The Crystal structure

Physical and Chemical Properties of Solids:

- Solids are incompressible, meaning the constituent particle is arranged close to each other, and because of that, there is negligible space between the constituent particles.
- Solids are rigid. This is due to a lack of space between the constituent particles that make it rigid or fixed.
- Solids have definite mass, volume, and shape due to which they have a compact arrangement of constituent particles.

Crystal: The word crystal derives from the Ancient Greek word ‘Krustallos’, meaning both ‘Ice’ and ‘Rock crystal’. A crystal or crystalline solid is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions.

Characteristics of a crystal:

- An ideal crystal is constructed by the infinite repetition of identical structural units in space.
- The structures of all crystals can be described in terms of a **lattice** (A), with a group of atoms (B) attached to every lattice point (**Basis**).
- The scientific study of crystals and crystal formation is known as crystallography
- The process of crystal formation via mechanisms of crystal growth is called “**crystallization**” or “**solidification**”.
- The scientific definition of ‘**crystal**’ is based on the microscopic arrangement of atoms inside it called the “**crystal structure,**” i.e., A crystal is a solid where the atoms form a periodic arrangement.
- Not all solids are crystals.

Crystals:

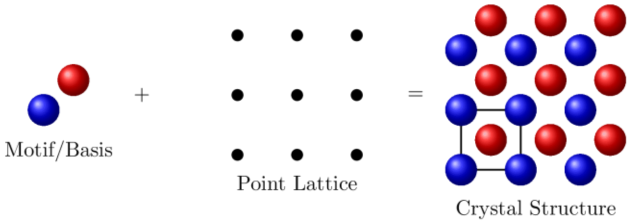
A. A simple lattice
B. Basis is the atoms
C. Crystal = Lattice + Basis

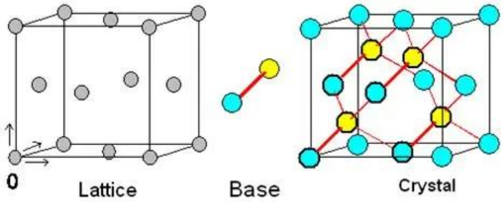
Lattice point: A lattice point is a single point in the lattice. It represents the position where an atom, ion, or group of atoms can be placed**.** There are many choices of lattice points.

Lattice: A regular and periodic arrangement of points is called a lattice. It gives the basic geometrical structure of a crystal. If you move from one lattice point to another with a translation vector, the environment looks the same.

Basis: The group of atoms is called the basis, and when repeated in space, it forms the crystal structure. A basis of atoms is attached to every lattice point.

Crystals: A crystal is a solid in which atoms, ions, or molecules are arranged in a regular, repeating, and orderly pattern throughout the entire material. Lattice + Basis = Crystal

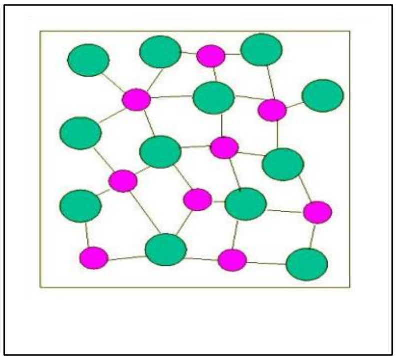




Classification of materials:

There are three different categories of crystal or crystalline solid (materials-solid), such as:

i. Amorphous state/solid
ii. Crystalline state/solid
iii. Polycrystalline state



Amorphous state/solid:

“A third category of solids is amorphous solids/materials, where atoms have no periodic arrangement even microscopically”.

Properties of Amorphous Solids:

1. Amorphous solids are gradually softened over a range of temperatures, and they can be molded into different shapes on heating.
2. Amorphous solids are pseudo-solids or super-cooled liquids, which means they tend to flow very slowly. If you observe that the glass pans, which are fixed to the windows of old buildings, are found to be slightly thicker at the bottom than at the top.
3. Amorphous solids have irregular shapes, i.e., their constituent particles do not have a definite geometry of arrangement.

