UNIT-1

CRYSTAL STRUCTURE – Solids: Amorphous & crystalline Materials. Lattice Translation Vectors. Lattice with a basis, Types of lattices, Unit cell, symmetry & symmetry elements. Miller Indices, Reciprocal lattice. Brillouin zones. Diffraction of x-rays: single crystal & powder Method, Bragg's law, Laue Condition, Ewald's construction, Atomic & Geometrical factor, Simple numerical problem on SC, BCC, FCC.

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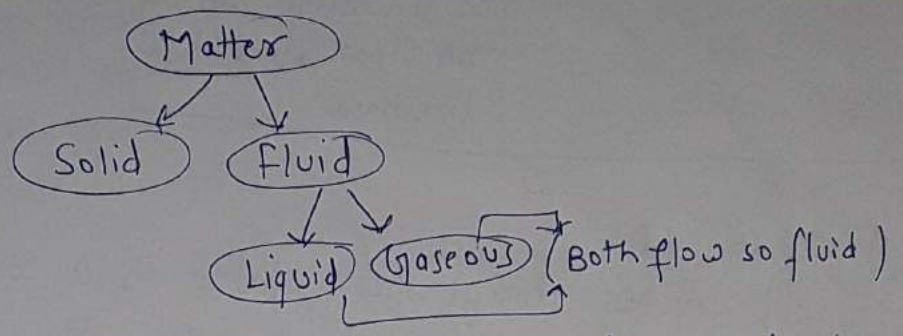
1) Amorphous & Crystalline Materials



Solid State Physics → study of physical properties of atomic matter in solid state

Physics of Condensed matter → study of liquids, particularly liquid metals, molten salts, solutions, liquid crystals and even substances like glycerine. At sufficiently low temp all matters condense in solid state.

Q) What is the main reason for diff. states of matter.

Ans: It is due to difference in nature of intermolecular forces

Ex:

Gas – Low Density, Negligible intermolecular force.

Liquid – Intermolecular forces are of short range and depend only on distance but not on direction.

Solids – Strong intermolecular forces & may be longe range (in crystals only).
Even small displacement of molecules from equillib. position is responsible for many properties of crystalline solids.

States b/w Solid & liquids

Liquid Crystals, Amorphous solids, Glass

Real Crystals	Liquid Crystals
Symmetry is present in the arrangement of atoms or molecules in all 3 directions	3 dimensional symmetry is not present Molecules are arranged in 1 or 2 dimensions but they can flow along other directions

Q) What is LCD

Ans: Liquid crystals change their state in a continuous way by small change of temp, electric pulse etc. These changes are characterised by change of colour & this property is utilised in liquid crystal display (LCD).

Amorphous Solids → Short range but strong inter-molecular force due to random arrangement of molecules. They are prepared from cooling molten matter. If the cooling is done very fast then the atoms do not have time to rearrange them in a crystal & arrange themselves in a random fashion to produce an Amorphous solids.

Glass → काँच → Frozen liquid. Randomness in the position of molecules is the same at all the times. As such there is no flow of molecules in a glass.

On the basis of structure, Solids → Crystalline
→ Non Crystalline (Amorphous)

Two broad catogories.

Q) Can we distinguish b/w Amorphous & crystalline solids by their external appearance / macroscopic form.

Ans: No

(3)

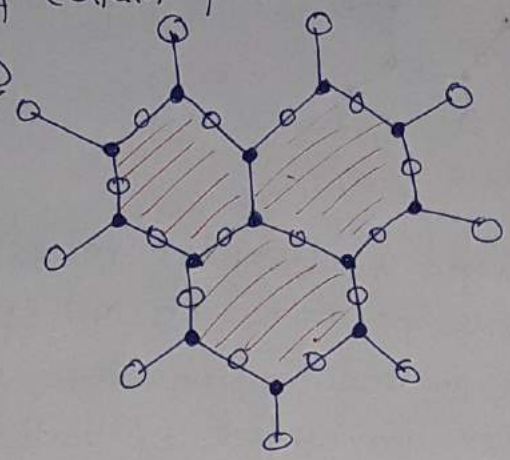
Q) How can they be distinguished.

Ans: By their degree of order shown by arrangement of fundamental particles, atoms, molecules or ions comprising them.

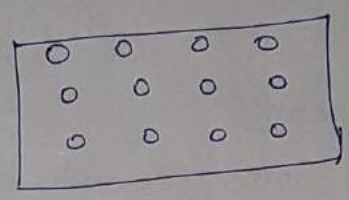
(A) Crystalline Solids

Ordered periodic arrangement of atoms, molecules or ions, forming the 3D pattern which may be obtained by a 3D repitition of certain pattern unit.

