Crystal Lattices

"The true test of crystallinity is not the superficial appearance of a large specimen of crystal, but whether on the microscopic scale, the atoms (or ions) are arranged in a periodic array."

References:

1) **Solid State Physics –**
   By N. W. Ashcroft and N. D. Mermin

2) **Crystallography Applied To Solid State Physics –**
   By A. R. Verma and O. N. Srivastava

3) **The Oxford Solid State Basics**
   By Steven H. Simon

Crystal Lattices

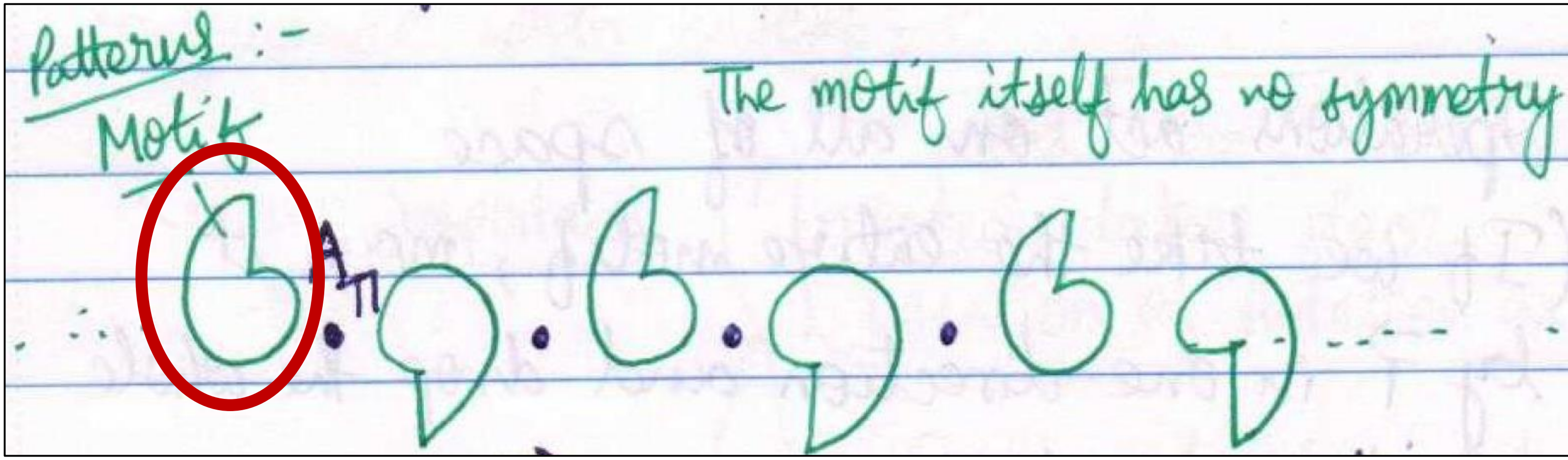
Things to discuss –

- Introduction to Symmetry Operations
- Bravais Lattice & Primitive Vectors
- Coordination number
- Primitive unit-cell & Conventional unit-cell
- Wigner-Seitz cell
- Reciprocal Lattice and Lattice Planes
- X-ray Diffraction and Neutron Diffraction

Symmetry Operations- A Brief Introduction

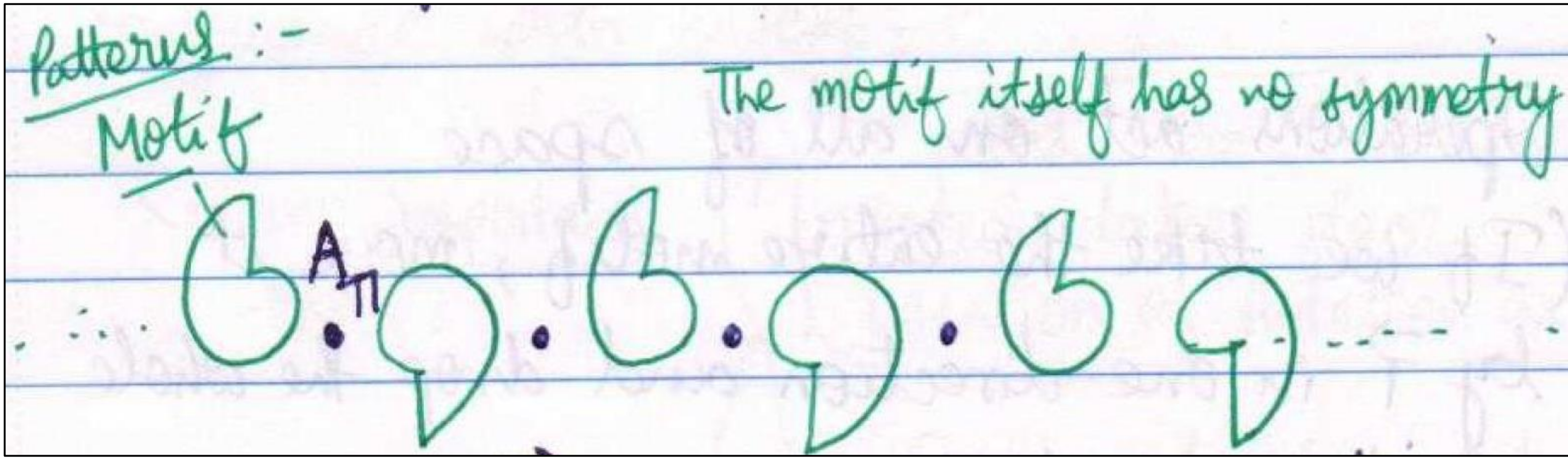
Patterns and their symmetry

1



Patterns and their symmetry

1



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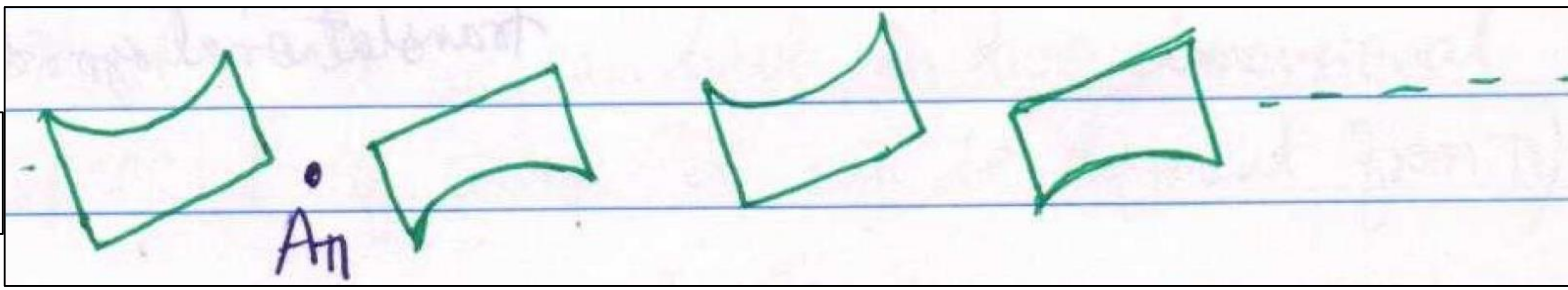

