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
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	$\alpha\neq\beta\neq\gamma$	$a\neq b\neq c$

Uniaxial crystal

Biaxial crystal

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)

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

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.

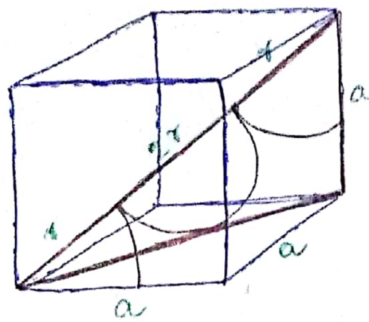
sc cell, coord. no. = 6.

bcc cell, coord no. = 8

fcc cell, coord no. = 4 × 3 = 12

1 plane ↳ XY, YZ, XZ plane

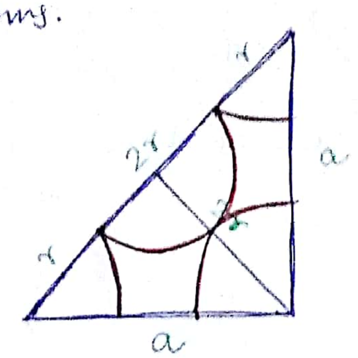
Atomic radius   Distance between centre of two touching atoms.



[bcc]

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

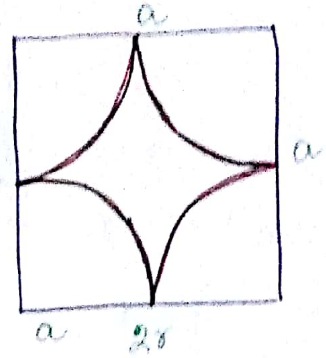
$$\text{or } r = \frac{\sqrt{3}}{4}a$$



[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, $r = \frac{\sqrt{3}}{4}a$

$\therefore$ Vol. of atoms $= 2 \times \frac{4}{3}\pi r^3$,   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, $r = \frac{a}{2\sqrt{2}}$.

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

example: nickel ~~barium~~, copper, aluminium, lithium, ~~chromium~~, ~~sodium~~, ~~iron~~,

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

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

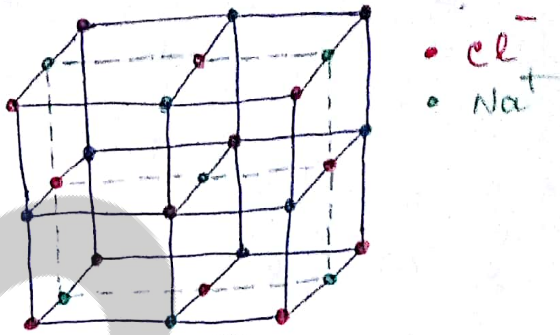
example : polonium, potassium chloride

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.

<u>NaCl structure</u>

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

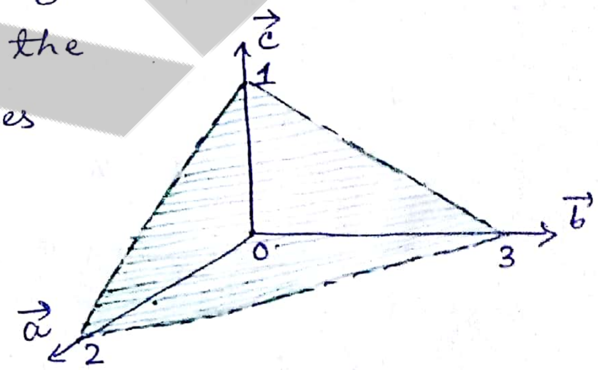
4 NaCl molecule in unit cube.

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

<u>Miller indices</u> 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)

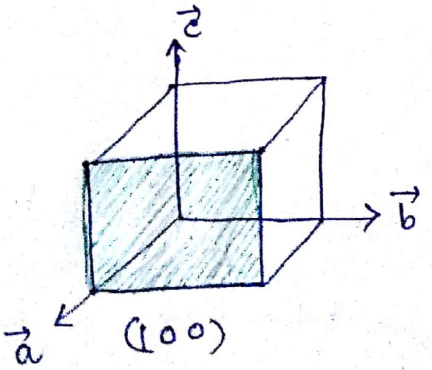
$(2,0,0)$, $(0,3,0)$, $(0,0,1)$ $\rightarrow$ $2a, 3b, c$.



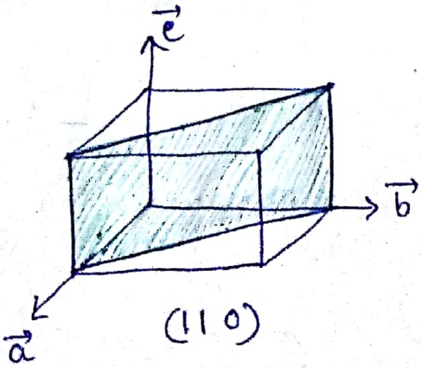
(b) Take reciprocals of them & reduce to smallest 3 integers, Denote with (h, k, l)

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

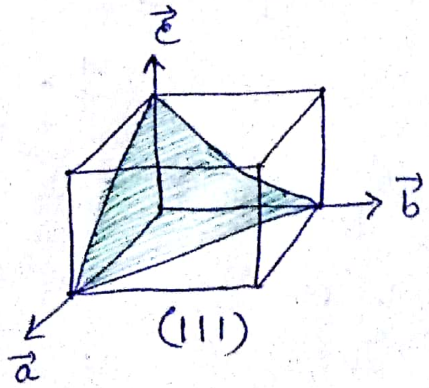
Miller index is $(3,2,6)$ plane.