Ex: 2D



2D



Properties

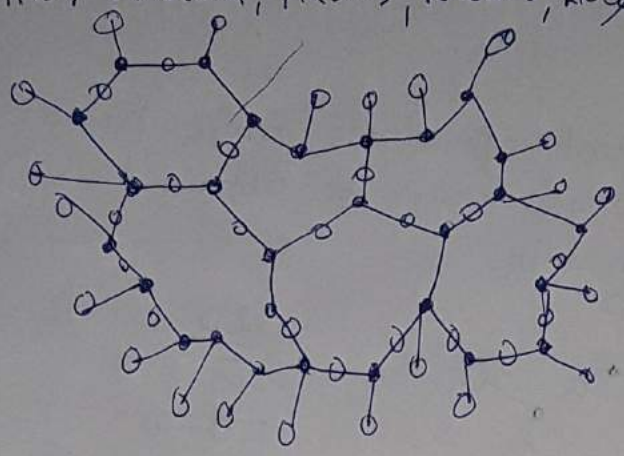
1. Internal arrangement of atoms/ions/molecules is in a definite geometrical order.
2. Sharp melting point
3. Below the temp of crystallization, materials are in a stable state. (Stable state → Min. energy state). Hence materials acquire a state of min. energy on crystallization.
4. Orderly arrangement is extended over a large volume of crystal
5. They are anisotropic → physical properties are different along diff directions, Hence crystallographic plane & directions become important. Properties like – refractive index, conductivity, thermal expansion, fall under this.
6. Uniform chemical composition throughout

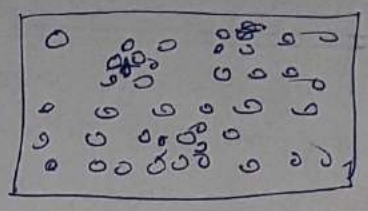
(B) Amorphous Solids :

Atoms/molecules are not arranged in regular/periodic atomic arrays and size of grains become comparable to the size of pattern unit. They have short range order, but in some cases they may possess small regions of orderly arrangement.
↓ known as crystallites

Ex – Glass, charcoal, plastics, Rubber, Wood

2D





Properties

1. Atoms/Molecules are arranged in irregular manner.
2. No sharp m.p., bcoz bonds b/w atoms are not equally strong.
3. Isotropic. → Various physical properties are same in all directions, due to random arrangement of particles.
4. They are supercooled liquids / pseudo solids

Types of crystal —

(A) SINGLE CRYSTAL – Same symmetry exists everywhere through out the crystal & is described in terms of three symmetry axis.

(B) POLYCRYSTAL – It consists of no of small crystallites having different symmetry axis & separated from one another by grain boundaries.
Sym. axis are different in diff. regions of specimen.

(C) Quasi-crystal – Ex – Al_6Mn, $FeTi_2$
Here 5 fold ~~sym~~ rotational symmetry exists which is prohibited in real 3D crystal.

Q) What is the reason for 5-fold rotational symmetry in quasi-crystals

(5)

Ans : 5-fold rotational symmetry in a structure called icosahedron exists due to small change in lattice parameter from one lattice point to another lattice point. They are known as quasi-crystals bcoz lattice parameters is not exactly constant in this material.

(d) Polymorphism — Diff. structure exists for same constituent elements. Ex — Zinc sulphide exists in cubic and hexagonal forms

e) Polytypes — Diff. no of layers of atoms in different sequences are stacked to get smallest unit cell in different ways. Ex- in polytype of SiC there may be 594 layers of atoms in a unit cell whereas in simple cubic structures of SiC there are only four molecules.

② Lattice Translation Vectors ③ Lattice With a Basis

In 1848 Bravais introduced the concept of space lattice.

Considering the translation of an object (symbolized by J) to a finite distance (say a) & then repeated along three crystallographic axes x, y, z

J J J J

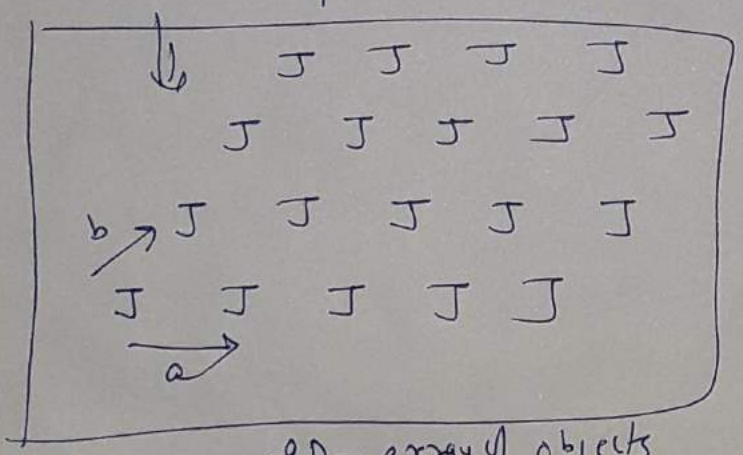
(Along x-direction only)

We obtain 1-D periodic array of J

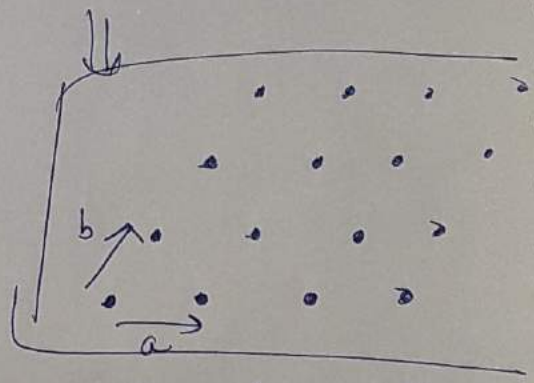
If we replace each J by an imaginary point in space, then resulting collection of points is called a lattice

(linear lattice)

If translation a is combined with another non-collinear translation b, then we get 2D array