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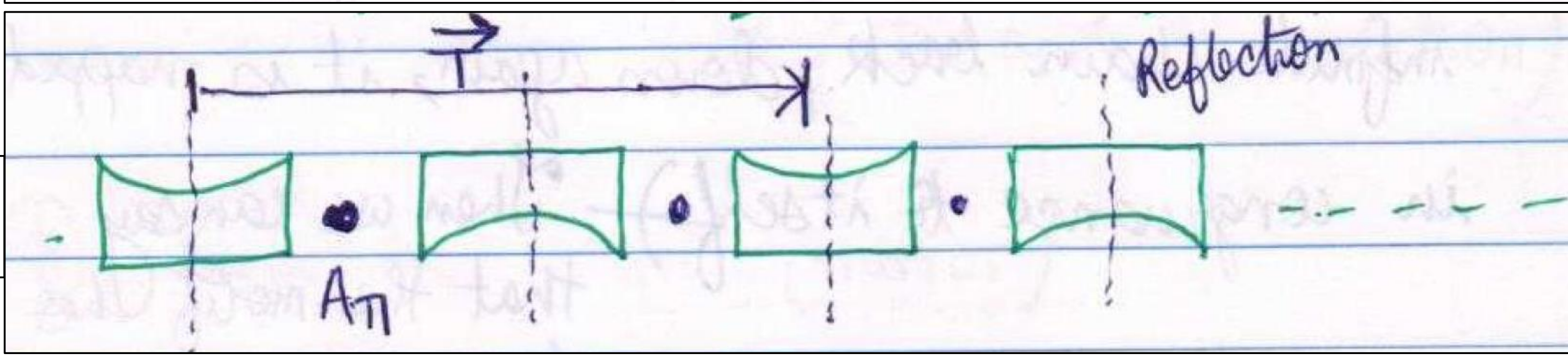
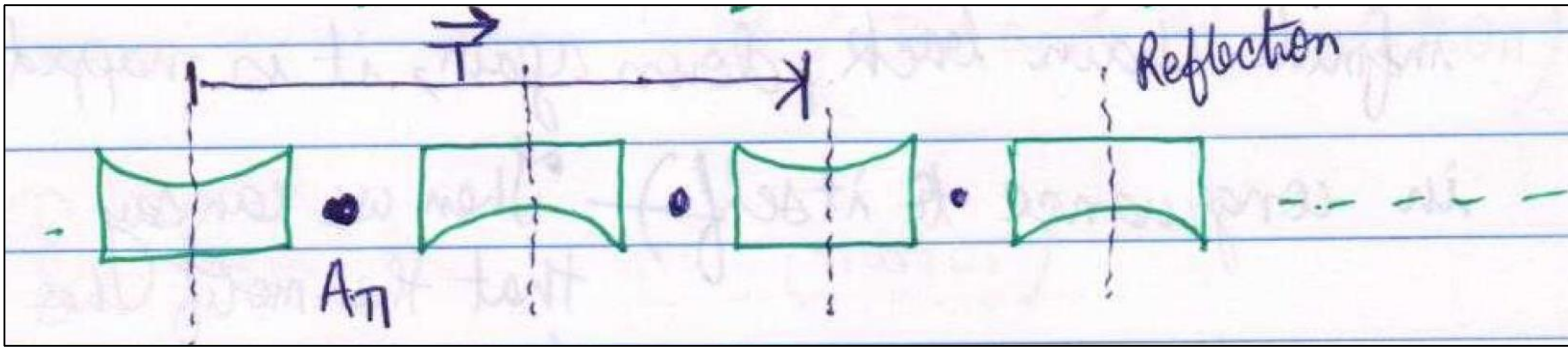


Crystals have Translational Periodicity

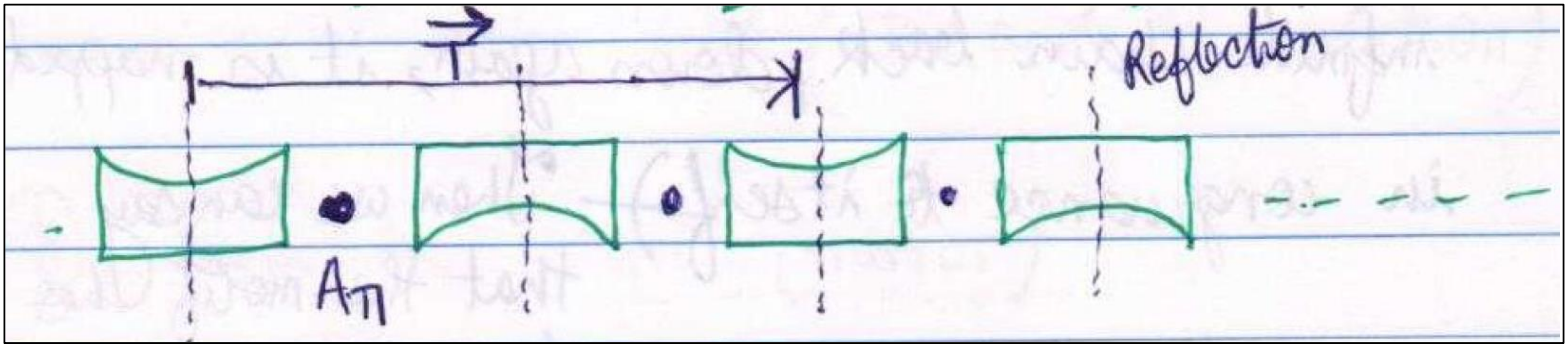
- Translation is a common operation for patterns from 1 to 3
- Translation has magnitude and direction, but no unique origin
- Crystals have translational periodicity

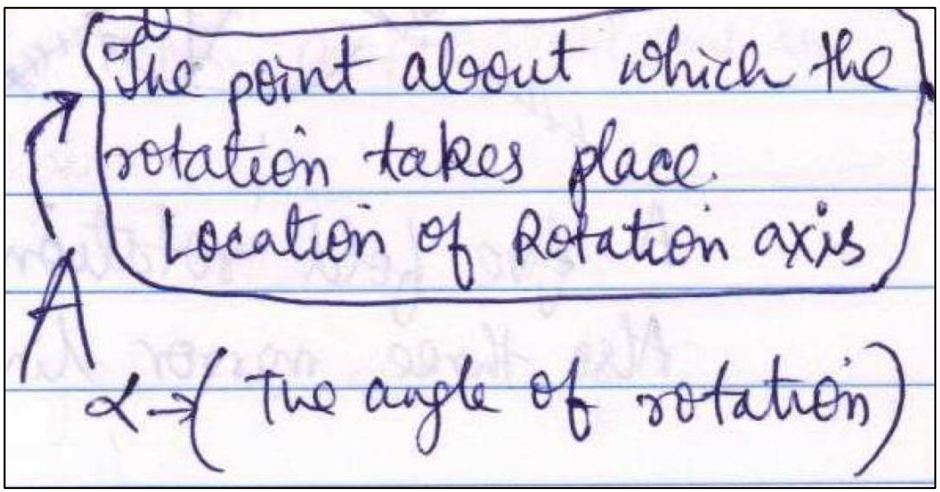


If we take the entire pattern, move it by $\vec{T}$ in one direction and drop the whole infinite chain back down again, it is mapped in congruence with itself ---- Then the pattern will be said to have translation periodicity $\vec{T}$.

Rotational Symmetry

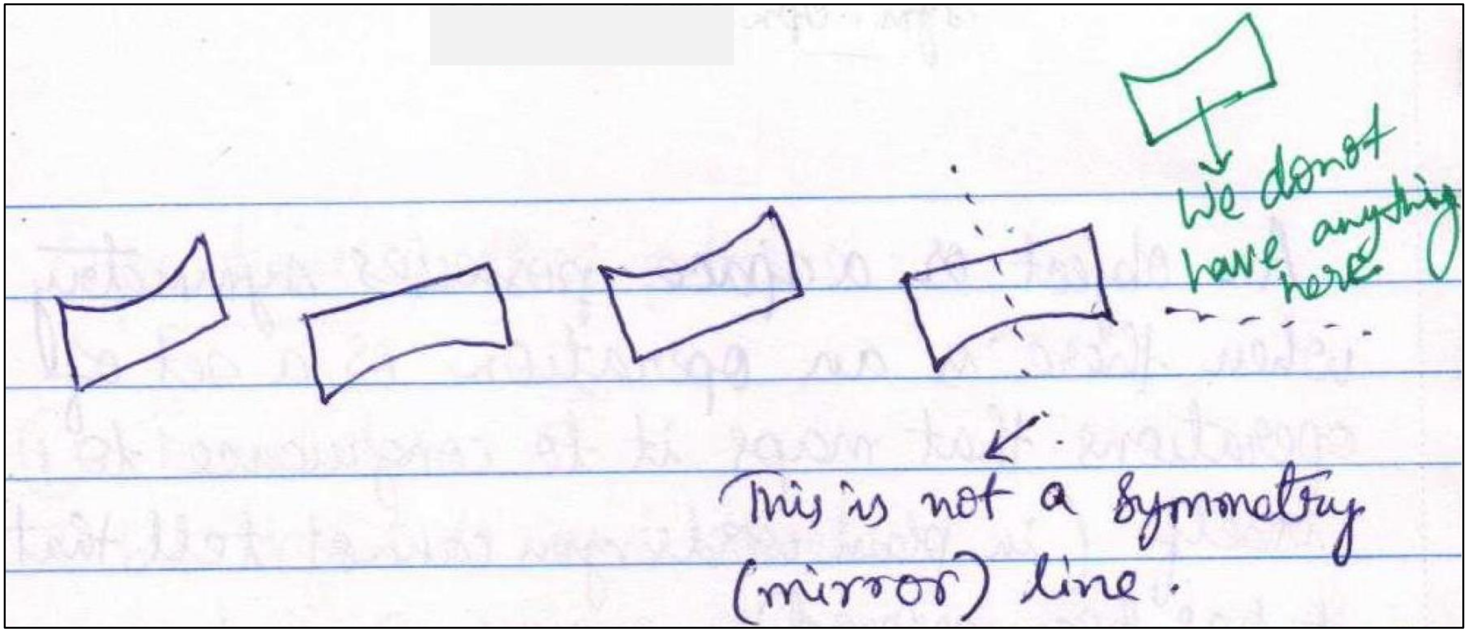
There are loci about which one can rotate one motif into its neighbor or flip the entire chain through 180° and it will be mapped into congruence with itself





