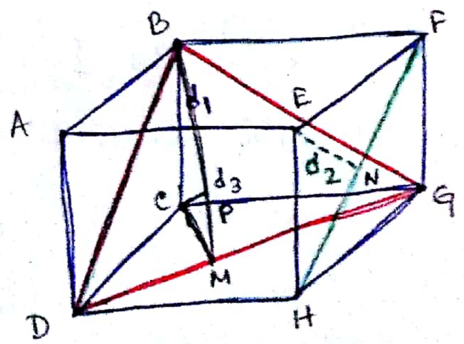
$$\theta_3 = 50.93^\circ.$$

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

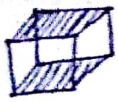
2. If X-rays with $\lambda = 0.5$ Å is diffracted at 5° in 1^{st} order, what is the spacing between adjacent planes of a crystal? At ~~and~~ what angle will 2^{nd} maximum occur?

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

Determination of crystal structure



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

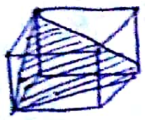


ABFE & CGHD.
d_1 distance apart. → Total 6 faces (100) plane.

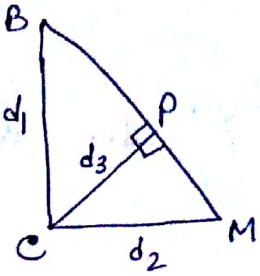
Diagonal plane BFHD inclined at $\pi/4$ to (100) planes

Scanned by CamScanner

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



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



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

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

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

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

θ_1 (from (100) plane) $= 5.22°$ θ_3 (from (111) plane) $= 9.05°$.

θ_2 (from (110) plane) $= 7.30°$

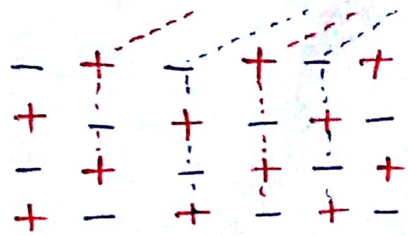
as $\frac{1}{d} = \frac{2\sin\theta}{\lambda}$ $\therefore \frac{1}{d_1} : \frac{1}{d_2} : \frac{1}{d_3} = \sin 5.22 : \sin 7.30 : \sin 9.05$

$= 0.0910 : 0.1272 : 0.1570$

$= 1 : 1.40 : 1.73 = 1 : \sqrt{2} : \sqrt{3}$.

So KCl has cubic crystal symmetry.

NaCl crystal



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

$\therefore$ Each ion of NaCl is shared between two adjacent cube & unit cell contain half a molecule of NaCl.

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

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

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

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

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

$= 1.12$ Å.

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

$= 1.12$ Å.

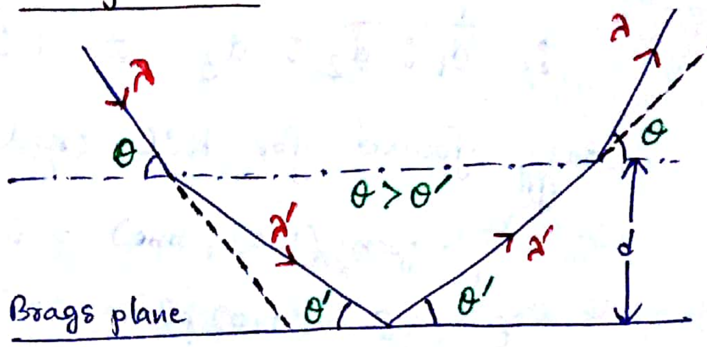
3rd order, $n=3$, $\theta = 36^\circ$, $\lambda = \frac{2d\sin\theta}{3} = \frac{2}{3}\times 2.814\times 10^{-10}\times \sin 36^\circ$

$= 1.12$ Å.

$\therefore$ Diffraction from NaCl crystal verifies 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.