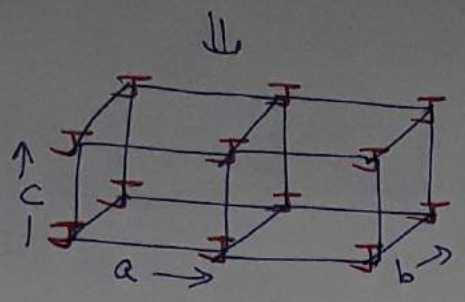


2D- array of objects

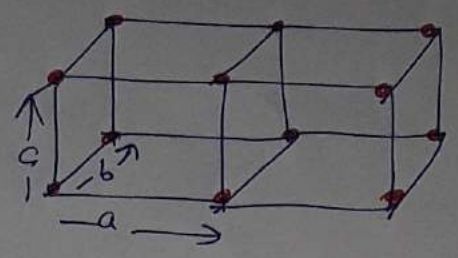


2D - Plane lattice

If further non-coplanar translation c is also combined then we get 3D array



3-D array of objects



3-D ~~array of~~ space lattice

$\boxed{\text{LATTICE}}$ ⟹ A lattice is a regular periodic arrangement of points in space which has the environment about any particular which in every way is same as that about any other point.

All points in a lattice are connected by a translational vector.

$\boxed{\text{Translational Vector}}$ ⟹ $\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

It is an operator.

n_1, n_2, n_3 → Arbitrary Integers

$\vec{a}, \vec{b}, \vec{c}$ → fundamental translational vectors

* Application of $\vec{T}$ operator to any point $\vec{r}$ (measured from some arbitrary origin) results in a point $\vec{r}'$

$$\vec{r}' = \vec{r} + \vec{T} = \vec{r} + (n_1\vec{a} + n_2\vec{b} + n_3\vec{c})$$

where $\vec{r}$ and $\vec{r}'$ are identical in all respects.

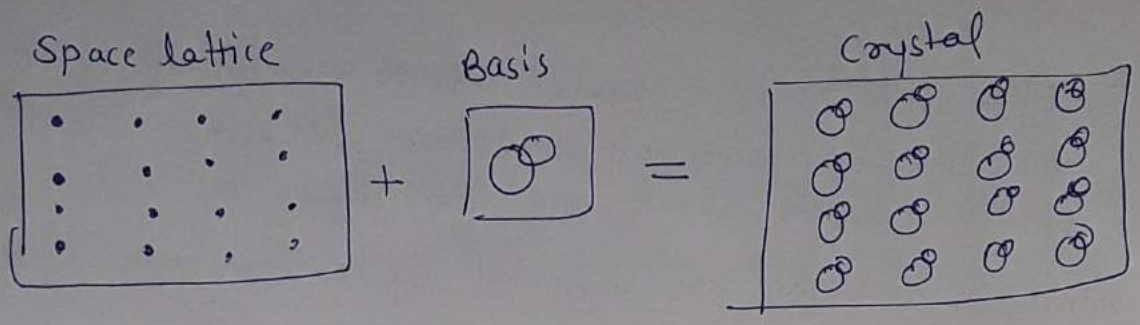
$\boxed{\text{LATTICE}}$ → Mathematical Concept

$\boxed{\text{Crystal}}$ → Physical picture

lattice + Basis = Crystal

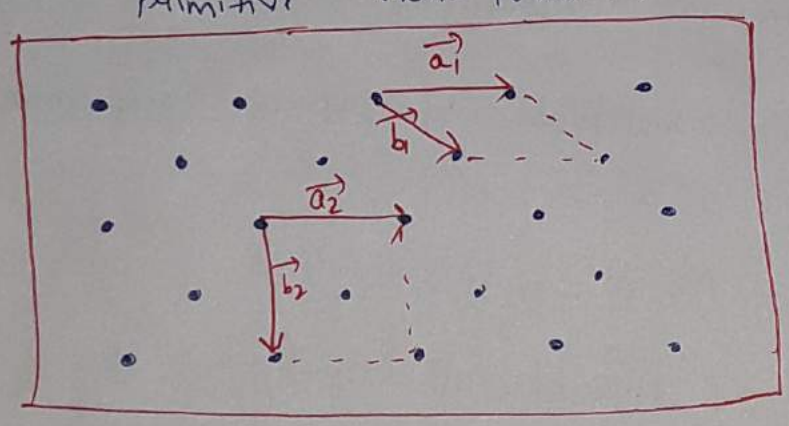
Basis → Every lattice point is associated with a structural or a building unit called basis. Basis consists of an atom or a group of atoms.

* If no $\vec{a}, \vec{b}, \vec{c}$ exists, then assembly of atoms can't be classified to be a crystal.
* Vectors $\vec{a}, \vec{b}, \vec{c}$ are often called crystal axes or basis vectors



* Translation vectors

Primitive Non-primitive



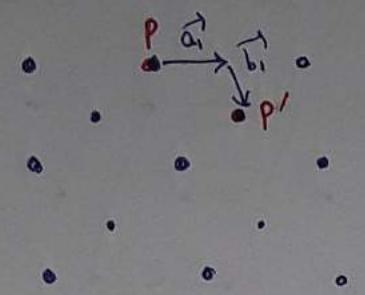
<u>Primitive Translational Vectors</u> : $\vec{a_1}, \vec{b_1}$ are such that every identical point in the crystal can be reached by an application of translation operation.

$$\vec{T} = n_1 \vec{a_1} + n_2 \vec{b_1}$$

$n_1, n_2 \longrightarrow$ can be $0, 1, 2$ - - only Integers

Non-Primitive Translational vectors: If n_1, n_2 etc are non-integral then $\vec{T}$ is called non-primitive translational vectors.