Reflection Symmetry

- The entire pattern should have the reflection (mirror) symmetry.
- Symmetry operation is a global operation and not a local operation



- If only the motif has reflection symmetry, however, the pattern lacks it, then reflection is not a symmetry operation for the pattern

In 2D – Single-step Symmetry operations

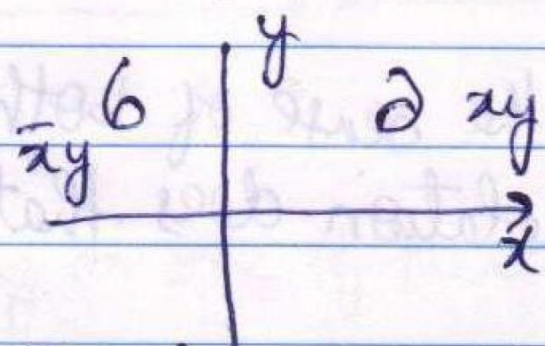
Three possible single-step operations in 2D-

- Translation $\vec{T}$

$$xy \rightarrow x+a,\ y+b \longrightarrow x+2a,\ y+2b$$

- Reflection ***m***

① Reflection



1st reflection

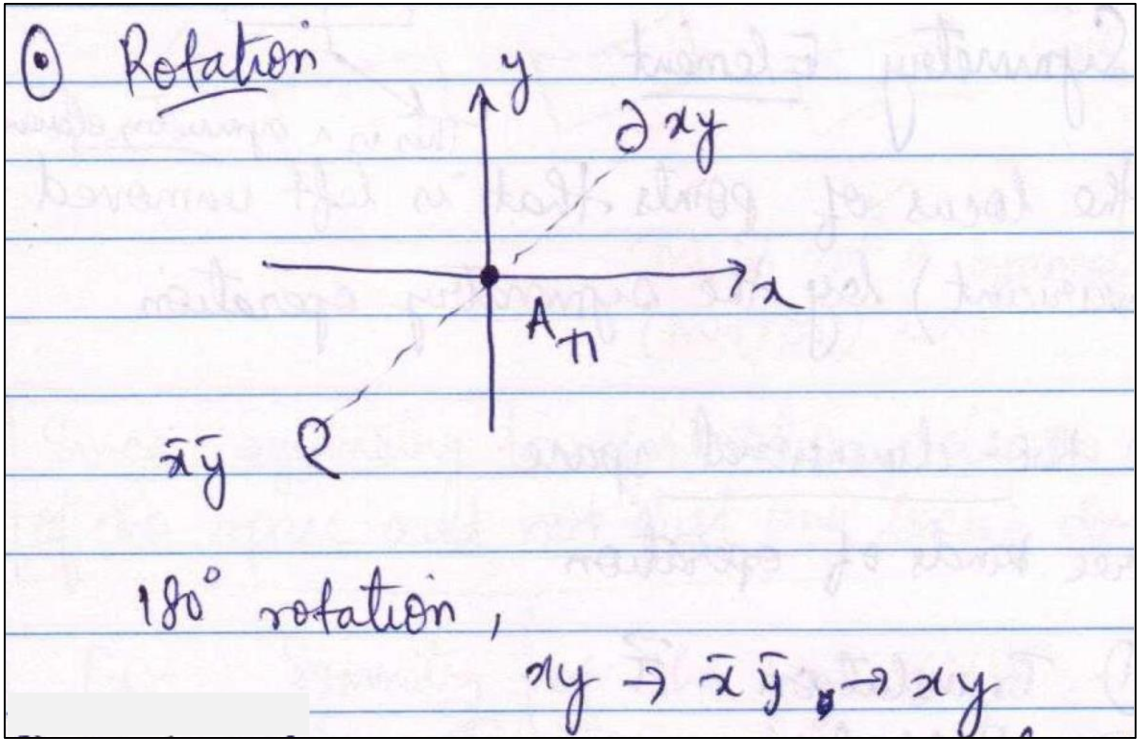
$xy \rightarrow \bar{x}y$ (mirror plane $m \perp x$ and passes through origin)

2nd reflection

$\bar{x}y \rightarrow xy$.

In 2D – Single-step Symmetry operations

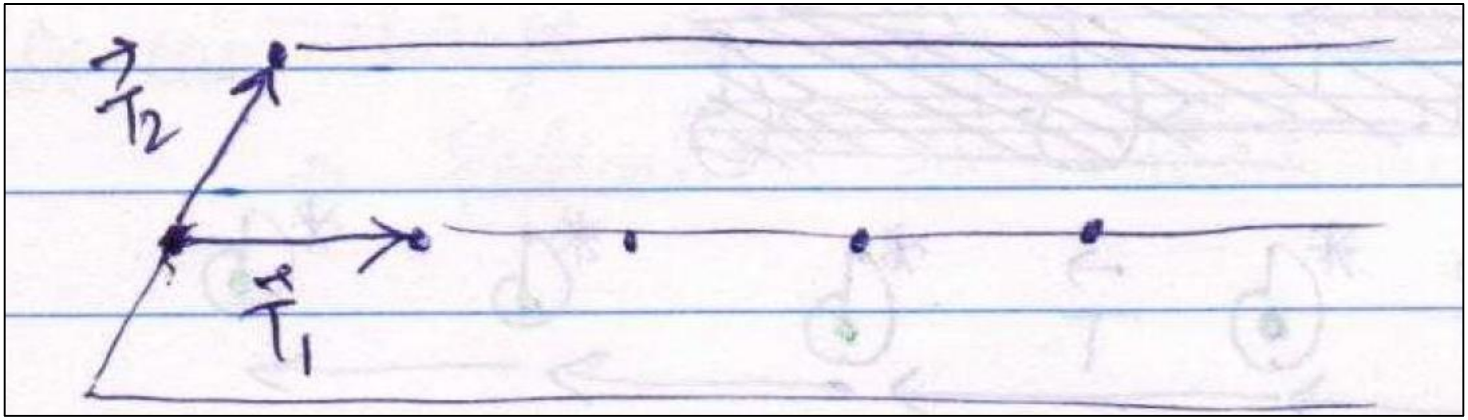
- Rotation



In two-dimensions (two coordinates) –

- We can change the sense of no coordinates – Translation does that
- We can change the sense of one coordinate – Reflection does that
- We can change the sense of both coordinates – Rotation does that

Non-collinear translations



$\overrightarrow{T_1}$ and $\overrightarrow{T_2}$ cannot be parallel, while they are unequal (not integral multiple), otherwise there will be no lattice

$\vec{T}_1, \vec{T}_2 \Rightarrow$ 2D - space lattice

$$n\vec{T}_1 + m\vec{T}_2$$

$$(-\infty \leftarrow n, m \rightarrow \infty)$$

In 3D – One-step symmetry operations

In 3D

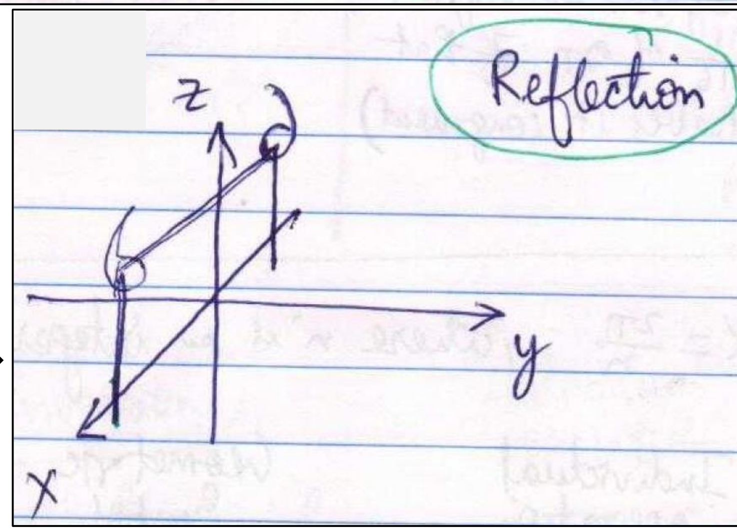
1. Translation

$x\,y\,z \rightarrow x+a,\ y+b,\ z+c \rightarrow x+2a,\ y+2b,\ z+2c$

(Changing the sense of no coordinate ⇒ Translational operator).

Changes the sense of no cordinates

Changes the sense of one coordinate (leaves the coordinates in the plane of the mirror unchanged)



In 3D – One-step symmetry operations- contd.

