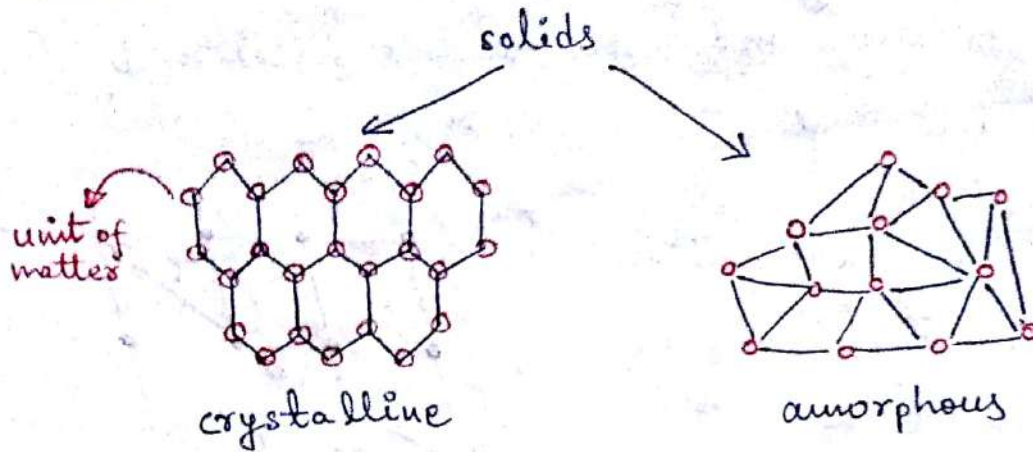


SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holo graph



(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

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.

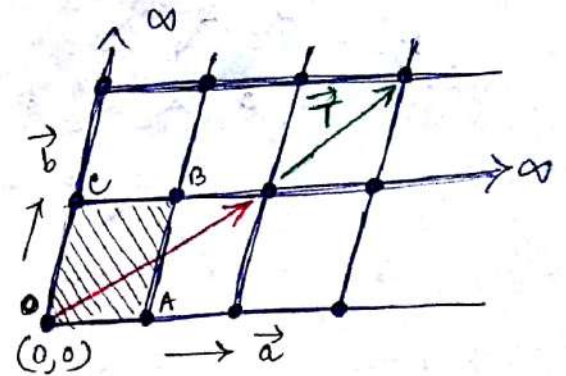
Example pitch, plastic, silicate glass.

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

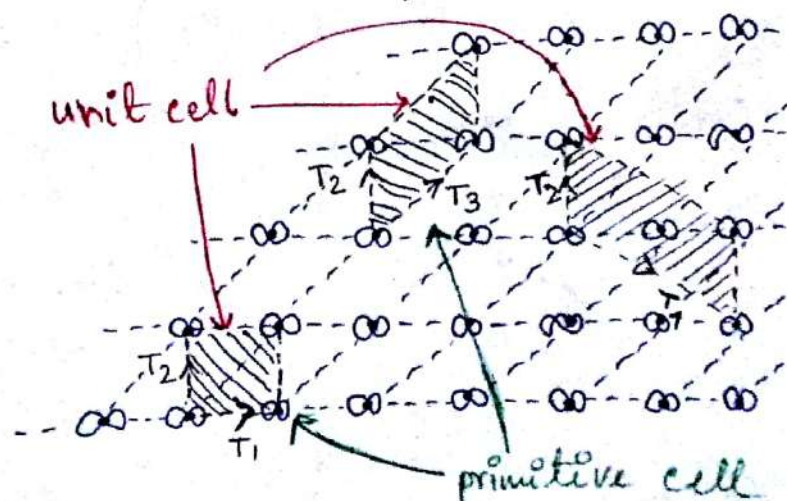
$$\begin{aligned} \text{Atomic position vector } \vec{r}' &= \vec{r} + \vec{T} \\ &= \vec{r} + n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \end{aligned}$$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

