

Crystallography :
 Arrangement of the atoms in solids.
 Spho → means to write
 ↓
 crystal structure → A solid of definite shape
 ↗

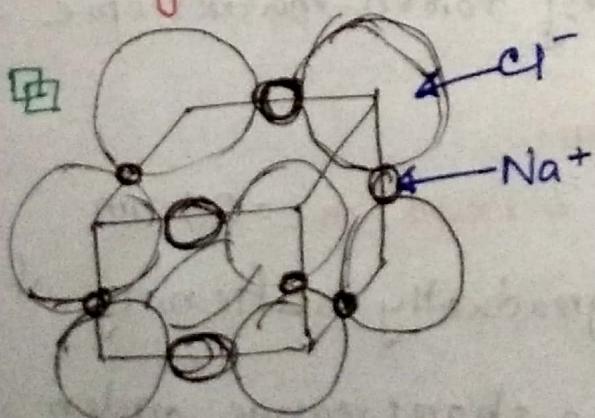
atoms or molecules arranged
 in regular repetition 3D
 pattern to termed as a
 crystal

grows
 in a constant
 environment

The shape
 remains unchanged
 during growth

appears as if identical
 building blocks are
 continuously added

Building blocks are atom or group of atoms



Solid are generally three types —
 (i) single crystalline
 (ii) Polycrystalline
 (iii) Amorphous "

Single Crystalline — can be distinguished from one another by the size of ordered region within the materials.

The periodicity extends throughout the materials

09/02/2020

Poly crystalline → materials solid is made of grains which are highly ordered crystalline regions of irregular size and orientation.

→ period periodicity does not extend throughout the crystal but is interrupted at grain boundaries.

are smaller crystallites than the size of the pattern, which form the periodicity

* size of the grains in which structure is periodic may vary from macroscopic dimension.

↳ several angstrom

$$A^\circ = 10^{-10} \text{ m} = 0.1 \times 10^{-9} \text{ m} = 0.1 \text{ nm}$$

Amorphous solids :

Substance without any regular form or shape

order in amorphous material is limited to a few molecular distance

→ there is gradually softening of the material

→ has only a short range order

→ isotropic in character

Ex → pitch
→ plastics
→ silicate glass etc.] → in which the molecules are in a more or less chaotic and random distribution throughout the solid

Crystalline Solids —

- has special regularity extending over a large volume
- there is a long range order in a substance
- have a sharp melting point

* the changing of long range order into short range orders takes place after breaking such bonds. whose strength is ~~nearby~~ nearly the same.

Properties along different directions of crystal axes

Like → Conductivity

→ Elasticity

→ Tensile Strength Anisotropic in character

Symmetry Considerations or Geometrical Symmetry :

→ A fundamental group of atoms or molecules known as motif.

↓
can be periodically repeated in a number of permissible ways without considering its intimate details

in space 4 ways → Types of symmetric operation

A lattice point \vec{r} under translation operation

\vec{T} is another point \vec{r}'

exactly identical to \vec{r}

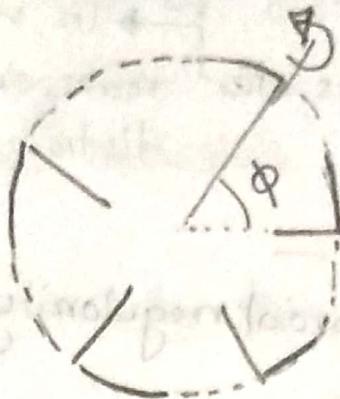
$$\vec{r}' = \vec{r} + \vec{T}$$

① Translational operation → repeats the motif an infinite number of times

Translation by an amount t as shown in figure

This operation (II) Rotation operation :
 repeats the motif
 a finite number
 of time \rightarrow

The motif can
 be through an
 angle ϕ about
 an axis of rotation



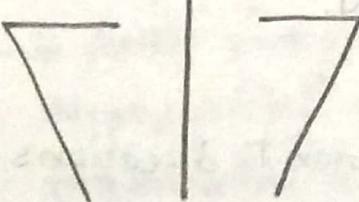
\rightarrow take angle ϕ as
 shown in figure

$$n\phi = 2\pi$$

$$\phi = \frac{n\pi}{n}$$

(III) Reflection operation :

across a line or plane
 changes the character of
 the lattice from
 left handed to
 right handed and
 vice versa