Changes the sense of two coordinates

Rotation ($\alpha = \frac{2\pi}{n}$, where n is an integer)

Analytic Symbol	Individual operation	Geometric Symbol
n	A_α	n-gon

180° (Two-fold axis)

Three-fold

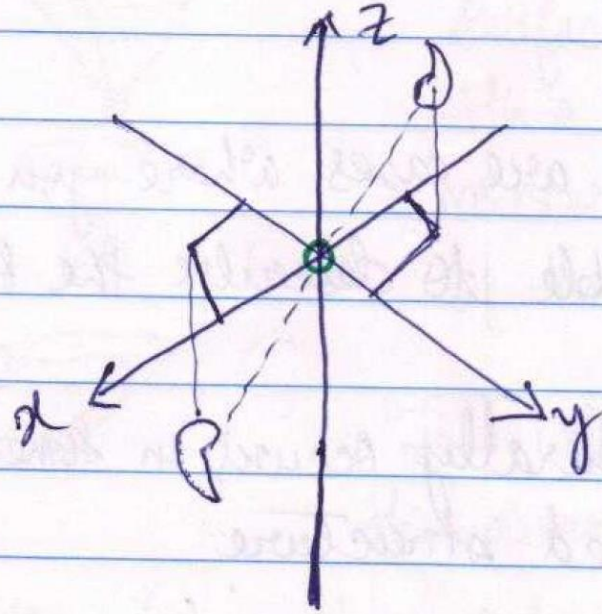
Four fold

Five fold

Six fold

In 3D – One-step symmetry operations- contd.

Changes the sense of all three coordinates



Inversion

$xyz \rightarrow \bar{x}\,\bar{y}\,\bar{z}$

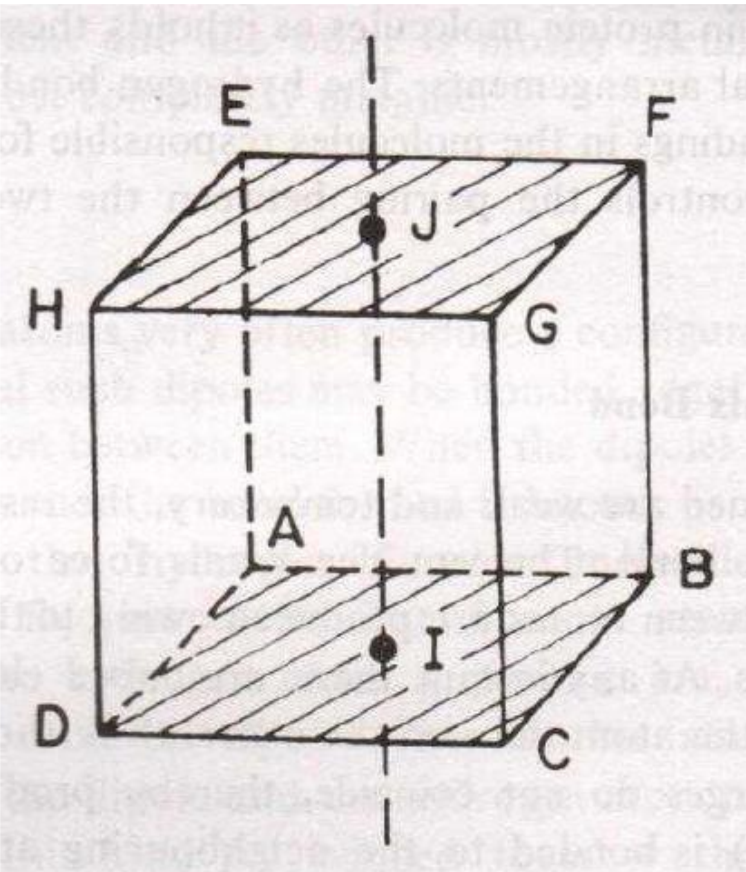
(Bounded the point of inversion is at the center)

Inversion

Analytic symbol	Individual operation	Geometric symbol
$\bar{1}$	$\bar{1}$	o (Tiny open circle)

Axis of Symmetry

Crystals always exhibit certain symmetries
We know cube is a symmetrical solid. How?



- If we rotate the cube about a vertical line parallel to the intersection edges and passing through center of the horizontal face, in one complete rotation of 360°, we get four positions of the cube coincident with its original position.

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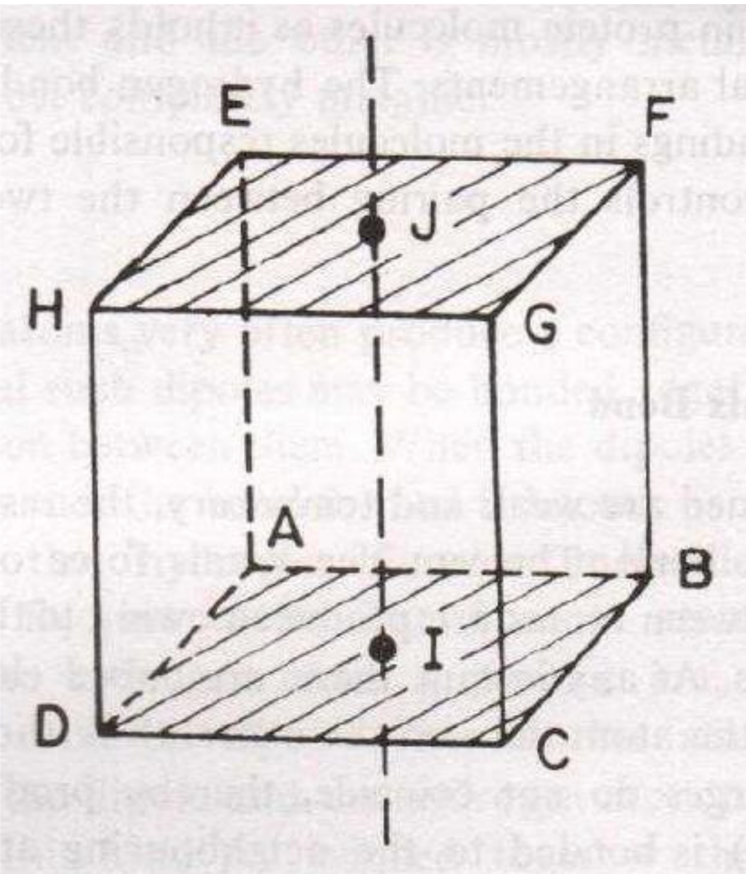

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- Such rotation axis is called axis of symmetry.

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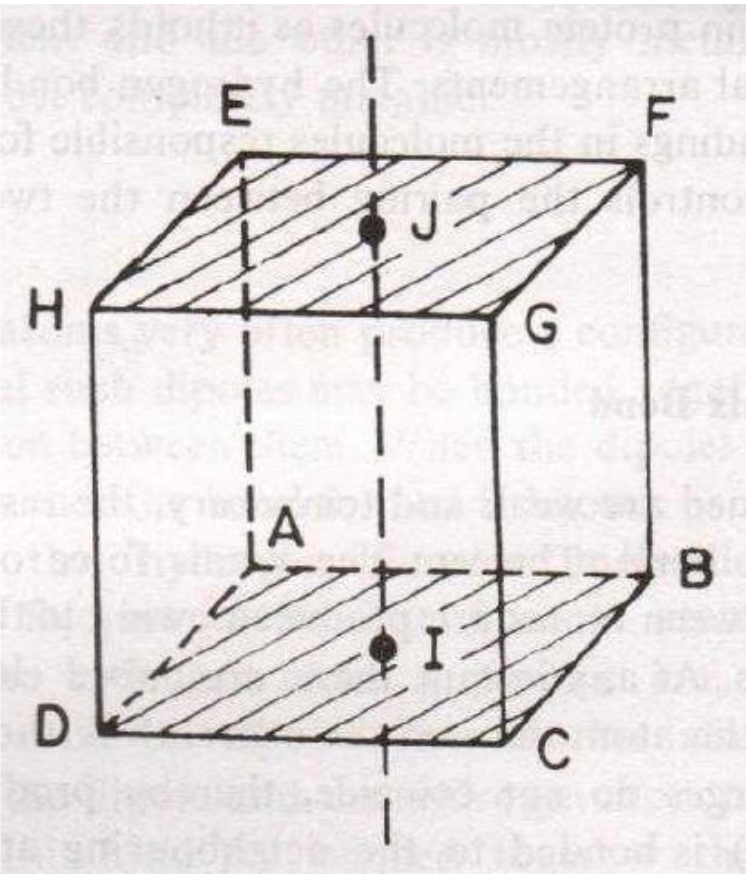