(100)



(110)



(111)

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

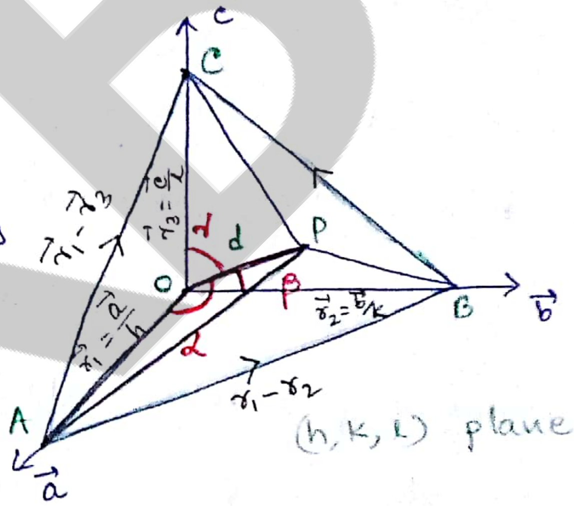
6-faces of cubic crystal, M-index $(1,0,0), (0,1,0), (0,0,1)$, $(\bar{1},0,0), (0,\bar{1},0), (0,0,\bar{1})$ $\equiv \{1,0,0\}$ because through rotation, all faces are equivalent & written in $\{\ \}$.

So $(2,0,0)$ plane (M-index) 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 & $OP = d$.

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

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

$\frac{OP}{OA} = \cos\alpha$ $\therefore$ $OP = OA\cos\alpha$ or $d = \frac{a}{h}\cos\alpha$ or $\cos\alpha = \frac{dh}{a}$

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

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

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

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

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

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

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

$= \vec{a}\cdot\vec{a} - \vec{b}\cdot\vec{b} = 0$. (as $|a| = |b|$)

Similarly $(\vec{r}_1 - \vec{r}_3)\cdot(h\vec{a} + k\vec{b} + l\vec{c}) = 0$ (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 & 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 → reciprocal lattice

For $\vec{a}, \vec{b}, \vec{c}$, we describe reciprocal basis vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$ (primitive) such that

$$\vec{a}\cdot\vec{a}^* = 2\pi, \quad \vec{b}\cdot\vec{a}^* = 0, \quad \vec{c}\cdot\vec{a}^* = 0$$
$$\vec{a}\cdot\vec{b}^* = 0, \quad \vec{b}\cdot\vec{b}^* = 2\pi, \quad \vec{c}\cdot\vec{b}^* = 0$$
$$\vec{a}\cdot\vec{c}^* = 0, \quad \vec{b}\cdot\vec{c}^* = 0, \quad \vec{c}\cdot\vec{c}^* = 2\pi.$$

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

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

property (i) reciprocal lattice is normal to lattice plane of direct crystal lattice.

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

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

(ii) direct lattice is reciprocal of reciprocal lattice.

sc = self-reciprocal.

bcc ⟷ 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 $e^{i\vec{K}\cdot\vec{\gamma}}$ which may not have the periodicity of Bravais lattice but $\vec{K}$ has that periodicity.

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

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

$$\therefore \vec{K}\cdot\vec{T} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3)$$

If $e^{i\vec{K}\cdot\vec{T}} = 1$, then $\vec{K}\cdot\vec{T}$ must be $2\pi \times$ 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.

<u>Reciprocal of reciprocal lattice</u>

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

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

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

<u>Reciprocal of sc lattice</u> $\vec{a} = a\hat{i}$, $\vec{b} = b\hat{j}$, $c = c\hat{k}$.

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

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

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

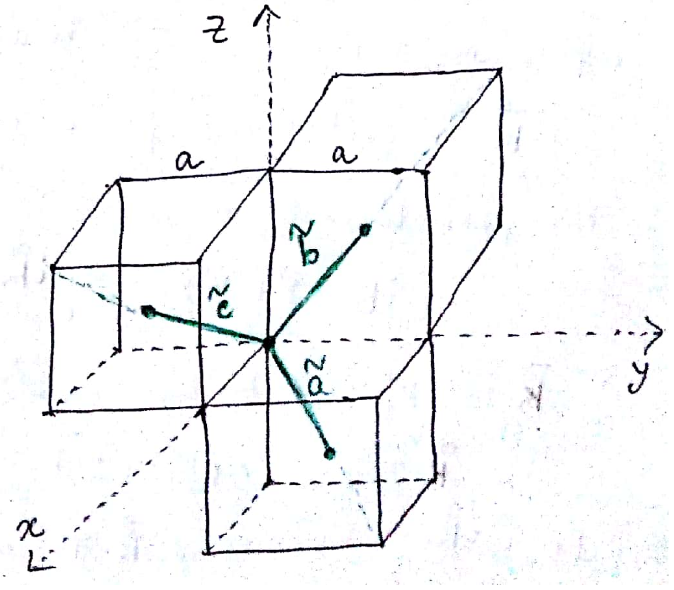
lattice constant $= 2\pi/a$.

<u>Reciprocal of bcc lattice</u>

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

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

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



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

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

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

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

<u>Reciprocal of fcc lattice</u> $\vec{a} = \frac{a}{2}(\hat{i}+\hat{j}),\quad \vec{b} = \frac{a}{2}(\hat{j}+\hat{k})$

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

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

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

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