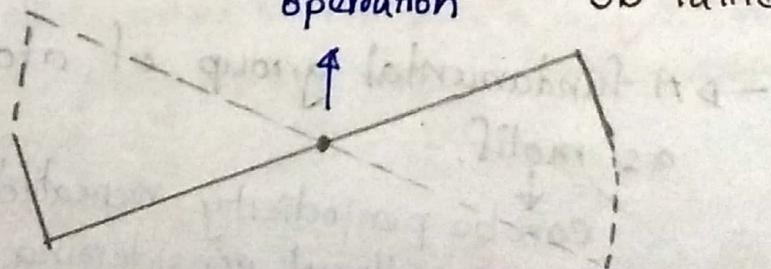


2D \rightarrow line

3D \rightarrow plane

(IV) Inversion operation :

point operation \rightarrow which is applicable to
 3D lattice only



Q

2D

7	7	7	7	7	7
7	7	7	7	7	7
7	7	7	7	7	7
7	7	7	7	7	7
7	7	7	7	7	7

$\frac{t_1}{a}$

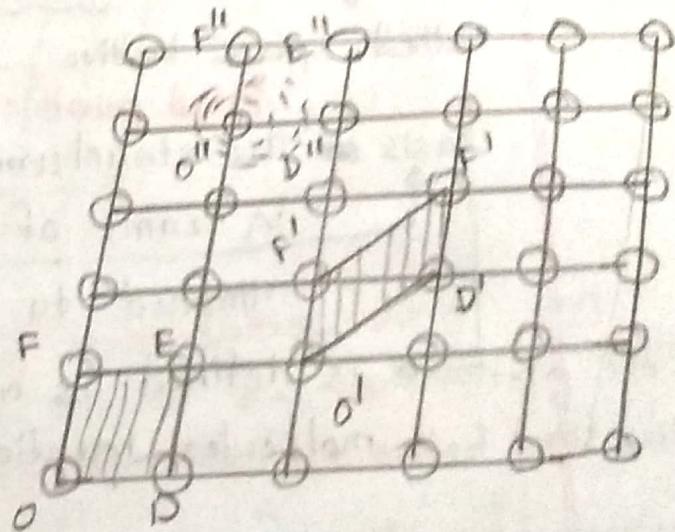
2D

0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0

$t_1 = t_2$

3D simulation cell:

0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0



Crystall lattice:

crystalline substance, the atoms are regularly arranged



The periodic arrangement of atoms in a crystal is called lattice or crystall lattice.

Lattice Parameters:

The length of the unit cell and the angles between the edges are called lattice P.

2D \bar{a}, \bar{b}

→ plane lattice

3D $\bar{a}, \bar{b}, \bar{c}$

→ space lattice

10/02/2020

$\bar{a}, \bar{b}, \bar{c}$
4

Space Lattice : on crystal lattice

The regular pattern of points which describe the arrangement of particles in a crystal structure is called space lattice.

► ions, molecules or atoms

$$\text{Fixed point} = n_1\bar{a} + n_2\bar{b} + n_3\bar{c}$$

Basis → The structure of all crystals can be described in terms of lattice with a group of atoms attached to each lattice point.

→ is defined as an assembly of atoms, ions or molecules identical in

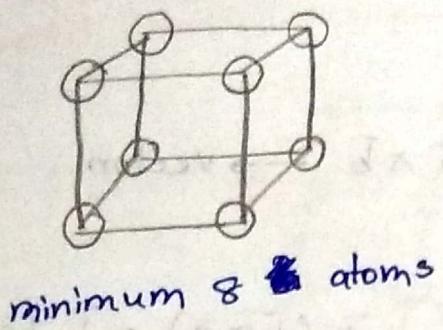
- composition
- arrangement
- orientation

Crystal Structure = Lattice + Basis

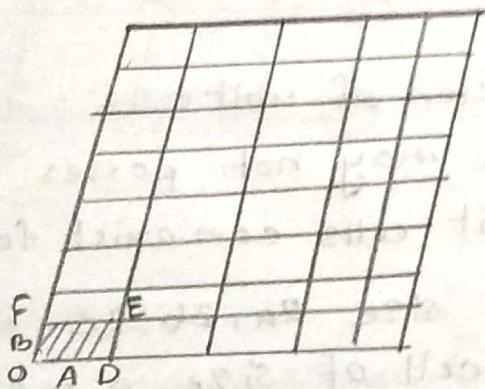
↳ is formed by the addition of a basis to every lattice point

Primitive cell → smallest unit of volume of a crystal

↓
minimum volume cell
which contains the least number of atoms required to completely specify the relative position of all atoms in a crystal



Unit cell →



→ The smallest portion of a space lattice which can generate the complete crystal by replicating its one dimension various direction is called unit cell.