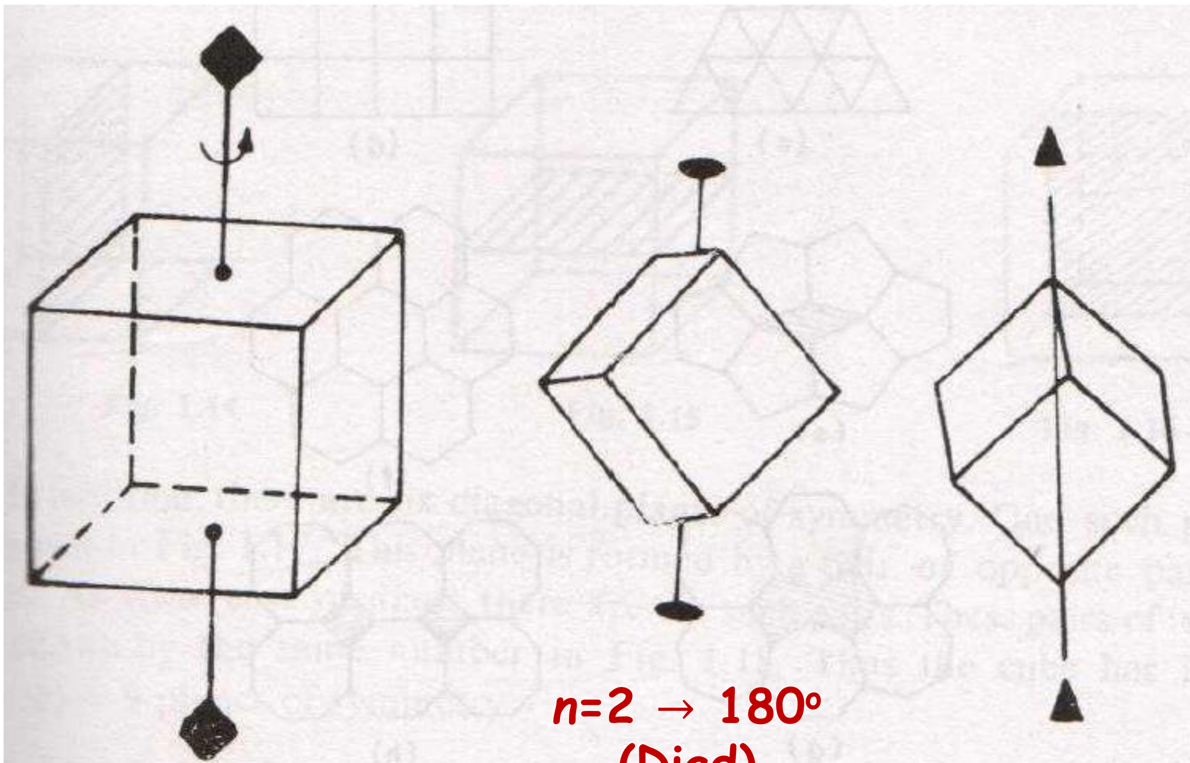
- If we rotate the cube about a vertical line parallel to the intersection edges and passing through center of the horizontal face, in one complete rotation of 360°, we get four positions of the cube coincident with its original position.

- Such rotation axis is called axis of symmetry.

- Since there are four congruent positions in one complete revolution, this is called fourfold axis of symmetry.

Axis of Symmetry

If a rotation through $\frac{2\pi}{n}$ about an axis brings a figure into congruent position, the axis is called an *n*-fold axis of symmetry.

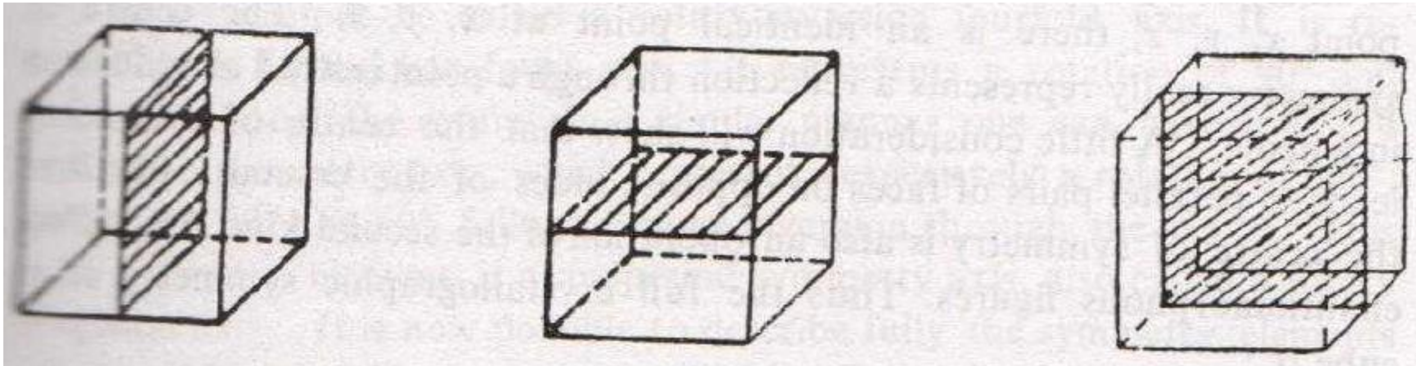


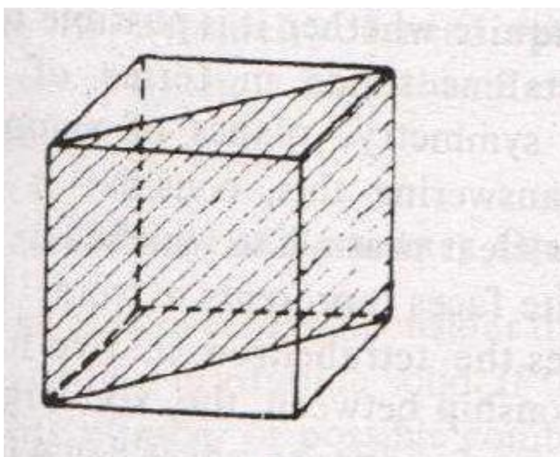
***n*=4 → 90°**
(Diad)

***n*=2 → 180°**
(Diad)

***n*=3 → 120°**
(Triad)

Planes of Symmetry





Symmetry

The full crystallographic symmetry of a cube is

$$\left.\begin{array}{l}3\ \text{tetrads}\\ 4\ \text{triads}\\ 6\ \text{diads}\end{array}\right\}\ 13\ \text{axes},$$

$$\left.\begin{array}{l}3\ \text{planes}\\ 6\ \text{diagonal planes}\end{array}\right\}\ 9\ \text{planes}$$

Centre of symmetry 1

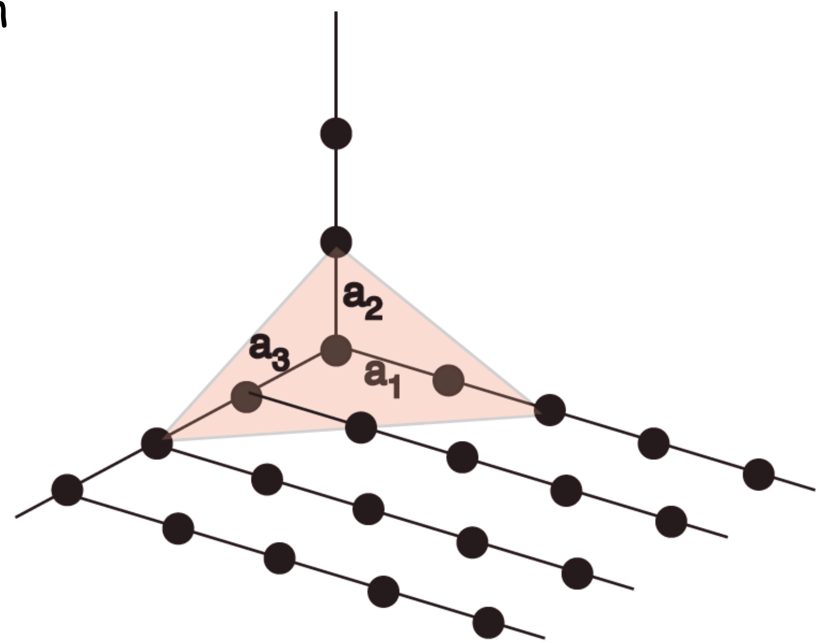
Total: $13+9+1 = 23$ elements of symmetry

Labelling Lattice-Planes

- For a given plane, first its intercepts with the axes in units of lattice vectors need to be determined
  (2 1 2)

- Reciprocal of these numbers are to be taken
  $(\frac{1}{2}, 1, \frac{1}{2})$

- Reduction of numbers to the smallest set of integers having the same ratio. These are called Miller indices
  (1 2 1)