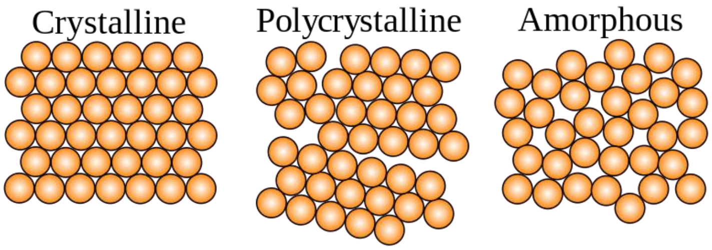
Properties of Amorphous Solids:

- When amorphous solids are cut with a sharp-edged tool, they form pieces with irregular surfaces.
- Amorphous solids do not have a definite heat of fusion due to their irregular arrangement of the particles.
- Amorphous solids are isotropic in nature, which means the value of any physical property would be the same along any direction because of the irregular arrangement of particles.

Amorphous Solids Uses:

Amorphous silicon, which is one of the best photovoltaic materials, converts sunlight into electricity.

Examples: Glass, Wax, Plastics, etc.



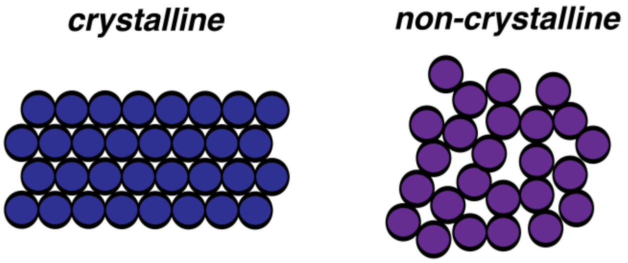
Crystalline state/solid:

“Microscopically, a crystalline (single crystal) has atoms in a near-perfect periodic arrangement.

Properties of Crystalline Solids

- ➢ Crystalline solids have a sharp melting point and begin to melt when they reach a specific temperature.

- The shape of crystalline solids is definite and has typical arrangements of particles.



They show cleavage property, i.e., when they are cut with the edge of a sharp tool, they split into two pieces and the newly generated surfaces are smooth and plain

Properties of Crystalline Solids

- They have definite heat of fusion (amount of energy needed to melt a given mass of solid at its melting point).
- Crystalline solids are anisotropic, which means their physical properties, like electrical resistance or refractive index, show different values when they are measured along different directions in the same crystal.
- Crystalline solids are true solids.

Examples: Examples of large crystals include Snowflakes, Diamonds, Table salt, etc.

Types of Crystalline Solids:

Based on the nature of intermolecular forces or chemical bonding, crystalline solids are further classified into four categories. They are,

i. Molecular Solids
ii. Ionic solids
iii. Metallic solids
iv. Covalent solids

Polycrystalline state:

A polycrystalline material is composed of many microscopic crystals (called **crystallites or Grains**). Most inorganic solids are not crystals but polycrystals.

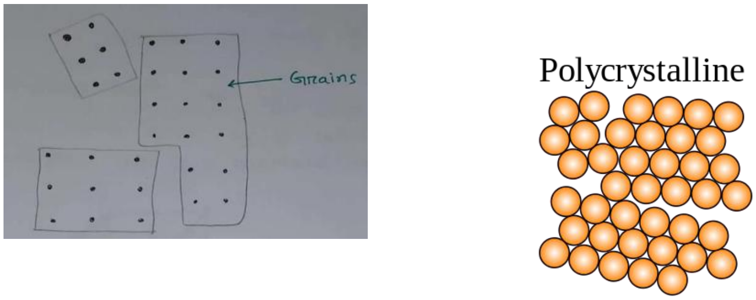
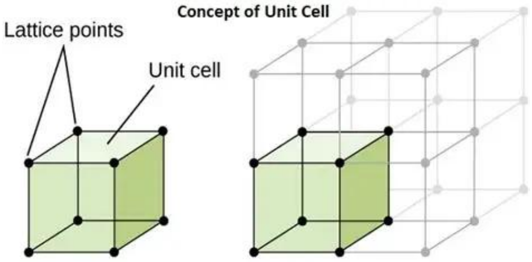


Figure III: Polycrystalline state

What is a Unit Cell?