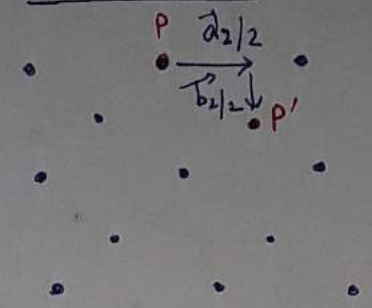
Primitive



from P to P'

$$\vec{T} = 1.\vec{a_1} + 1.\vec{b_1}$$

Non-Primitive



from P to P'

$$\vec{T} = \frac{1}{2}\vec{a_2} + \frac{1}{2}\vec{b_2}$$

1D $\rightarrow$ $\vec{T} = n_1\vec{a}$

2D $\rightarrow$ $\vec{T} = n_1\vec{a} + n_2\vec{b}$

3D $\rightarrow$ $\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

(4) UNIT CELL

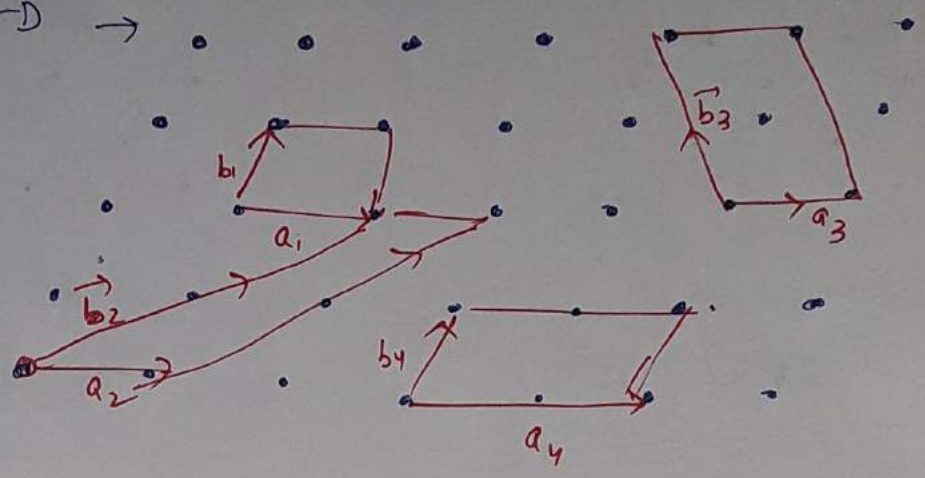
Smallest volume/structure which when repeated in all directions builds the crystal.

(10)

Ex: Wall (crystal) is made of bricks (unit cell)
& shape of wall depends on the shape of brick

Similarly shape of crystal depends on the shape of unit cell.

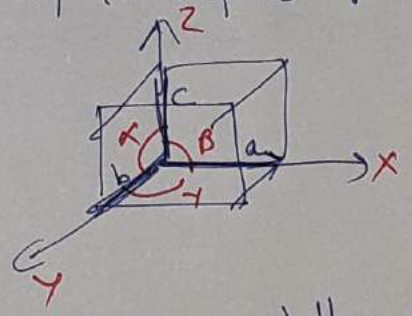
Unit cells in 2-D →



PARAMETERS OF UNIT CELL

(1) Crystallographic axes – These are defined as the line, drawn ∥ to the lines of intersection of any three faces of the unit cell which do not lie in same plane.

X, Y, Z → Crystl axis

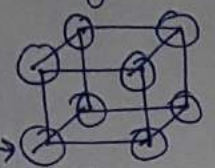


(2) Interfacial Angle – Angles b/w three crystallographic axis shown as α, β, γ.

(3) Primitives – There are 3 sides a, b, c of unit cell along x, y, z axes. Its not ~~nece~~ necessary that all primitives are equal.

Unit Cell → Primitive
Unit Cell → Non-Primitive

Primitive Unit Cell : Lattice density of one point is associated with cell. Or its a type of unit cell which contains lattice points at the corners only & is a minimum volume cell. It fills all space under the action of suitable crystal translation operator.

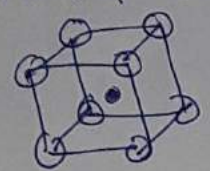


Primitive Basis

No of lattice points in this cell $= 8 \times \frac{1}{8}^{th}$ of each atom

$= 1$ atom / unit cell.

Non-Primitive Unit cell : lattice density of more than 1 point is associated with the cell.



No of lattice points/atoms in this cell $= 8 \times \frac{1}{8}^{th}$ of each atom at corner $+ 1$ (at centre)

$= 1 + 1 = 2$

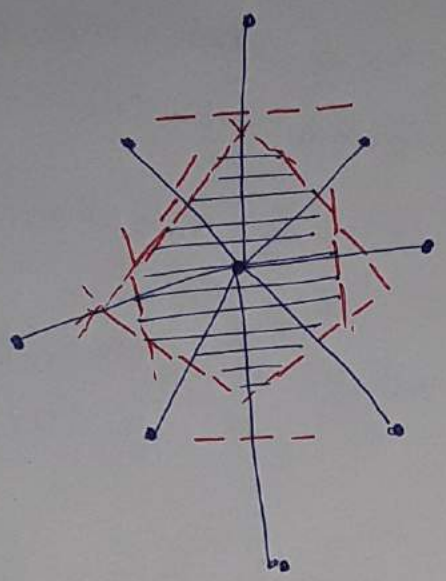
Ex : BCC → Non-primitive unit cell
→ ~~Its another~~ But it also has a rhombohedral symmetry structure

★ A primitive cell can also be constructed using the following procedure –

(i) Connect a given lattice point to all the nearby lattice points.

