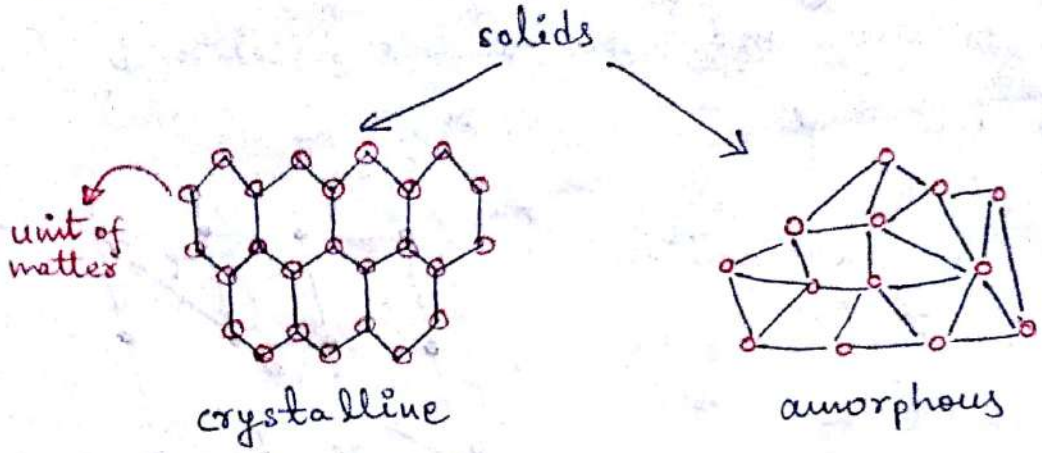
SOLID STATE PHYSICS

Crystal structure, direct lattice & (un)holy grail



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

whats "solid"? → elasticity

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

x = displacement

l = length of lattice

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

But $\frac{1}{2}K\bar{x}^2 = \frac{1}{2}K_BT$ (equipartition theorem)

$$\therefore \bar{x}^2 = \frac{K_BT}{K} = \frac{K_BT}{Kl}$$

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

amorphous solids ⟷ highly viscous, supercooled liquids.

Example pitch, plastic, silicate glass.

SALIENT FEATURES

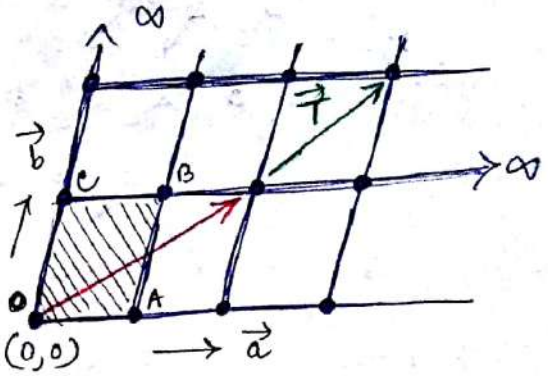
(i) molecular motion is irregular but distance is more or less same with elastic solid.

(ii) no regular shape → 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 $\vec{r}' = \vec{r} + \vec{T}$

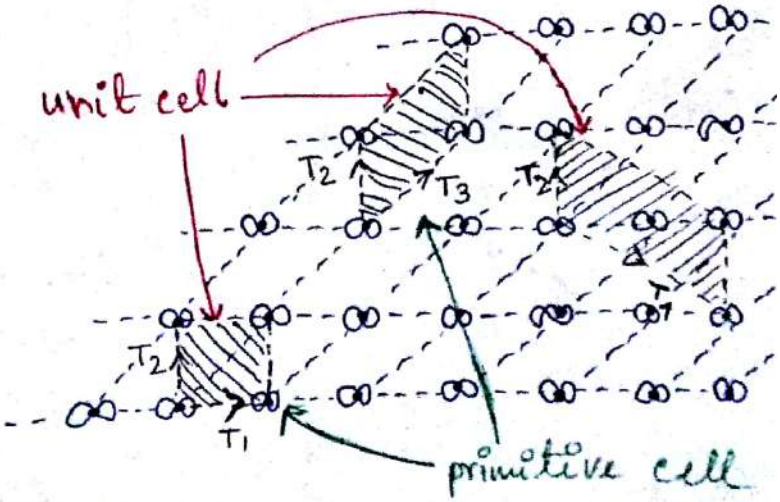
$= \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

where n_1, n_2, n_3 are integers.

primitive lattice & Unit cell

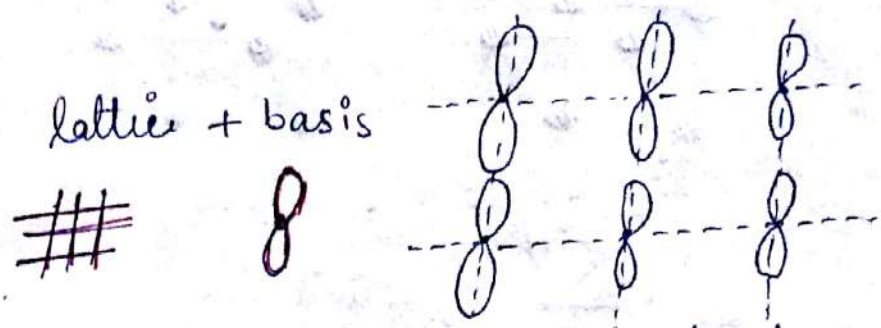
Unit cell is volume from which entire crystal can be constructed by translational repitition. (OABC parallelogram)