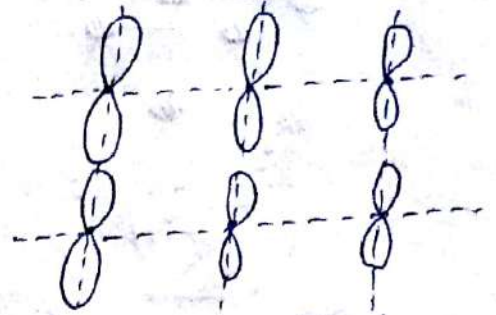
Unit cell is volume from which entire crystal can be constructed by translational repetition. (OABC parallelogram)

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)

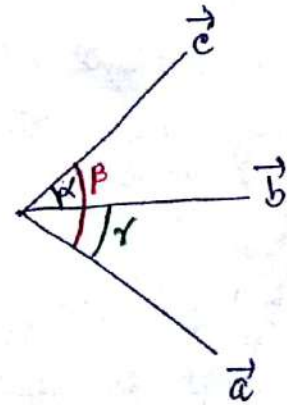
$$n(\vec{r}) = \sum_{\vec{T}} \delta(\vec{r} - \vec{T})$$

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} .

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

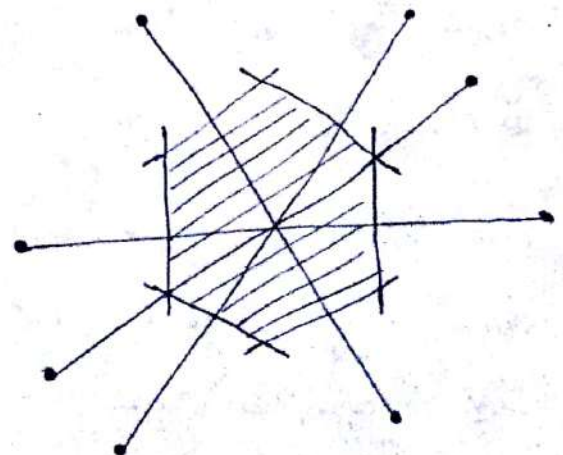
For cubic structure $|\vec{a}| = |\vec{b}| = |\vec{c}|$
 $\alpha = \beta = \gamma = \frac{\pi}{2}$