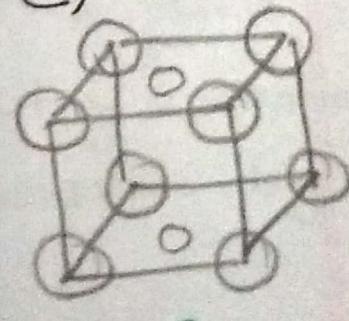
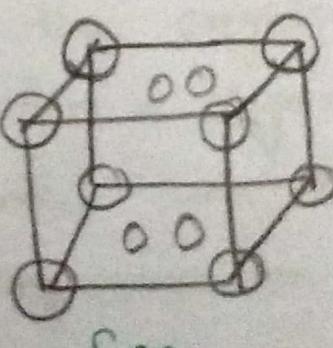
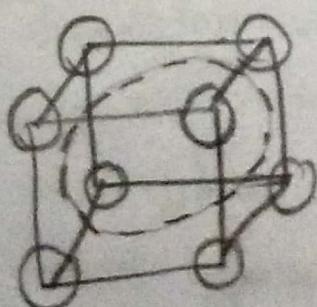
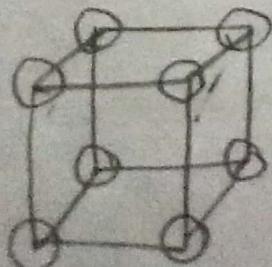
Types of unit cell → Based on the unit cell length and angles, there can be 4 different types of unit cell.

(I) Simple cubic structure → (SC)

(II) Body centered Cubic Structure → (BCC)

(III) Face " " " → (FCC)

(IV) Base " " " → (B)



Translations Vectors :

$$2D \longrightarrow \bar{a}, \bar{b}$$

$$\text{Area of the unit cell} = \bar{a} \times \bar{b} \rightarrow \text{vector}$$

$$3D \longrightarrow \bar{a}, \bar{b}, \bar{c}$$

$$\text{Volume of the unit cell} = \bar{a} (\bar{b} \times \bar{c}) = \bar{b} (\bar{c} \times \bar{a})$$

$$= \bar{c} (\bar{a} \times \bar{b})$$

Important factors of unit cells :

- ① A crystal may not possess a unique unit cell.
- ② Many unit cells can exist for the same structure.
- ③ A cell of size $2a, 2b, 2c$ is as much correct as the cell of size a, b, c .
- ④ For certain structures unit cells of completely different geometry are possible.

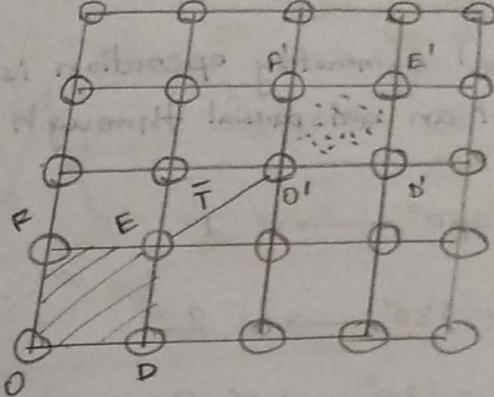
Primitive Basis Vectors :

$\bar{a}, \bar{b}, \bar{c}$ \longrightarrow define primitive cell

Primitive crystal axis is called

$\vec{a}, \vec{b}, \vec{c}$

Crystal Translation Vectors :



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

n_1, n_2 and n_3 are arbitrary integers.

Crystal Translation operation :

The displacement of a crystal to itself by \vec{T} is called a crystal T. ope.

In a crystal in addition to the geometrical arrangement of atoms or function $f(r)$,

Symmetry Operation : is that which transforms the crystal to itself i.e. a crystal remains in various under a symmetry operation. Crystal lattice can be carried into themselves by \vec{T} and by various other symmetry operation.



$$= 2\pi = 360^\circ$$

Typical symmetry operation is that of rotation about an axis parallel through a lattice.

$$\therefore \frac{2\pi}{1} = \frac{360^\circ}{1} = 360^\circ \rightarrow \nu 1$$

$$\frac{2\pi}{2} = \frac{360^\circ}{2} = 180^\circ \rightarrow \nu 2$$

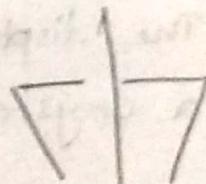
$$\frac{2\pi}{3} = \frac{360^\circ}{3} = 120^\circ \rightarrow \nu 3$$

$$\frac{2\pi}{4} = \frac{360^\circ}{4} = 90^\circ \rightarrow \nu 4$$

$$\frac{2\pi}{5} = \frac{360^\circ}{5} = 72^\circ \rightarrow \times$$

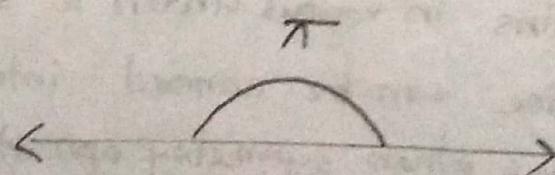
$$\frac{2\pi}{6} = \frac{360^\circ}{6} = 60^\circ \rightarrow \times$$

Rotation Symmetry operation!