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

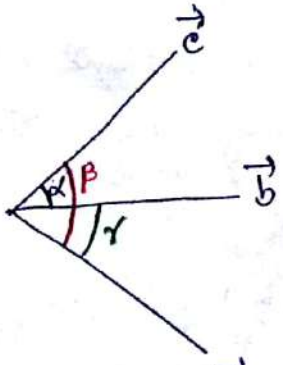
density $\rho(\vec{r}) = \sum_{\vec{T},\alpha} m_\alpha \delta(\vec{r} - \vec{T} - \vec{c}_\alpha)$

where m_α is mass of atom at lattice site $\vec{c}_\alpha$.

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

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

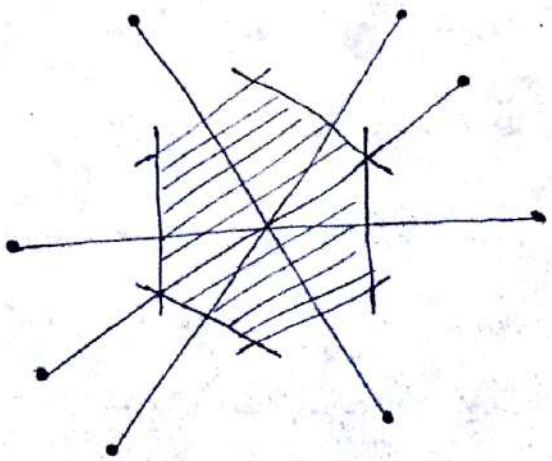
$$\alpha = \beta = \gamma = \frac{\pi}{2}$$

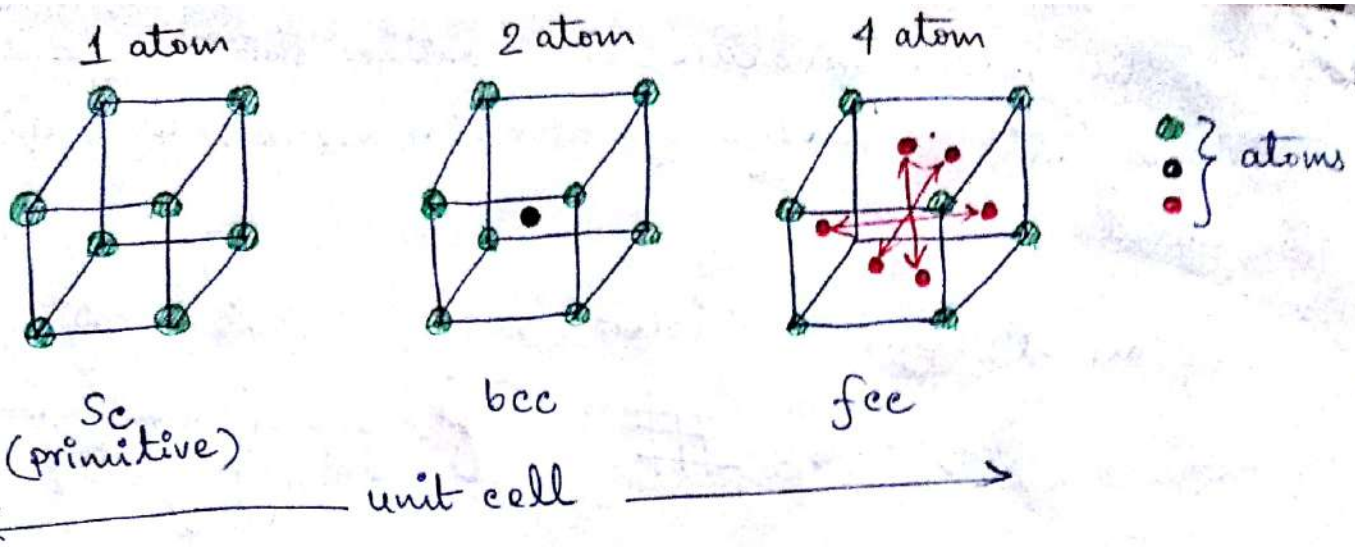


Wigner - Sietz primitive cell

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

This is WS primitive cell.

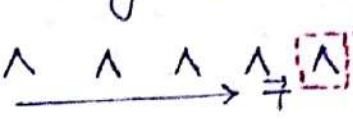




Elements of symmetry

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.