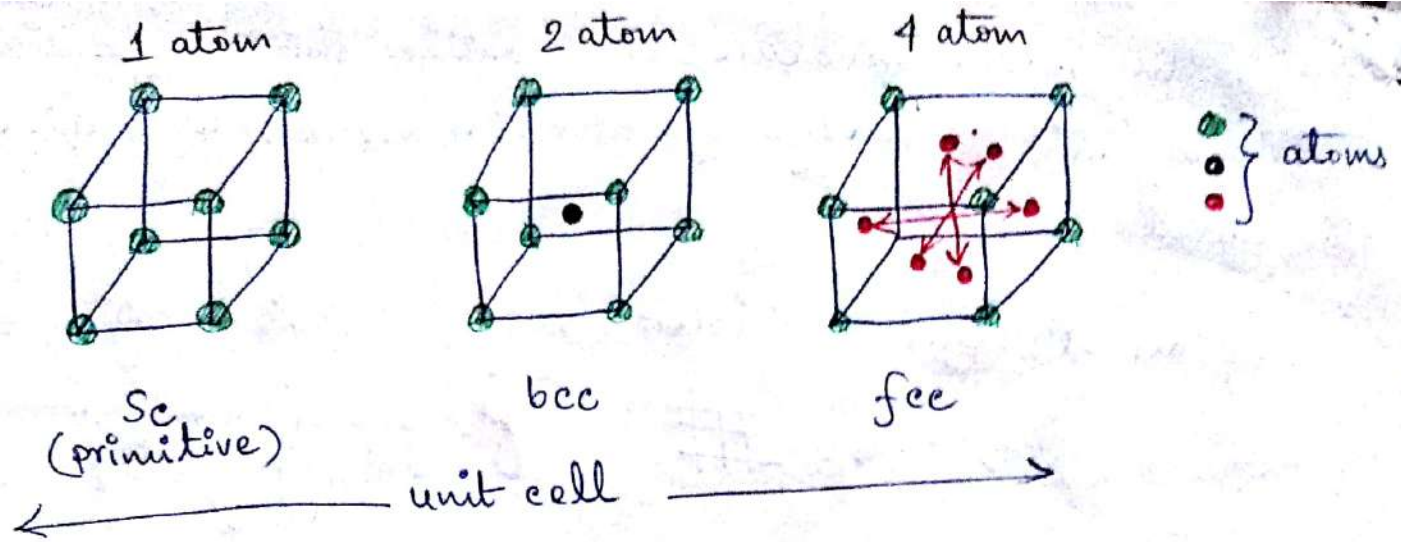


Wigner-Sietz primitive cell

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

This is WS primitive cell.

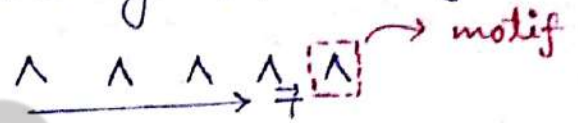




Elements of symmetry

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.



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

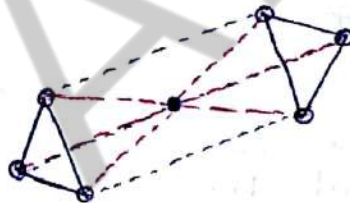
A 2D square lattice has 4-fold rotational symmetry.

(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 $-1, 0, 1, 2, 3$

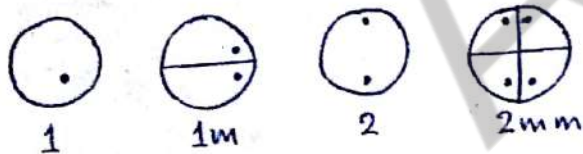
$$\{q = -1, \theta = \frac{2\pi}{2}\}, \{q = 0, \theta = \frac{2\pi}{3}\}, \{q = 1, \theta = \frac{2\pi}{4}\}$$