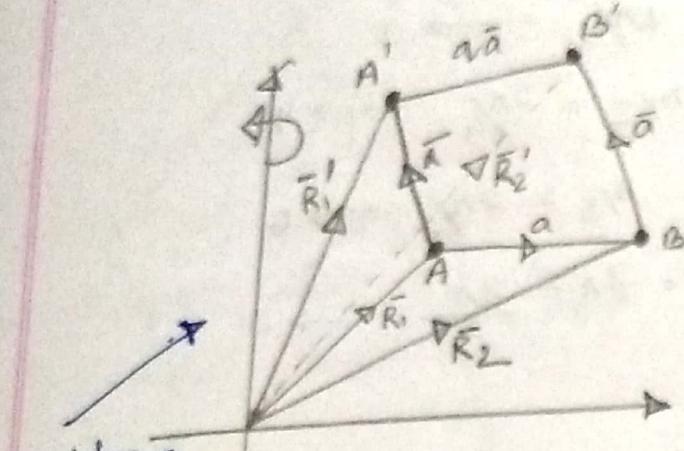


(i) Mirror reflection about a plane through a lattice point.

(ii) Inversion operation which is a combination of rotation through π followed by a reflection in a plane normal to the rotation axis.



A crystal cannot have 5-fold symmetry



~~AA'~~ $\bar{a} \bar{a}$ = \bar{a} primitive translation vector

$\bar{OA} = \bar{R}_1$ The two lattice vectors connecting the origin to A and B
 $\bar{OB} = \bar{R}_2$ the two closest lattice points of the crystal

Consider a line perpendicular to the plane of the paper and passing through the lattice point

Vector \bar{a} be rotated about the line an axis through an angle θ

$$\therefore \theta = \frac{2\pi}{n}$$

clockwise ↗
anticlockwise ↘

$$\theta = \frac{2\pi}{n}$$
 is clockwise

$$\therefore \text{New lattice } \bar{OB}' = \bar{R}_2'$$

$$\bar{OA}' = \bar{R}_1'$$

Rotating 2 to zero

$$AA' = BB' = |\bar{a}|$$

$$\angle BAA' = \angle LABB' = \theta$$

Quadrilateral $ABB'A'$ is Trapezium with

$$A'B' \parallel AB$$

$$\begin{aligned} A'B' &= q|\bar{a}| \\ &= |\bar{R}_1' - \bar{R}_2'| \end{aligned}$$

$$= |\bar{a}| \sin \pi/2 + |\bar{a}| \sin(\theta - \pi/2) + |\bar{a}| \sin(\theta - \pi/2)$$

$$q = 1 - 2 \cos \theta$$

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

$\therefore \cos \theta < 1 \rightarrow$ above relation can be satisfied only when
 $q = 3, 2, 1, 0, -1$

$$q = 3, \cos\theta = -1, \theta = \pi = \frac{3\pi}{2} \rightarrow 2$$

$$q = 2, \cos\theta = -\frac{1}{2}, \theta = 2\pi/3 \rightarrow 3$$

$$q = 1, \cos\theta = 0, \theta = \pi/2 = \frac{2\pi}{4} \rightarrow 4$$

$$q = 0, \cos\theta = 1/2, \theta = \pi/3 = \frac{2\pi}{6} \rightarrow 6$$

$$q = -1, \cos\theta = 1, \theta = 2\pi = \frac{3\pi}{3} \rightarrow 1$$

Symmetry elements of a crystal

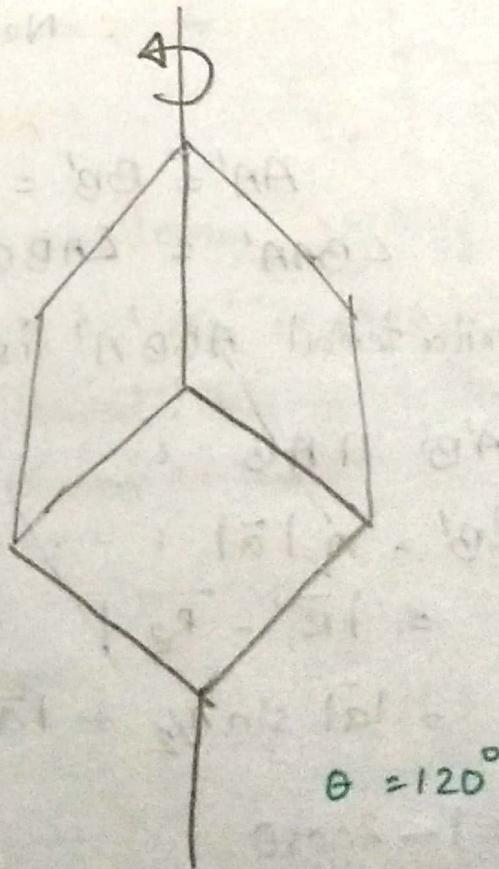
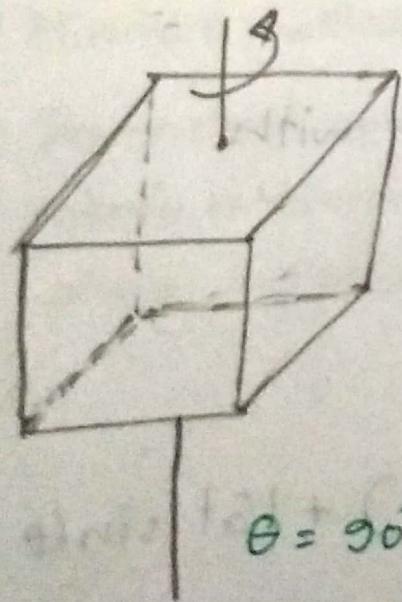
Solid