(ii) Draw normals at the mid points of lines connecting the lattice pts.

The smallest volume enclosed by the normals is the reqd. primitive cell. Such a cell is called wigner–Seitz cell



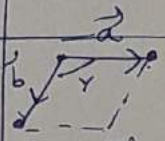
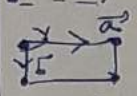
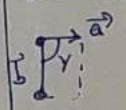
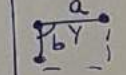
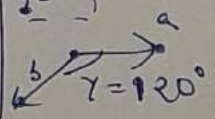
Construction of wigner–seitz primitive cell.

BRAVAIS LATTICE : Its a 3D lattice, A bravais lattice tiles the space without any gaps or holes.

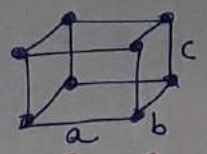
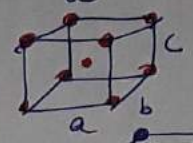
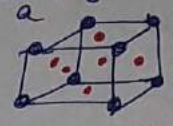
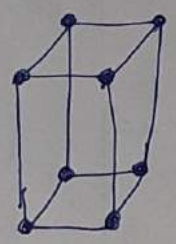
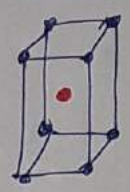
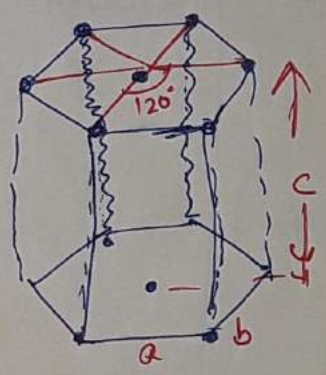
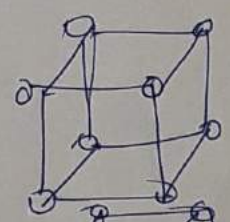
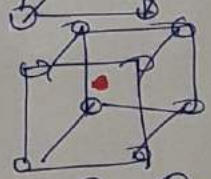
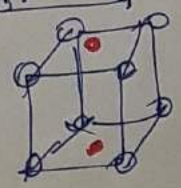
2D → 5 types

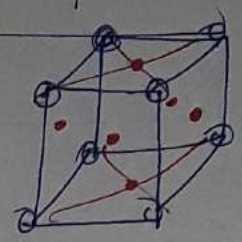
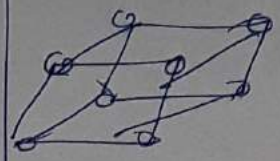
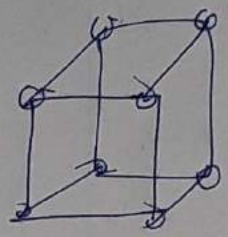
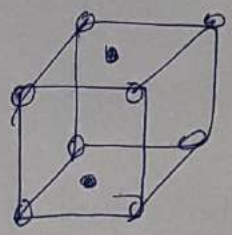
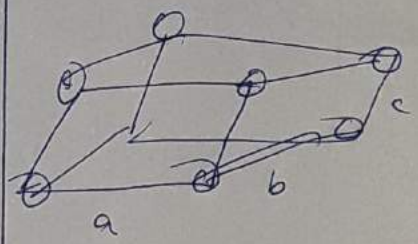
3D → 14 types

2D – Bravais Lattice

S.No	Name	Characteristics	Conventional Unit cell	
1.	Oblique	$\lvert a\rvert \neq \lvert b\rvert$, $\gamma \neq 90^\circ$	||gm	
2.	Rectangular	$\lvert a\rvert \neq \lvert b\rvert$, $\gamma = 90^\circ$, $a > b$	Rectangle.	
3.	Centred Rectangular	$\lvert a\rvert \neq \lvert b\rvert$, $\gamma = 90^\circ$, $a < b$	Rectangle	
4.	Square	$\lvert a\rvert = \lvert b\rvert$, $\gamma = 90^\circ$	Square	
5.	Hexagonal	$\lvert a\rvert = \lvert b\rvert$, $\gamma = 120^\circ$	60° Rhombus	

3D—Brayais lattice

S.NO	NAME of lattice	Lattice Parameters	Figure
	Cubic → SC, FCC, BCC		
1.	Simple Cubic	$a=b=c$, $\alpha=\beta=\gamma=90^\circ$	
2.	Body Centered Cubic	$a=b=c$, $\alpha=\beta=\gamma=90^\circ$	
3.	Face centered Cubic	$a=b=c$, $\alpha=\beta=\gamma=90^\circ$	
	Tetragonal → Simple, Body Centered		
4.	Simple Tetragonal	$a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$	
5.	Body Centered Tetragonal	$a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$	
6.	Hexagonal	$a=b\neq c$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$	
	Orthorhombic → Simple, BCC, Base centered, Face centered		
7.	Simple orthorhombic	$a\neq b\neq c$, $\alpha=\beta=\gamma=90^\circ$	
8.	Body Centered orthorhombic	$a\neq b\neq c$, $\alpha=\beta=\gamma=90^\circ$	
9.	Base centered orthorhombic	$a\neq b\neq c$, $\alpha=\beta=\gamma=90^\circ$	

S.No	Name of lattice	Lattice Parameters	Figure
10.	Face Centered orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$	
11.	Rhombohedral	$a = b = c$ $(\alpha = \beta = \gamma \neq 90^\circ) < 120^\circ$	
	Monoclinic Simple, Base Centered		
12.	Simple Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	
13.	Base-centered Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	
14.	TRICLINIC	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	

Symmetry & Symmetry Elements

Symmetry operation → It transforms the crystals to itself i.e. a crystal remains invariant under a symmetry operation.