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

So, $n = 1, 2, 3, 4, 6 \rightarrow$ hexad.
 \downarrow
 diad triad tetrad

Point group & space group

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

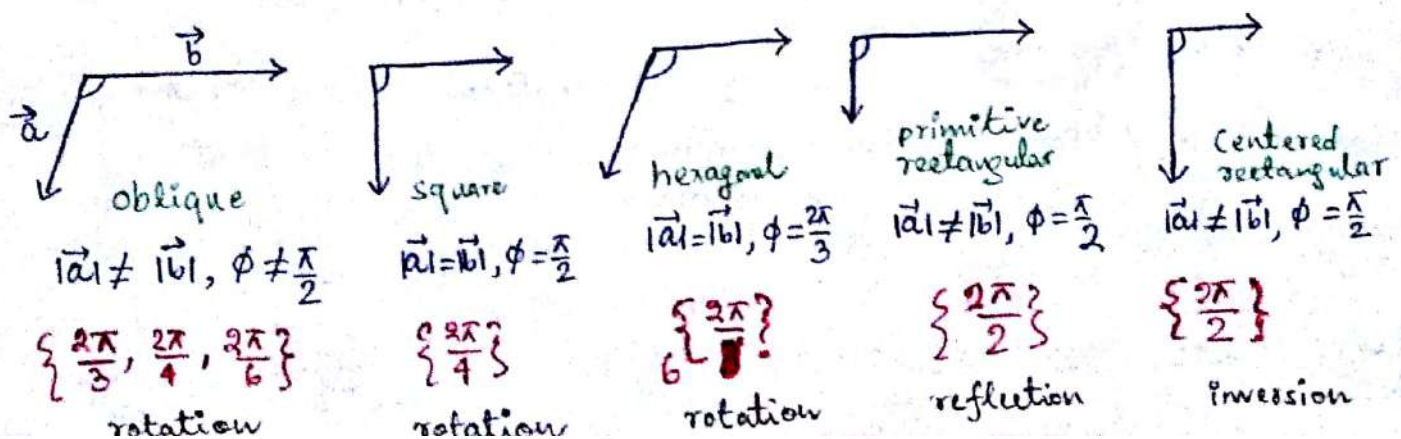


Total 32 point groups.

Group of all symmetry elements is space group.

In 2D: 17, 3D: 230.

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



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.

sc cell, coord no. = 6.

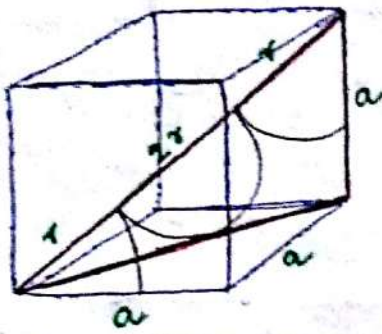
bcc cell, coord no. = 8

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

1 plane \rightarrow xy, yz, xz plane

Atomic radius

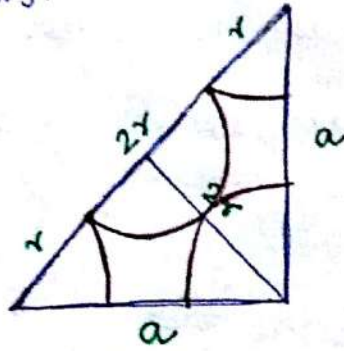
Distance between centre of two touching atoms.



[bcc]

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

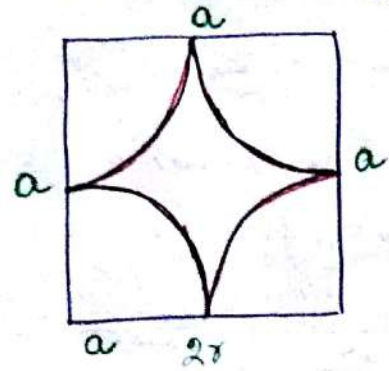
$$\text{or } r = \frac{\sqrt{3}}{4}a$$



[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 $\vec{a} = \frac{\sqrt{3}}{2} \hat{a}_1 + \frac{a}{2} \hat{j}$, $\vec{b} = -\frac{\sqrt{3}}{2} \hat{a}_1 + \frac{a}{2} \hat{j}$, $\vec{c} = c \hat{k}$. Compute the volume of the primitive cell.

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

NaCl structure

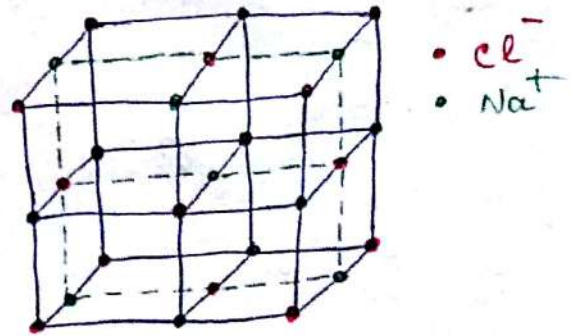
ionic crystal Na^+ & Cl^- , fcc Bravais lattice

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

4 NaCl molecule in unit cube.

Na^+ $(0,0,0)$ & $\text{Cl}^- (\frac{a}{2}, 0, 0) \rightarrow 6$ 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 intercept of the plane on crystal axes