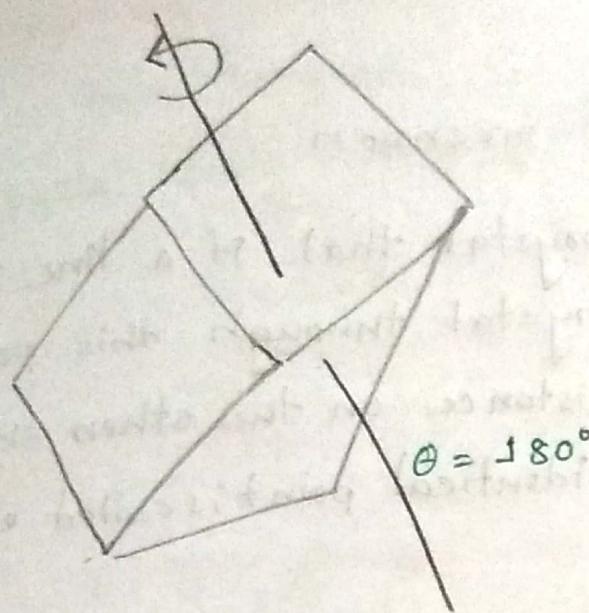
(I) Axis of Symmetry

(II) Planes of " $\Rightarrow \frac{\pi}{2} = \theta$

(III) Centre of "

Axis of Symmetry

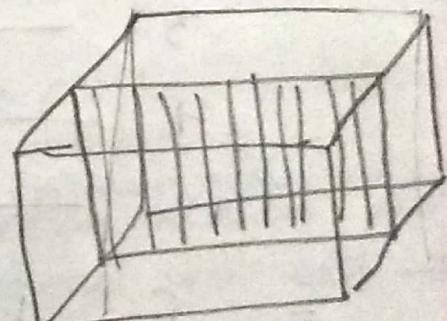
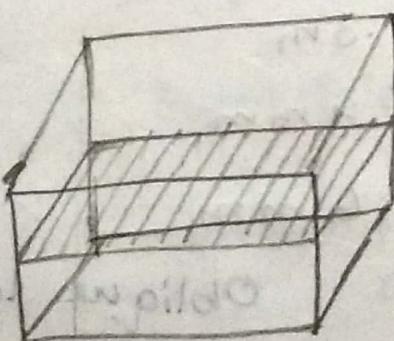
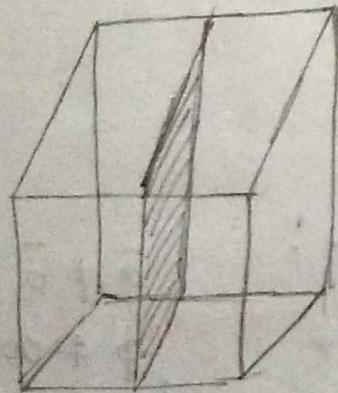




if $n=1$, the crystal has to be rotated through 360° to achieve self confidence. Such an axis is called an Identity axis.

Each crystal possesses an infinite no of such axis.

Plane of Symmetry :



Centre of Symmetry

↓
also called centre of inversion

such a point in a crystal that if a line is drawn from any point on the crystal through this point and produced an equal distance on the other side of this centre, it meets an identical point is called centre of symmetry.