These operations are —

Translations, Rotations, Reflection, Inversion (only applicable to 3D crystal)

Translations → Apply to lattice.

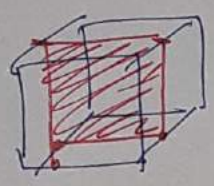
Rotations, Reflection, Inversion → Applies to all objects & are collectively known as point symmetry operations.

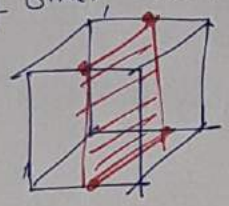
Symmetry element : The geometrical locus about which a group of finite operations act is known as "symmetry element".

- Plane of sym.
- Axis of sym.
- Centre of sym.

Plane of sym.

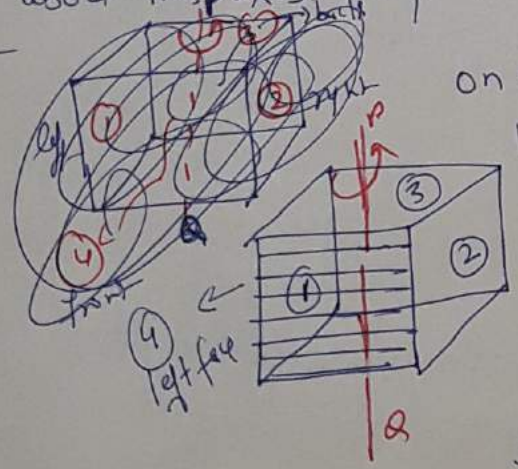
If a crystal is divided by an imaginary plane into two halves, such that one is mirror image of other, then such a plane is plane of symmetry





Axis of sym.

This is an axis passing through crystal such that if crystal is rotated about this axis, crystal remains invariant.



On rotation by $\pi/2$, 4th face comes to front at 1's position. But we can't distinguish b/w new & old position. Thus each rotation of $\pi/2$ bring cube into self-coincidence or congruent position

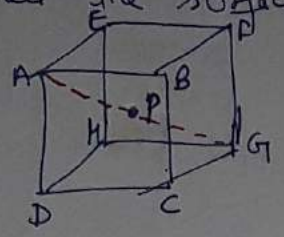
Hence PQ is axis of symmetry

Its $\frac{360^\circ}{\pi/2} = \frac{360^\circ}{4}$ → 4 fold axis of symmetry

4 congruent positions in a complete 360° rotation

centre of symtry

It's a point in crystal such that any line passing through it will meet the surface of crystal at equal distances on either side



$AP = PG$

$P \rightarrow$ centre of sym.

Symtry operations

(1) Translations

It follows from orderly arrangement of a lattice. It means that a lattice point $\vec{r}$, under lattice translation vector operation $\vec{T}$, gives $\vec{r}'$ exactly identical to $\vec{r}$

$$\vec{r}' = \vec{r} + \vec{T} \qquad \text{where } \vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

(2) Rotations

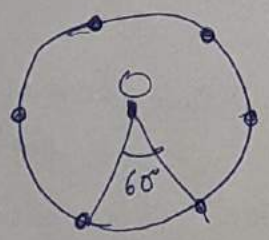
A lattice is said to possess rotation symmetry if its rotation by an angle θ about an axis transforms lattice to itself.

$n\theta = 2\pi$

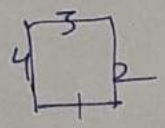
$\theta = 2\pi/n$ $\qquad n \rightarrow$ multiplicity of rotation axis

Ex $\Rightarrow n = 6 \Rightarrow \theta = \frac{2 \times \pi}{6} = \pi/3 = 60^\circ$

$\Rightarrow$ lattice repeats itself with a min. rotation of 60°.



$n \rightarrow$ n-fold rotation

Ex $\Rightarrow$ 2D-square lattice  $\Rightarrow$ 4-fold rotation symtry.

* A rotation axis may/may not pass through a lattice point

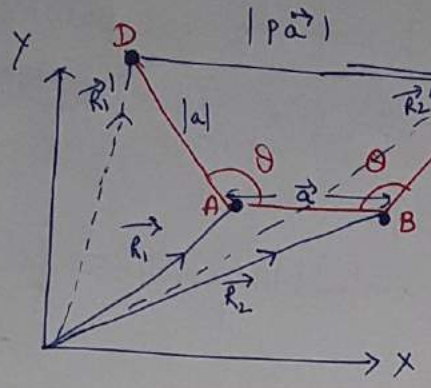
$n=1 \longrightarrow$ crystal should be rotated through 360° to achieve congruency. Such an axis is also called identity axis

(17)

$n=2 \rightarrow \theta = 180°$, two rotations, 2-fold symmetry.
Such an axis is called diad - axis
Represented as ⬭

$n=3 \rightarrow \theta = 120° \longrightarrow$ 3-fold $\rightarrow$ △
$n=4 \rightarrow \theta = 90° \longrightarrow$ 4-fold $\rightarrow$ □
$n=6 \rightarrow \theta = 60° \longrightarrow$ 6-fold $\rightarrow$ ⬡

Suppose $\vec{r}$ point is rotation axis. Then to satisfy translation symmetry $\vec{r}+\vec{T}=\vec{r}'$ should also be rotation axis. But for five fold its not right. Certain rotations are not compatible with translation operation.