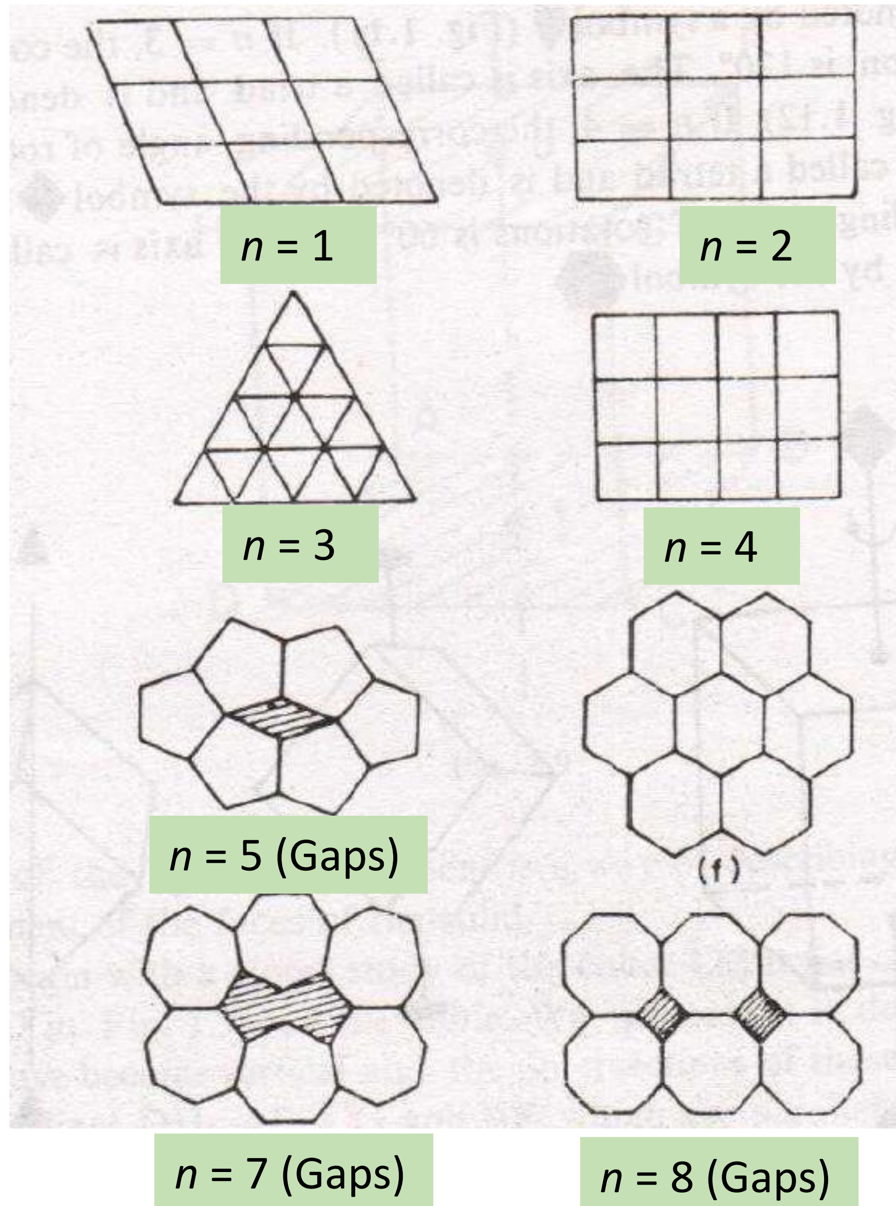


Symmetry

One can construct a solid model (from glass, wood, clay etc.) where *n* can have any values 1, 2, 3, 4, 5, 6, 7, 8 …

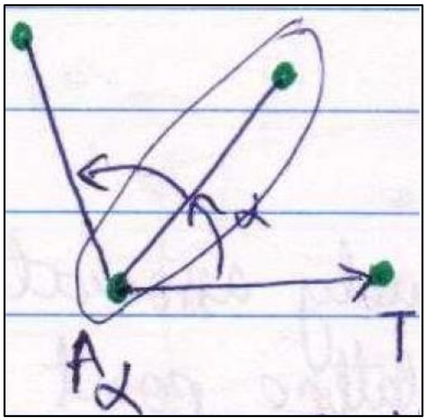
A crystal is not just a solid body but is one in which the internal atomic or molecular arrangement is periodic in three dimensions.

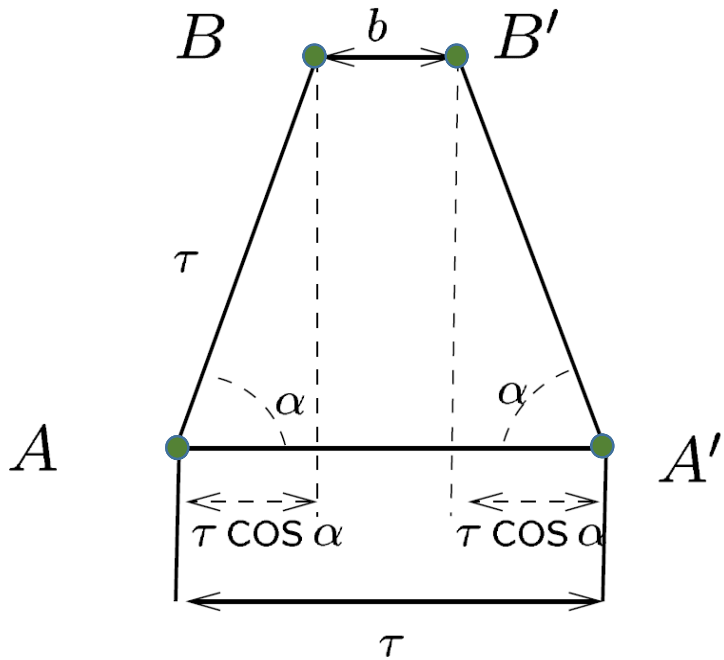
The above puts a constraint on *n* for crystals and we can have only 1, 2, 3, 4 and 6 fold symmetries.