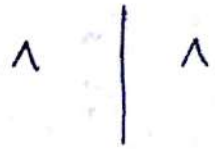
= 1, 2, 3, 4, ~~5~~, 6.

$\phi = 60^\circ$

$= \frac{2\pi}{6}$

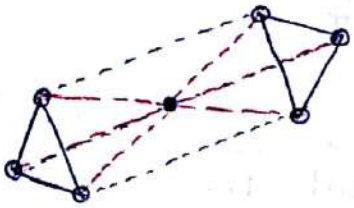
A 2D square lattice has 4-fold rotational symmetry.

(iii) Reflection mirror image



(iv) Inversion

(only for 3D lattice)



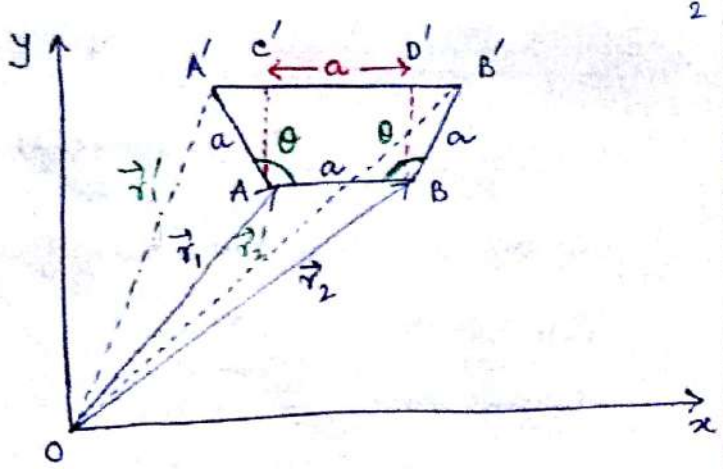
Symmetry operation performed about a point / line are called point group symmetry. 3 type of point group (i) plane of symmetry (reflection), (ii) axis of symmetry (rotation), (iii) centre of symmetry (inversion)

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 = integer)

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

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

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

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

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

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

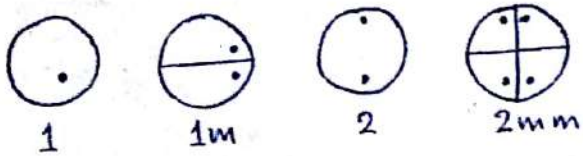
$\{q=2,\ \theta = \frac{2\pi}{6}\}$, $\{q=3,\ \theta = \frac{2\pi}{1}\}$.

So, $n = 1, 2, 3, 4, 6$ → hexad

↓ diad, ↘ triad, → tetrad

Point group & space group

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

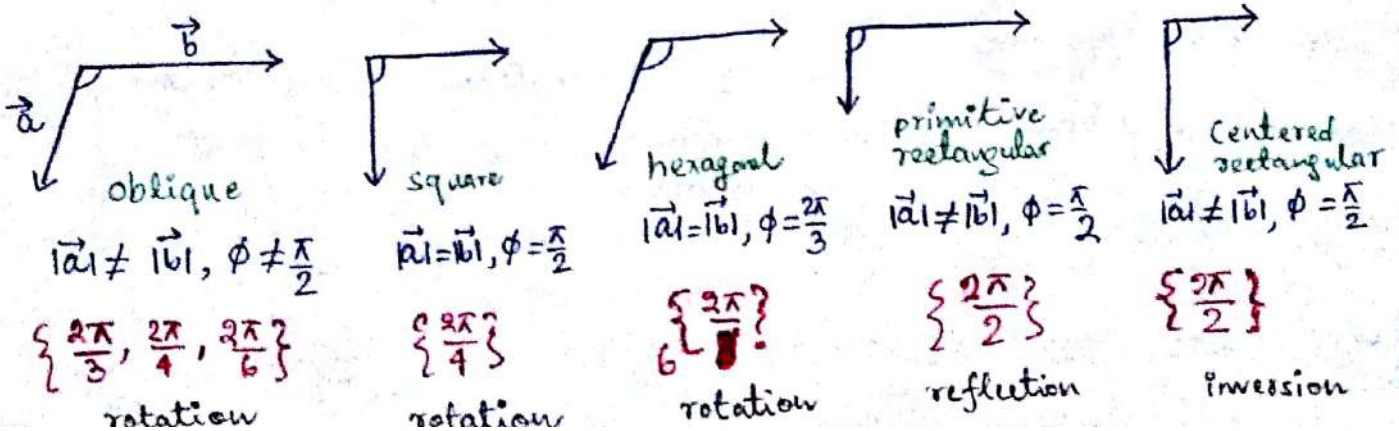


Total 32 point groups.

Group of all symmetry elements is space group.

In 2D : 17, 3D : 230.

Bravais lattice : $|\vec{a}|, |\vec{b}|, \phi$ 5combination : symmetry operation 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)
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)

$$\#\text{ of atoms / unit cell} = \frac{8}{8} + 1\frac{6}{2} = 2$$

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 → 3 XY, YZ, XZ plane