Suppose $\vec{R}_1$ and $\vec{R}_2$ are two vectors drawn to two closest lattice points.

Let these points are in the direction of primitive translation vector $\vec{a}$

$|\vec{a}| = |\vec{R}_1 - \vec{R}_2|$ = Min separation b/w lattice points

Assume that a line ⊥ to page & passing through the lattice point defined by $\vec{R}_1$ is n-fold axis of rotation.

As all lattice points are equivalent, there must also be a similar axis through tip of $\vec{R}_2$.

let $\theta = 2\pi/n$.

AB → Rotated Anti-clockwise ⇒ AD (through angle θ)

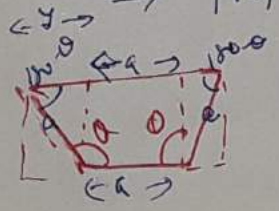
AB → Rotated clock-wise ⇒ BC (clockwise through θ)

D → New lattice point at $\vec{R}_1'$

C → " " " " $\vec{R}_2'$

$\Rightarrow |\vec{R}_1' - \vec{R}_2'|$ should also be a lattice vector

$\Rightarrow |\vec{R}_1' - \vec{R}_2'| = |pa|$ where p is integer



$$\boxed{\cos(180-\theta) = \frac{y}{a} \Rightarrow y = a\cos(180-\theta)}$$

$$\Rightarrow |pa| = a + 2\times a\cos(180-\theta)$$

$$|Pa| = a + 2a\cos(180-\theta) = a + 2a(-\cos\theta)$$

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

$$|\cos\theta| = \left|\frac{1-P}{2}\right|$$

Above eqn can be satisfied only for $|\cos\theta| \leq 1$

i.e. for $P = 3, 2, 1, 0, -1 \; ---$

$$\theta = \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}, \frac{2\pi}{1}$$

or $n = 1, 2, 3, 4, 6, \; --$

Hence only 1, 2, 3, 4, 6, - fold axis of rotation are possible

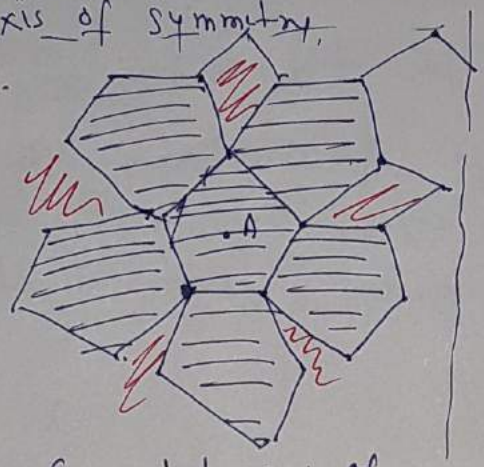
Above eqn is not satisfied for $n=5$ or 5-fold rotatn axis ~~symmetry~~

$n=7$

or 7-fold does not exist

Result $\longrightarrow$ Translational symmetry is not compatible with 5-fold axis of symmetry.

Ex:



Array has 5-fold symtry about point A, but there exists no set of vectors that satisfies translation operation & thus array can't be classified as a lattice.

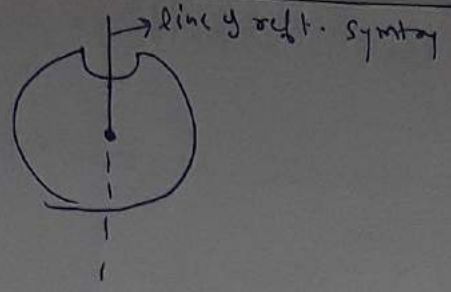
Connected array of pentagons does not fill all the space.

(3) Reflections:

A body is said to possess reflection symmetry if a plane can be drawn in the body dividing it into two exactly similar parts, so that half is reflection of other half.

Plane/line which divides the body is denoted by m

Ex



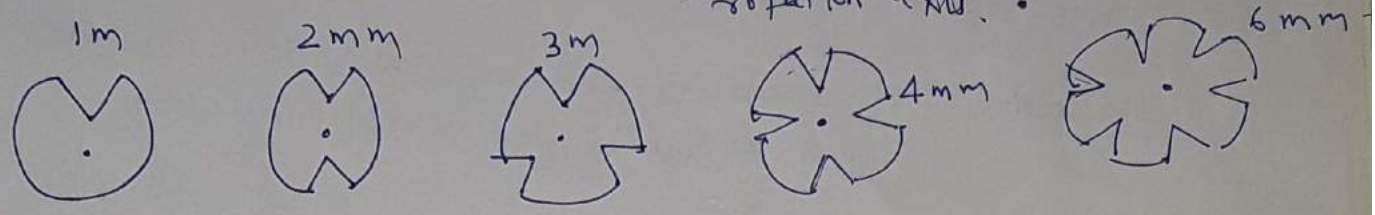
Now consider, combinations of reflections with allowed rotations.
Each allowed rotation axis can be associated with two possibilities