Bravais Lattice in 2D

Various combinations of allowed rotation and reflection operations are found to give rise to 10 different 2D point groups permissible in a crystal.

$$1 \longrightarrow 1m$$

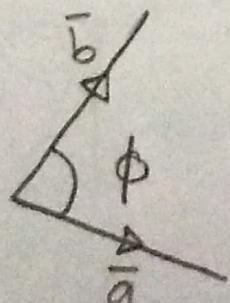
$$2 \longrightarrow 2mm$$

$$3 \longrightarrow 3m$$

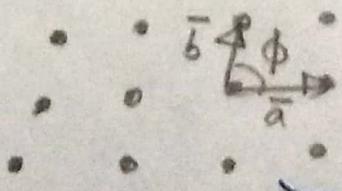
$$4 \longrightarrow 4mm$$

$$6 \longrightarrow 6mm$$

$$\bar{a}, \bar{b}, \phi$$



Oblique lattice:



$$\bar{a} \neq \bar{b}$$

$$\phi \neq 90^\circ$$

arbitrary
symmetries

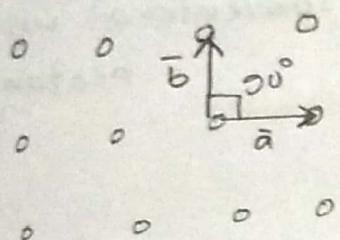
2-fold rotation

1. Conventional unit cell

Parallelogram

spacial lattice \rightarrow oblique invariant under rotation
 \downarrow
 $2\pi/3$, $2\pi/4$ and $2\pi/6$

2. square lattice :



$$\bar{a} = \bar{b}$$

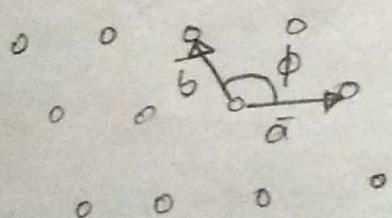
$$\phi = 90^\circ$$

Symmetries \rightarrow 4-fold rotation
reflection

invariant under a rotation $\rightarrow 2\pi/4$

Conventional unit cell \rightarrow square

3. Hexagonal Lattice :



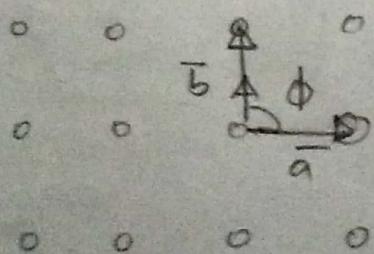
$$\bar{a} = \bar{b}$$

$$\phi = 120^\circ$$

Symmetries \rightarrow 6-fold rotation
reflection

invariant under ~~rotation~~ ^{mirror reflection} $\rightarrow 60^\circ$
conventional unit cell \rightarrow rhombus

4. Rectangular lattice :

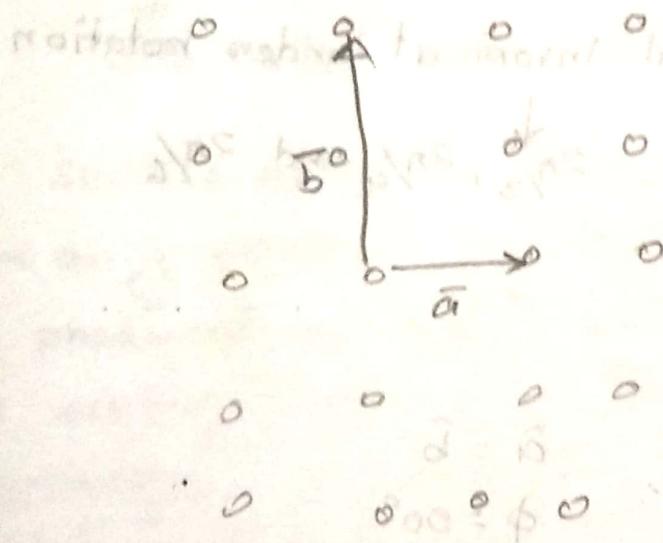


$$\bar{a} \neq \bar{b}$$

$$\phi = 90^\circ$$

Symmetries \rightarrow 2-fold rotation reflection
invariant under mirror reflection
conventional unit cell \rightarrow rectangle

5. centered rectangular lattice:



$$a \neq b, a < b$$

$$\phi = 90^\circ$$

symmetrical \rightarrow 2-fold notation

invariant under inversion operation

conventional unit cell \rightarrow rectangular

zurück zum \rightarrow zentriertem ZG
richtung

\leftarrow zentriertes rechteckiges Gitter
 \rightarrow (Hoch-Zwei-Längsachsen)