Combination of translation and rotation operations

Start with a translation and add a rotation operation A_α





$$b = \tau - 2\tau\cos\alpha$$

For the lattice to exist in the horizontal direction -

$$m\tau = \tau - 2\tau\cos\alpha$$ m is an integer

Permissible periods of crystallographic axes

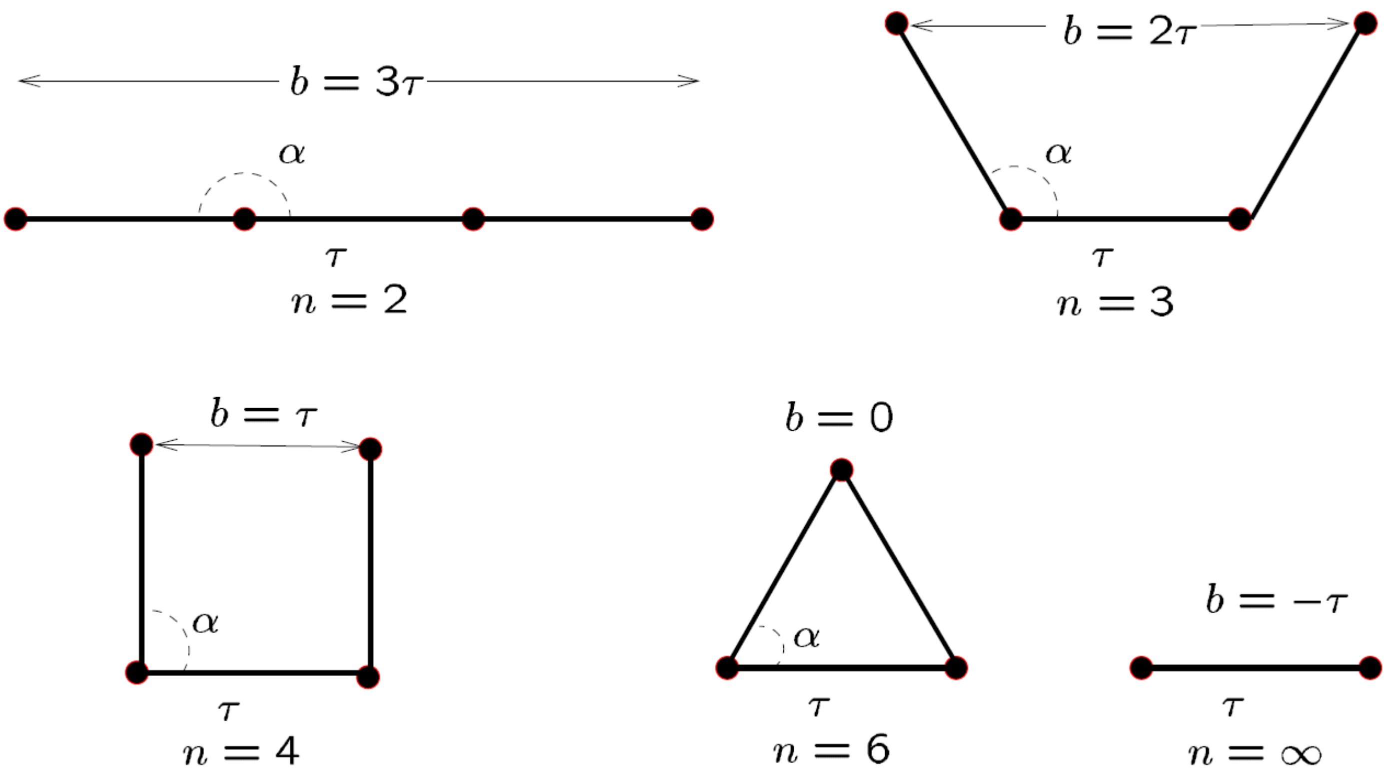
$$m\tau = \tau - 2\tau\cos\alpha$$

$$\mathbf{2\cos\alpha = M}$$

M = 1-*m*, is also an integer

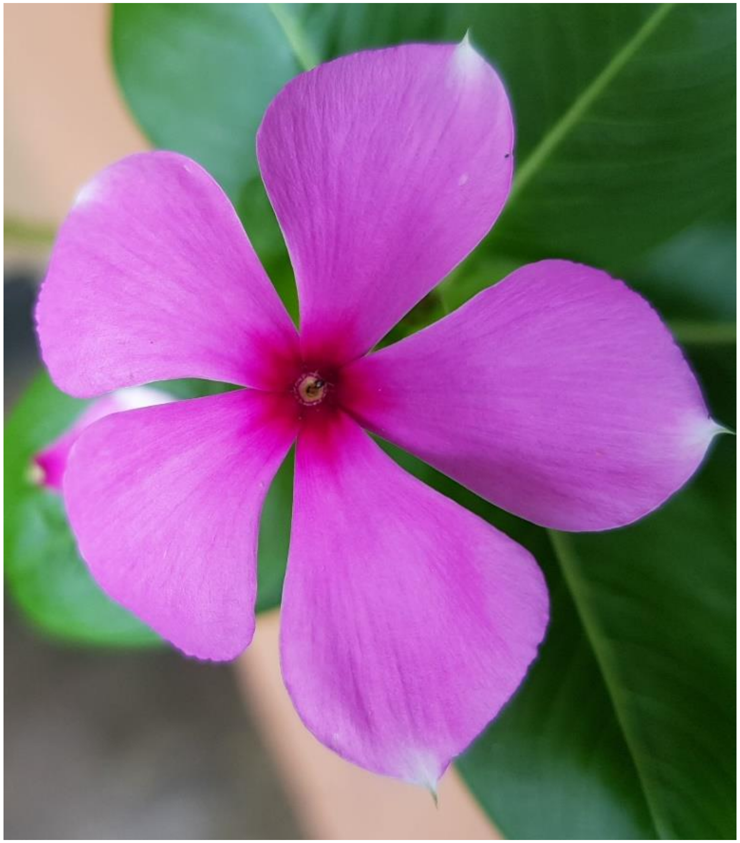
M	$\cos\alpha$	α	$n = 2\pi/\alpha$	$b = \tau - 2\tau\cos\alpha$
-3	-1.5	$-$	$-$	$-$
-2	-1	π	2	3τ
-1	-0.5	$2\pi/3$	3	2τ
0	0	$\pi/2$	4	τ
1	0.5	$\pi/3$	6	0
2	1	0	∞	$-\tau$
3	1.5	$-$	$-$	$-$

Permissible periods of crystallographic axes

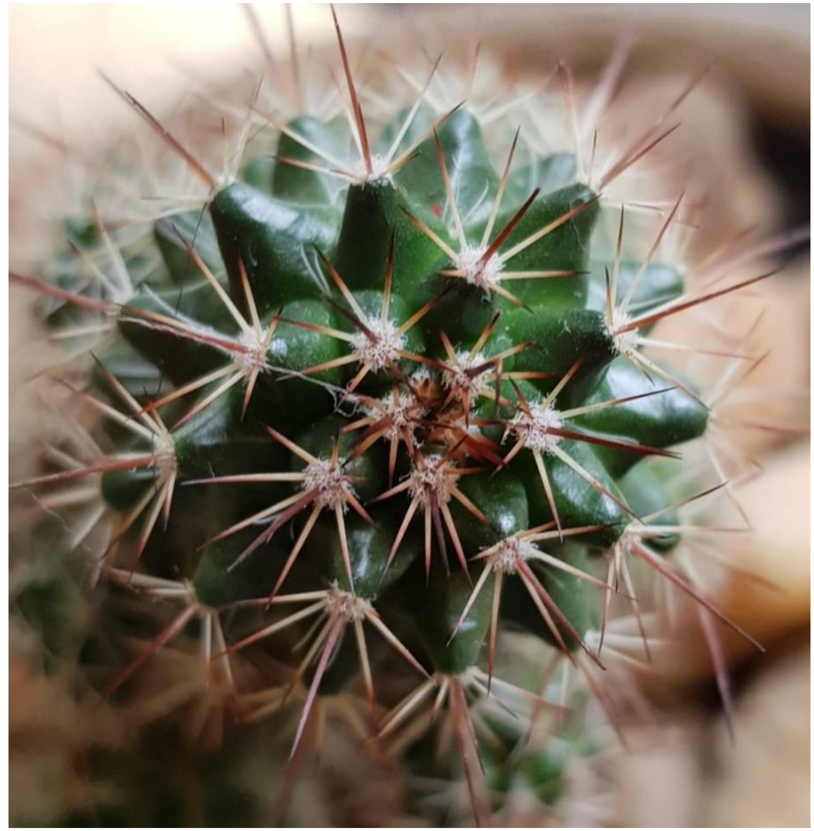


Because of translational repetition, crystals can only have 1-fold, 2-fold, 3-fold, 4-fold and 6-fold rotation axes