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

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

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

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

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

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

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

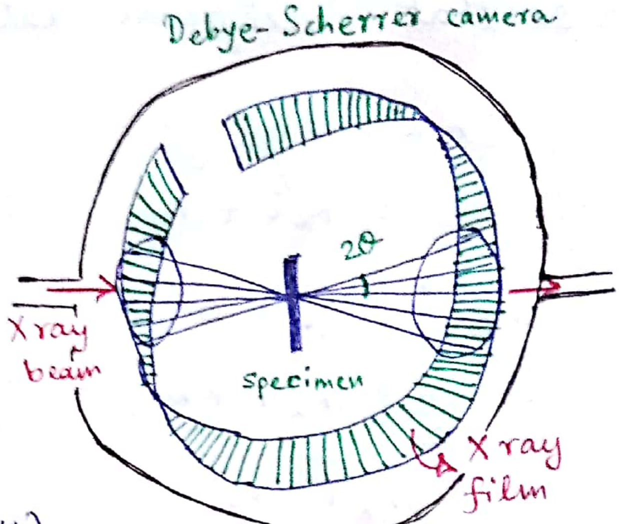
$[1-\mu^2 = (1+\mu)(1-\mu) \simeq 2(1-\mu)$ as $\mu \simeq 1]$

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

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

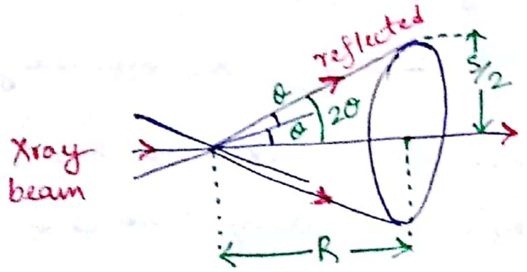
~~Largest~~ The correction term $\frac{4d^2(1-\mu)}{n^2\lambda^2}$ is small & becomes more small as "n" increases.

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

$\frac{S}{2R} = 2\theta$ or $\theta = \frac{S}{4R}$ & $\sin\theta \simeq \theta$

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

$\simeq 2d\theta = \lambda$

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

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)

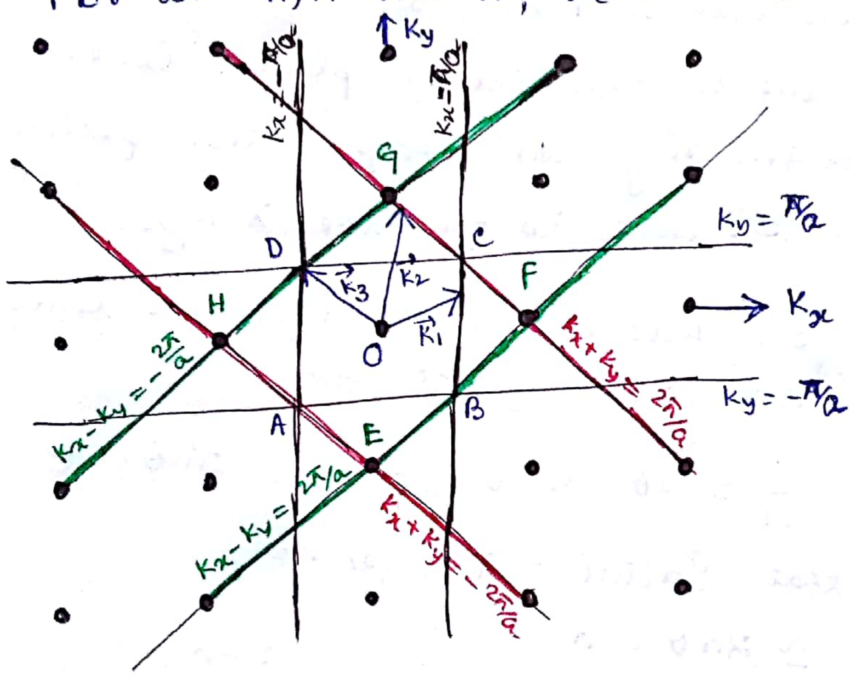
$\vec{k} = k_x\hat{i} + k_y\hat{j}$. ∴ from Bragg's vectorial condition

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

or $$\frac{4\pi}{a}(hk_x + kk_y) + \frac{4\pi^2}{a^2}(h^2+k^2) = 0$$

or $$\boxed{hk_x + kk_y = -\frac{\pi}{a}(h^2+k^2)}$$

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



If $h = \pm 1, k = 0$ then
$k_x = \pm\frac{\pi}{a}$ (k_y arbitrary)

If $h = 0, k = \pm 1$, then
$k_y = \pm\frac{\pi}{a}$ (k_x 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.

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 $\vec{k}$ that obey Bragg's law, meaning they're the reflecting planes. ABCD ⇒ $2d\sin\theta = \lambda$. EFGH ⇒ $2d\sin\theta = 2\lambda$ & so on.

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

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

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

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

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

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 $\perp$ 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 <u>bcc</u> lattice.

Brillouin zones of bcc lattice

primitive translation vectors of bcc lattice are

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

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

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