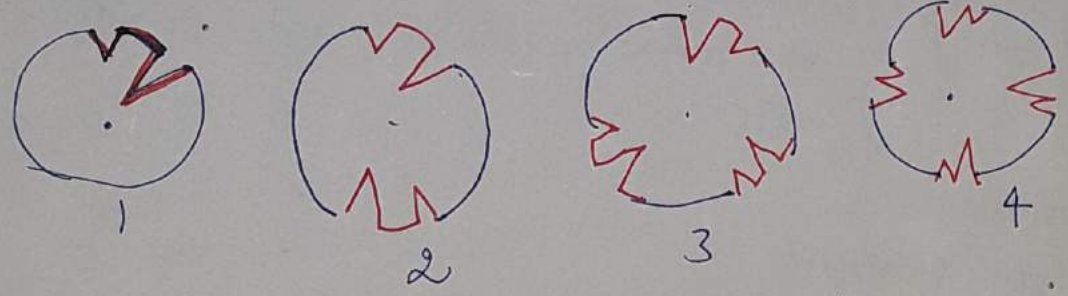
- Rotation with reflection
- Rotation without reflection.

There are 5 - allowed rotation axis
⇓ Possible combinations. 1, 1m, 2, 2mm, 3, 3m, 4, 4mm, 6, 6mm

⇓

1, 2, 3, 4, 6 → rotational symm.
m → plane / line ∥ to rotation axis
second m ⇒ Another plane/line ⊥ to rotation axis.





Above → 10 Groups of sym. operations

(4) Inversions

Its a point operation which is applicable to 3-D lattices only.

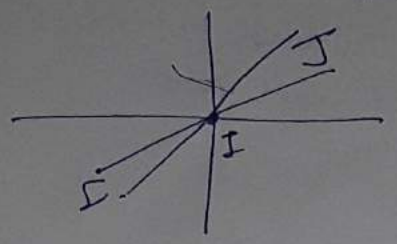
⇒ Each point located at $\vec{r}$ relative to a lattice point has an identical point at $-\vec{r}$ relative to same lattice.

→ $\vec{I}$ is centre of inversion

(4) Inversion is equivalent to reflection through a point called Inversion centre / centre of symmetry.

Enantiomorphous pair of figures in this case is related ~~to~~ by inversion centre lying half way b/w the two.

(20)



Reflectn through centre + symtrically Inverted.

⇒ Inversion centre / centre of symmetry has the property of inverting all space through a point.

(5) Improper Rotation

It is possible to have a rotational operation relating enantiomorphous objects. Such an operation is called improper rotation.

Rotoreflection Rotoinversion

(A) Rotoreflection: If a rotation and reflection are combined to form a ~~hyb~~ single hybrid operation

$\tilde{1}, \tilde{2}, \tilde{3}$ → Tilde symbol is used to distinguish b/w rotation axis only and rotoreflection axis

(B) Rotoinversion

~~Reflection through a point~~

Inversion + Rotation axis

$\bar{1}, \bar{2}, \bar{3}$ → Distinguish b/w proper rotation axis & rotoinversion axis

Q) Find out total no of symmetry elements in a cube.

Ans : (i) 2 → fold axis ∥ to face diagonal, passing through centre of cube. (6 such axis exist)

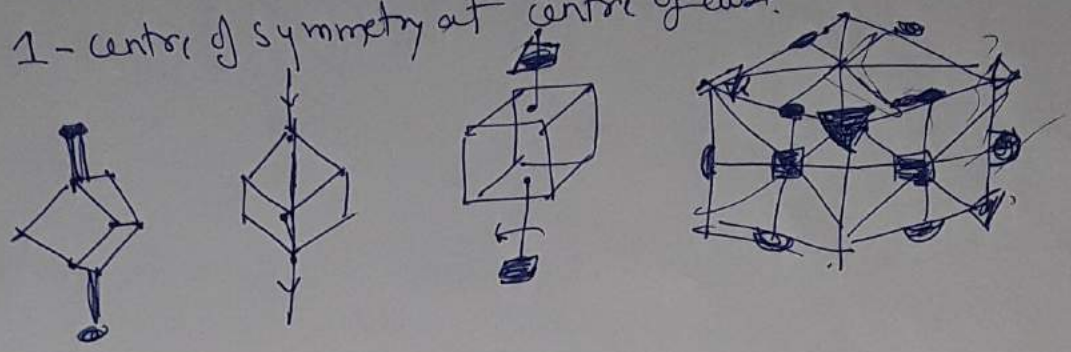
(21)

(ii) 3-fold rotoinversion axis through body diagonal. (4 such axis)

(iii) 4-fold symmetry about an axis through centre of two opposing faces. (3 such axis)

(iv) 9 mirror planes bisecting ∥ faces & connecting diagonal edges. All of them passing through centre of cube

(v) 1-centre of symmetry at centre of cube.



Point Groups & Space Groups

Main 4 types of symmetry operations → Translation
→ Rotation, Reflection, Inversion → Point operation.

The last 3 operations are point operations which collectively & their combinations give certain symmetry elements determine symmetry of space around a point. The group of such symmetry operations at a point is called a "Point group".

In 3-D there are additional point operation, such as inversion. The group of all sym. elements of a crystal is called space group.