Non-crystallographic symmetry in nature



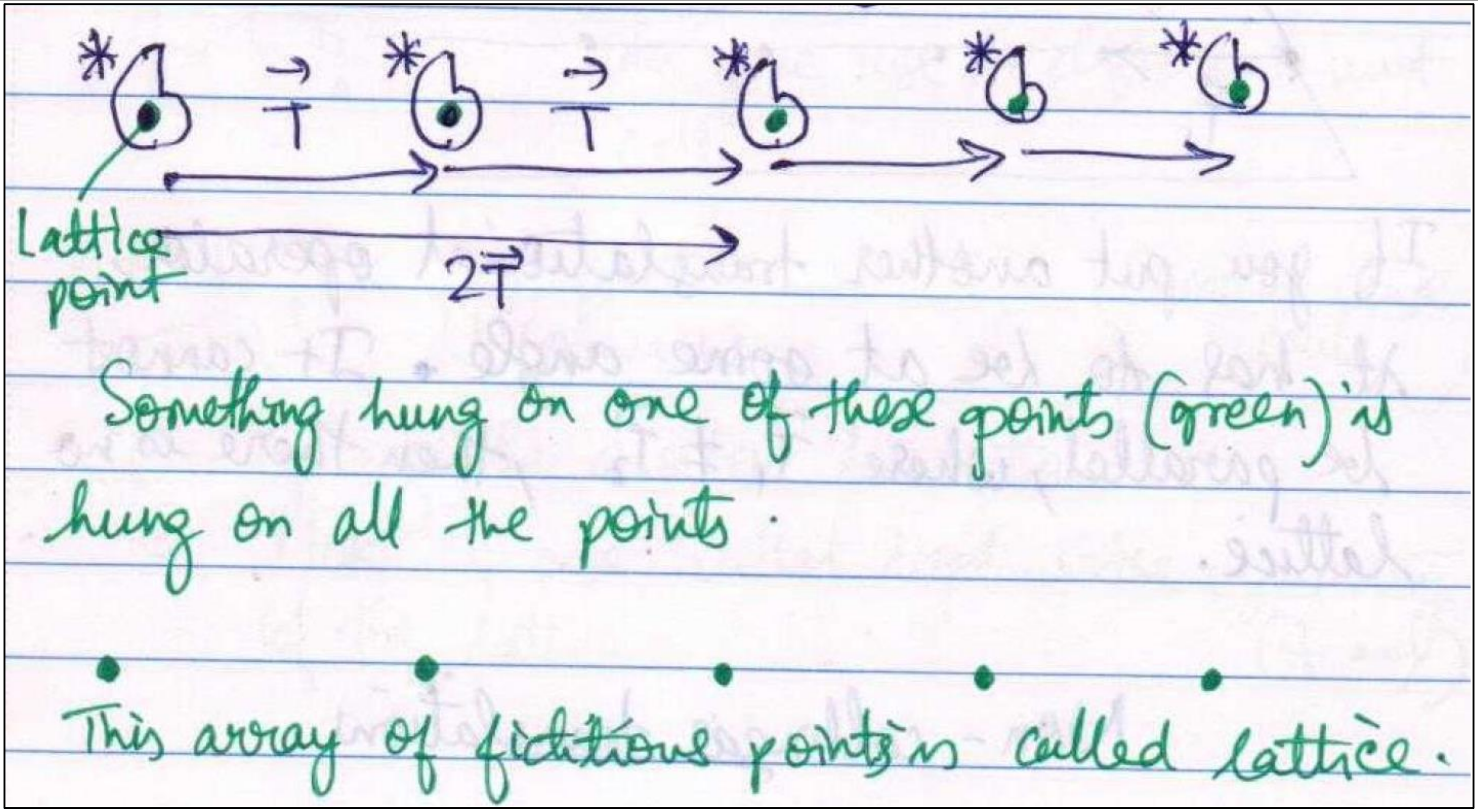
Periwinkle

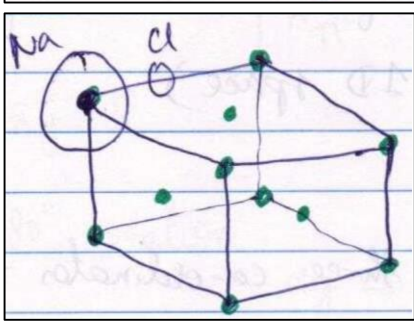


Cactus

Cells inside the above things cannot be translationally invariant

Translational Symmetry - Lattice





A lattice is an array of fictitious points which summarizes the translational symmetry of the lattice

Bravais Lattice

- It specifies the periodic array in which the repeated units (single atom, group of atoms, ions etc.) of the crystal are arranged.

- It summarizes the geometry of the underlying periodic structure.

Two equivalent definitions –

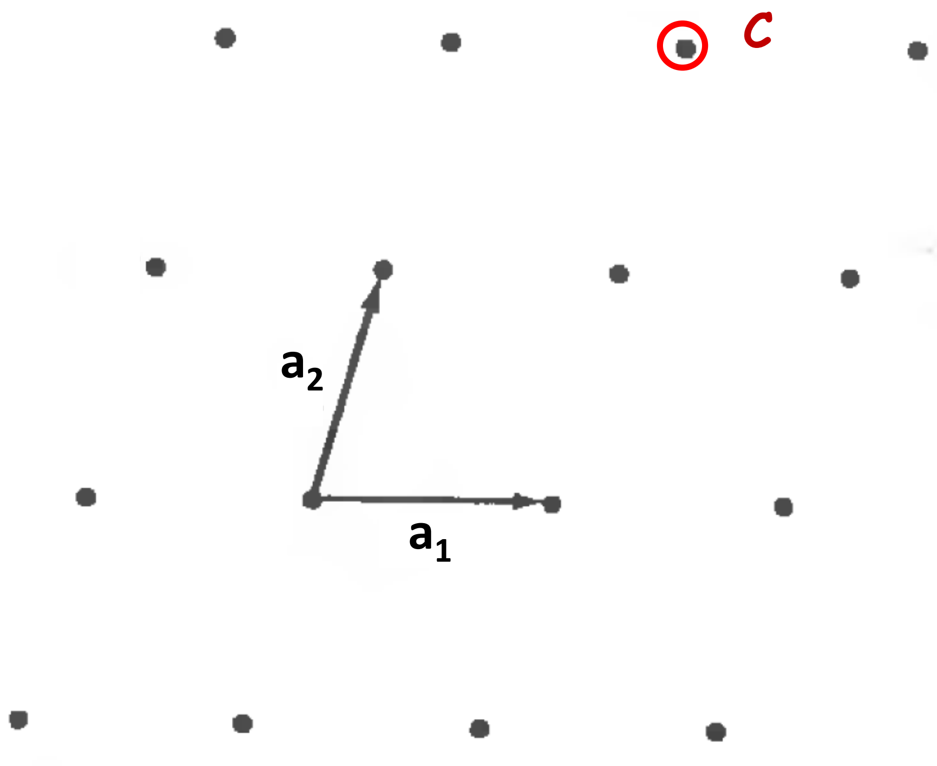
1) A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.

2) A Bravais lattice consists of all points with position vectors ***R*** of the form –

$$\boldsymbol{R} = n_1\,\mathbf{a}_1 + n_2\,\mathbf{a}_2 + n_3\,\mathbf{a}_3$$

Here $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are any three vectors not all in the same plane. These are called **primitive vectors** and they span the lattice.
n_1, n_2 and n_3 are any integers (positive as well as negative)

Bravais Lattice

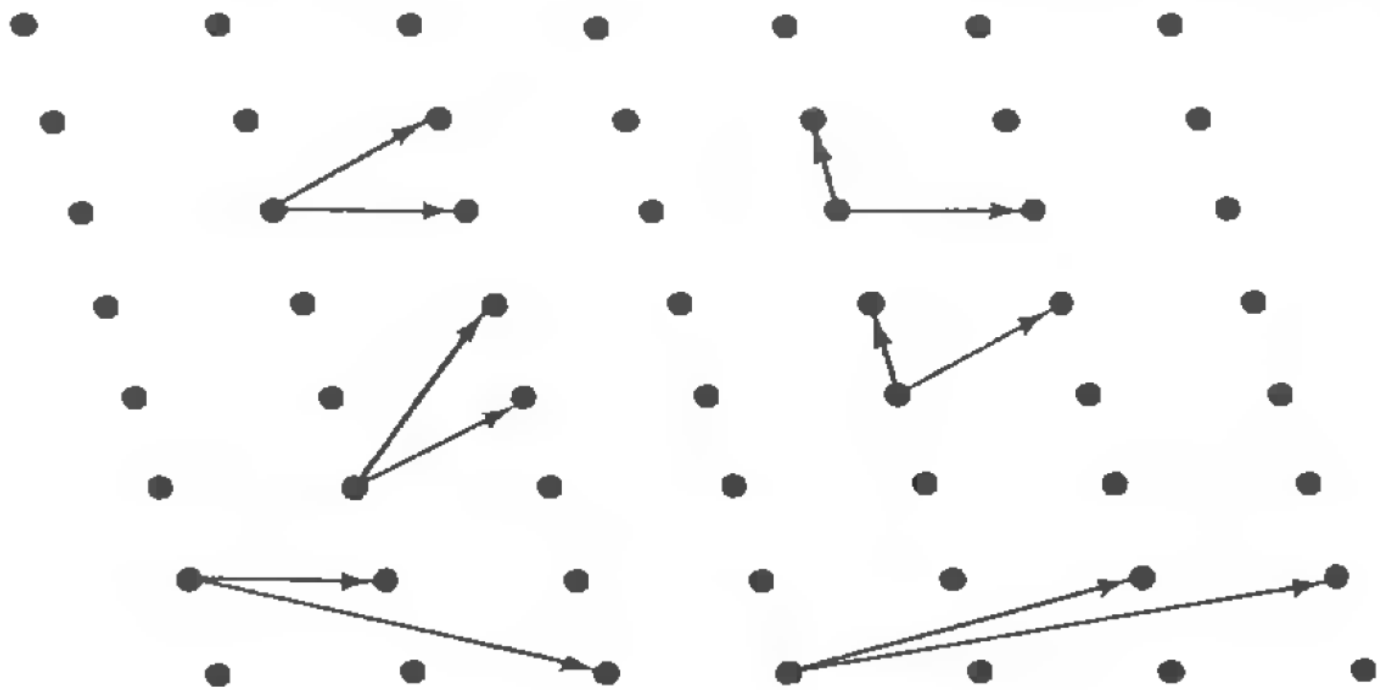


Point C can be reached by $(2a_2 + a_1)$

Similarly any other point on this lattice can be reached with suitable choices for n1 and n2

A general 2D Bravais lattice
$\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive vectors

Bravais Lattice



Primitive vectors are not unique
Several possible choices for $\mathbf{a}_1$ and $\mathbf{a}_2$

Coordination Number

- The points in a Bravais lattice that are closest to a given point are called its nearest neighbours.
- Because of periodic nature of Bravais lattice, each point has the same number of nearest neighbours.
- This number is a property of lattice and called coordination number.
- Coordination number for Simple cubic lattice – 6, Body-centered cubic lattice– 8, Face-centered cubic lattice – 12…
- The notion can be extended to a simple array of points, which are not Bravais lattice.