The smallest repeating unit of the crystal lattice is the unit cell, the building block of a crystal. A unit cell can either be primitive cubic, body-centred cubic (BCC), or face-centered cubic (FCC).In this section, we will discuss the three types of unit cells in detail.



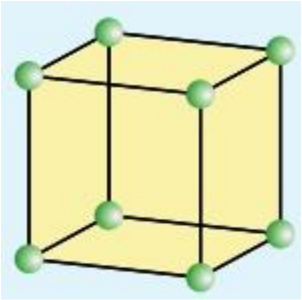
Types of Unit Cell

Numerous unit cells together make a crystal lattice. Constituent particles like atoms and molecules are also present. Each lattice point is occupied by one such particle.

- **Primitive Cubic Unit Cell**
- **Face-centered cubic unit cell (FCC)**
- **Body-centered Cubic Unit Cell (BCC)**

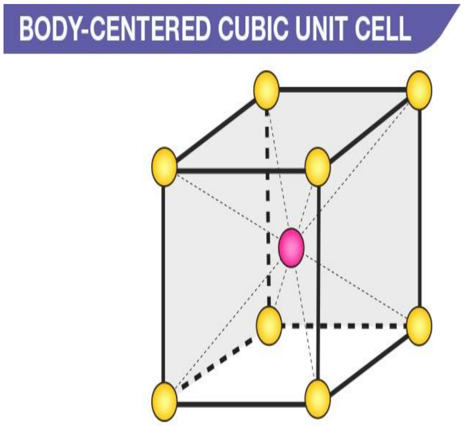
Primitive Cubic Unit Cell

In the primitive cubic unit cell, the atoms are present only at the corners. Every atom at the corner is shared among 8 adjacent unit cells. There are 4 unit cells in the same layer and 4 in the upper (or lower) layer. Therefore, a particular unit cell has only $1/8^{th}$ of an atom. Each small sphere in the following figure represents the center of a particle that occupies that particular position and not its size. This structure is known as an open structure. In each cubic unit cell, there are 8 atoms at the corners. Therefore, the total number of atoms in one unit cell is 8 × 1/8 = **1 atom**.



Body-centred Cubic Unit Cell (BCC)

- A BCC unit cell has atoms at each corner of the cube and an atom at the center of the structure. The diagram shown below is an open structure. According to this structure, the atom at the body center wholly belongs to the unit cell in which it is present.
- In the BCC unit cell, every corner has atoms.
- There is one atom present at the center of the structure
- The diagram is an open structure
- According to this structure atom at the body center wholly belongs to the unit cell in which it is present.



Number of Atoms in BCC Cell:

Thus, in a BCC cell, we have:

8 corners × 1/8 per corner atom = 8 × 1 /8 = 1 atom,

1 body centre atom = 1 × 1 = 1 atom

Therefore, the total number of atoms present per unit cell = **2 atoms.**

Face-centred Cubic Unit Cell (FCC)

An FCC unit cell contains atoms at all the corners of the crystal lattice and at the center of all the faces of the cube. The atom present at the face center is shared between 2 adjacent unit cells and only 1/2 of each atom belongs to an individual cell.

- In the FCC unit cell, atoms are present in all the corners of the crystal lattice
- Also, there is an atom present at the center of every face of the cube
- This face-center atom is shared between two adjacent unit cells

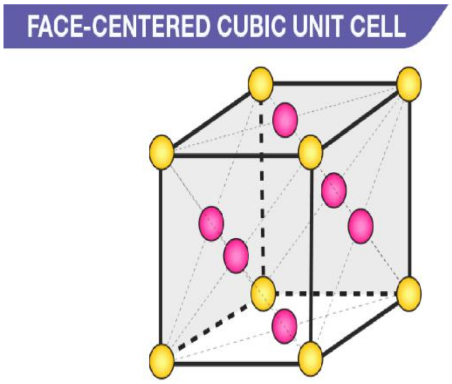


Figure: Face-centered cubic unit cell.