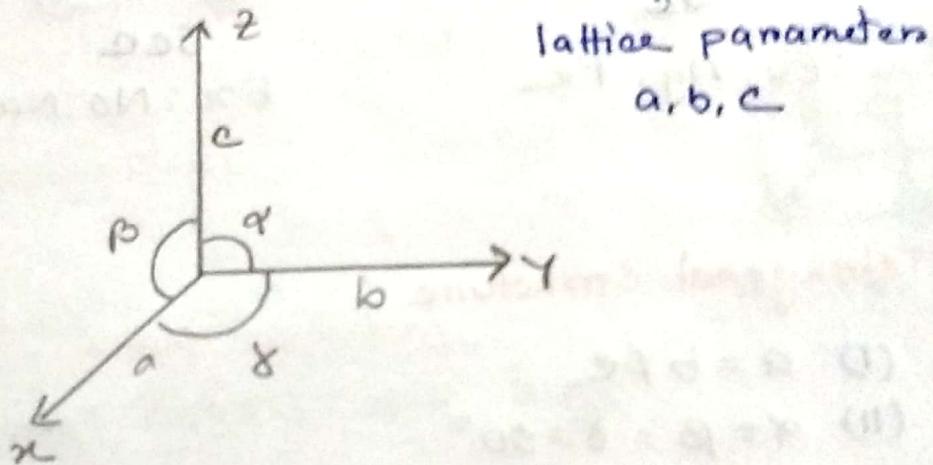
$$90^\circ - \phi$$

Bravi's Space lattice (3D) :

→ 1880 introduced the space lattice

* 14 possible types of space lattice

1 general 13 special → G system
Triclinic lattice 7 system of crystal



lattice parameters
 a, b, c

$$\begin{aligned} a \wedge b &\rightarrow \gamma \\ b \wedge c &\rightarrow \alpha \\ c \wedge a &\rightarrow \beta \end{aligned}$$

(i) Cubic Structure :

$$(i) a = b = c$$

$$(ii) a = \beta = \gamma = 90^\circ$$

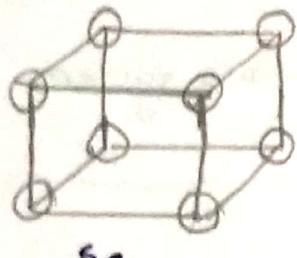
Cubic Lattice : four 3-fold rotation axis,

Cube diagonal
 $M, 3m$

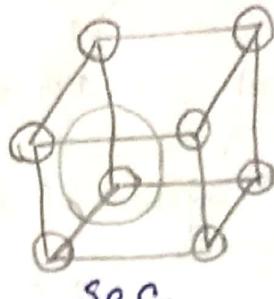
Example : $\text{NaCl}, \text{CaF}_2, \text{NaClO}_2$ etc.

3 types :

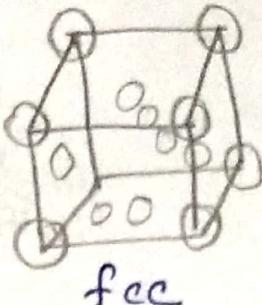
- (i) Simple Cubic (sc) or primitive (P) structure
- (ii) Body centered cubic (bcc)
- (iii) Face " " " (fcc)



Ex : Cu, Ag, Fe



Ex : Na, NaCl



Ex : CsCl

(2) Tetragonal structure :

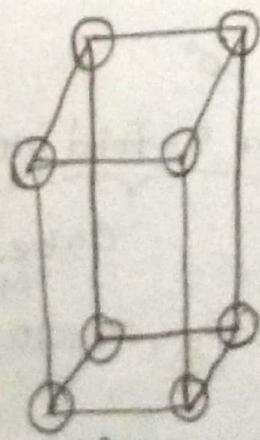
(i) $a = b \neq c$

(ii) $\alpha = \beta = \gamma = 90^\circ$

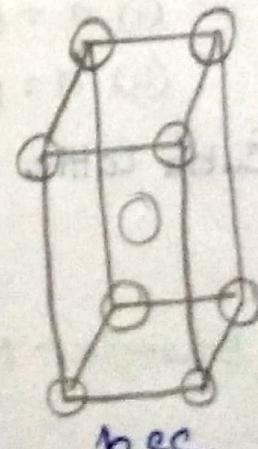
Lattice : One 4-fold rotation axis on
a 4-fold rotation inversion axis

Ex : NiSO_4 , SnO_2 etc.

Two types : (i) sc
(ii) bcc



Ex : $\rho\text{-Sn}$



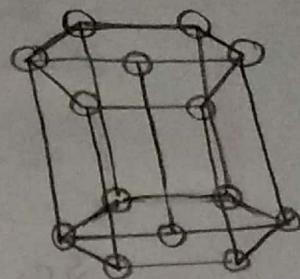
Ex : TiO_2

(3) Hexagonal Structure :

- (I) $a = b \neq c$
(II) $\alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$

Ex : SiO_2 , AgI etc

Lattice : one 6-fold rotation axis
 $6/m, m, m$



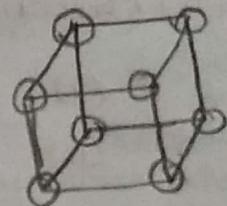
$\text{Mg}, \text{Zn}, \text{Cd}$ etc

(4) Trigonal Structure :