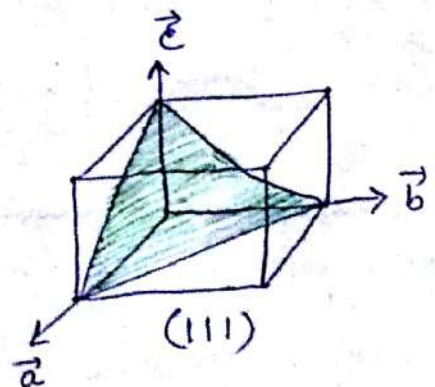
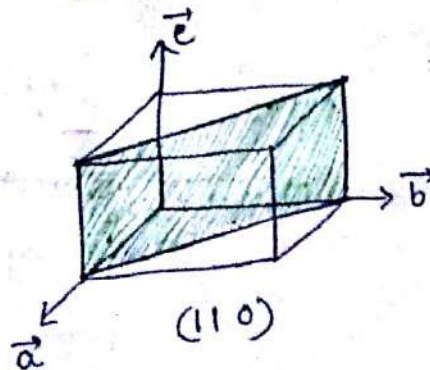
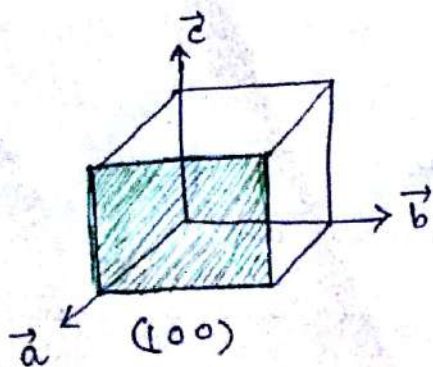
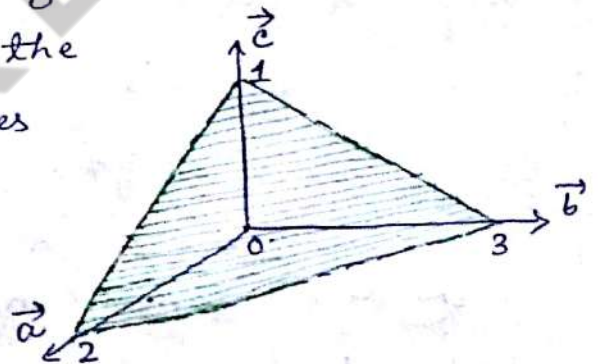
$\vec{a}, \vec{b}, \vec{c}$ (primitive or nonprimitive)

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

(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 $(1, 0, 0), (0, 1, 0), (0, 0, 1)$
 $(\bar{1}, 0, 0), (0, \bar{1}, 0), (0, 0, \bar{1}) \Rightarrow \{1, 0, 0\}$
 because through rotation, all faces are equivalent & written in $\{ \}$.

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

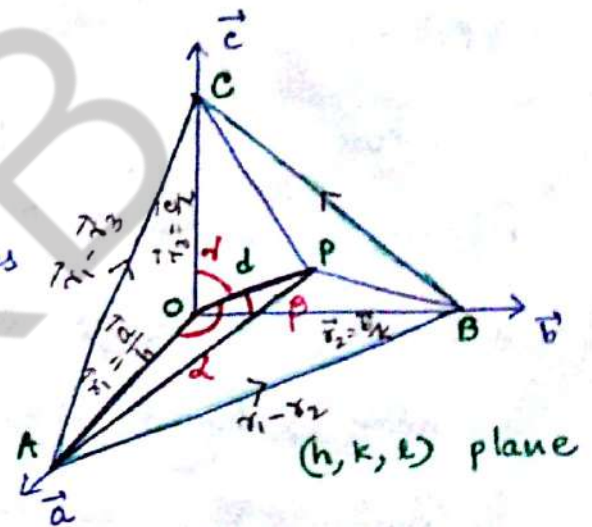
simple unit cell $\vec{a} \perp \vec{b} \perp \vec{c}$ & a plane (h, k, l) (Miller index).

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 $[h, k, l]$

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

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) .