↓
on Rhombohedral

- (I) $a = b = c$
(II) $\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$

Lattice : One 3-fold rotation axis $\bar{3}m$



$\text{As}, \text{Sb}, \text{Bi}$

(5) Orthogonal Structure :

on
orthorhombic

- (I) $a \neq b \neq c$
(II) $\alpha = \beta = \gamma = 90^\circ$

Ex : $\text{KNO}_3, \text{BaSO}_4, \text{MgSO}_4$ etc

Lattice : 3 \perp 2-fold rotation axis

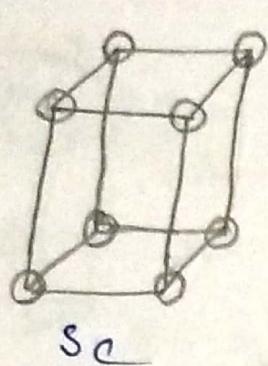
m, m, m

4 types - ① sc

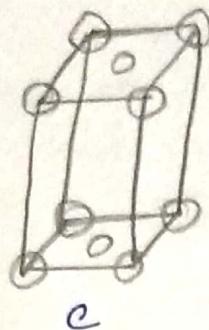
② Base Centred (c) structure

③ bcc

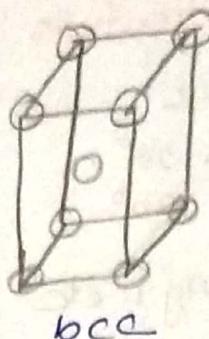
④ fcc



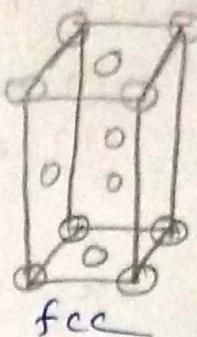
Ex: Cu



Ex: PuBr_3



Ex: Fe_3C



Ex: Mg_2Cu

(6) Monoclinic Structure:

$$(I) \quad a \neq b \neq c$$

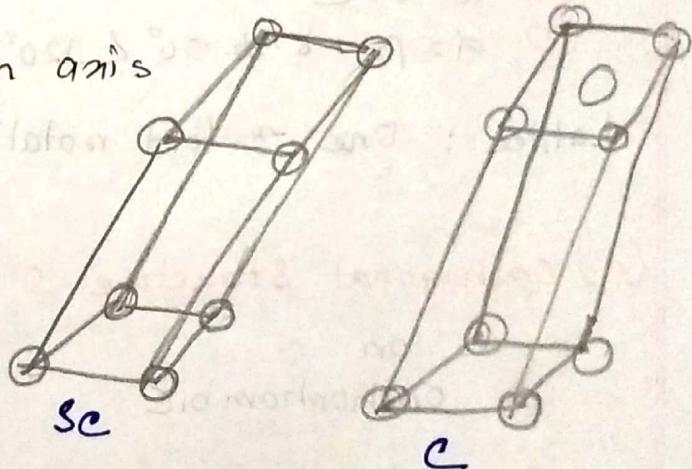
$$(II) \quad \alpha = \gamma = 90^\circ \neq \beta$$

Lattice: One 2-fold rotation axis

$\bar{2}/m$

Ex: Na_2SO_4 , FeSO_4 etc

Two types :
 (I) Sc
 (II) c



Ex: $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$

Ex: $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

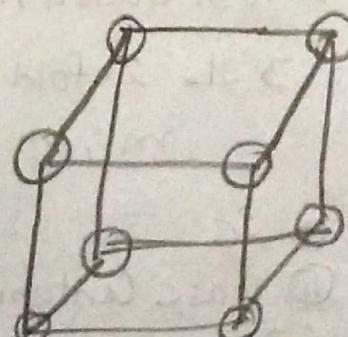
(7) Triclinic Structure:

$$(I) \quad a \neq b \neq c$$

$$(II) \quad \alpha = \beta = \gamma \neq 90^\circ$$

Lattice: None

Ex: CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$



$\text{K}_2\text{Cr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

No of atoms or lattice per unit

i.e., Volume of a unit cell = V in cm^3

Density of the crystal = ρ in gm/cm^3

The weight of the matters in the

unit cell = ρV in gm

No of atoms or molecules per unit cell = n

The atomic (molecular) weight of one atom or molecule = M

The weight of the matters in the unit cell = $(nM) \times 1.66 \times 10^{-24}$ gm

the weight of
hydrogen atoms in
gms in converting
molecular weight in gms

dm of conservation :

$$nM \times 1.66 \times 10^{-24} = \rho V$$

$$n = \frac{\rho V}{M \times 1.66 \times 10^{-24}}$$

$$n = \frac{\rho V \times 6.023 \times 10^{23}}{M}$$

→ Avogadro's Number

$$n = \frac{N \rho V}{M}$$