Primitive lattice cell: The parallepiped defined by primitive axes a_1, a_2, and a_3 is called a primitive cell.

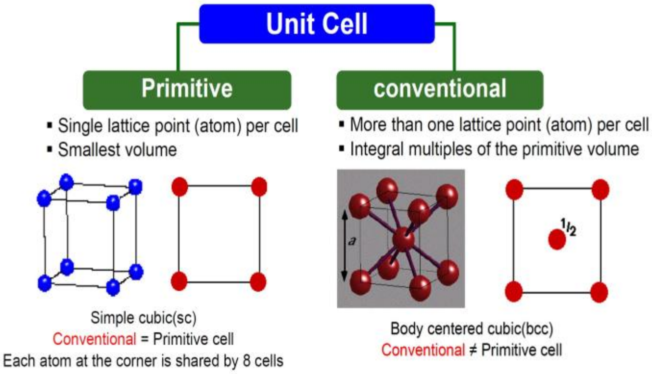
Can a unit cell be primitive?

A primitive cell is a unit cell that contains exactly one lattice point. It is the smallest possible cell. If there is a lattice point at the edge of a cell and thus shared with another cell, it is only counted as half.

What is the difference between a primitive cell and a unit cell?

Primitive unit cells contain only one lattice point, which is made up of the lattice points at each of the corners. Non-primitive unit cells contain additional lattice points, either on the face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell.

Primitive Cell and Conventional cell



Wigner-Seitz cell:

A Wigner-Seitz cell is an example of another kind of primitive cell which has only one lattice point. This Wigner-Seitz cell can be constructed as follows:

1. Draw lines to connect a given lattice point to all nearby lattice points.
2. Draw new lines or planes at the midpoint and normal to these lines.

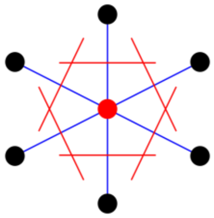


Fig.: Wigner-Seitz cell

Bravais Lattice:

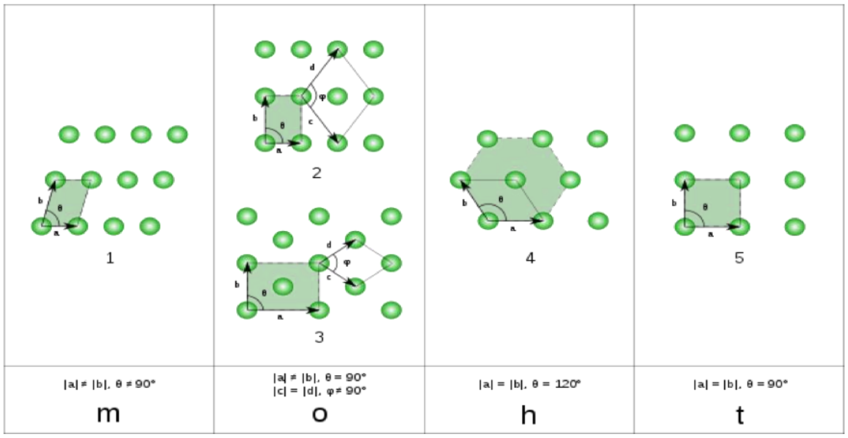
A good definition of a Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears the same regardless of the point from which the array is viewed. The Bravais lattice is the periodic array in which the repeated units of the crystal are arranged. Because there are only 14 distinct arrangements, the Bravais lattice system provides a convenient mechanism for classifying the structural diversity that occurs in nature.

In geometry and crystallography, a Bravais lattice, named after Auguste Bravais (1850), is an infinite array of discrete points generated by a set of discrete translation operations described in three-dimensional space".

In 2 dimensions:

In two-dimensional space, there are 5 Bravais lattices grouped into four crystal families. They are

1. Oblique (monoclinic)
2. Rectangular (orthorhombic)
3. Centered rectangular (orthorhombic)
4. Hexagonal, and
5. Square (tetragonal).



In 3 dimensions

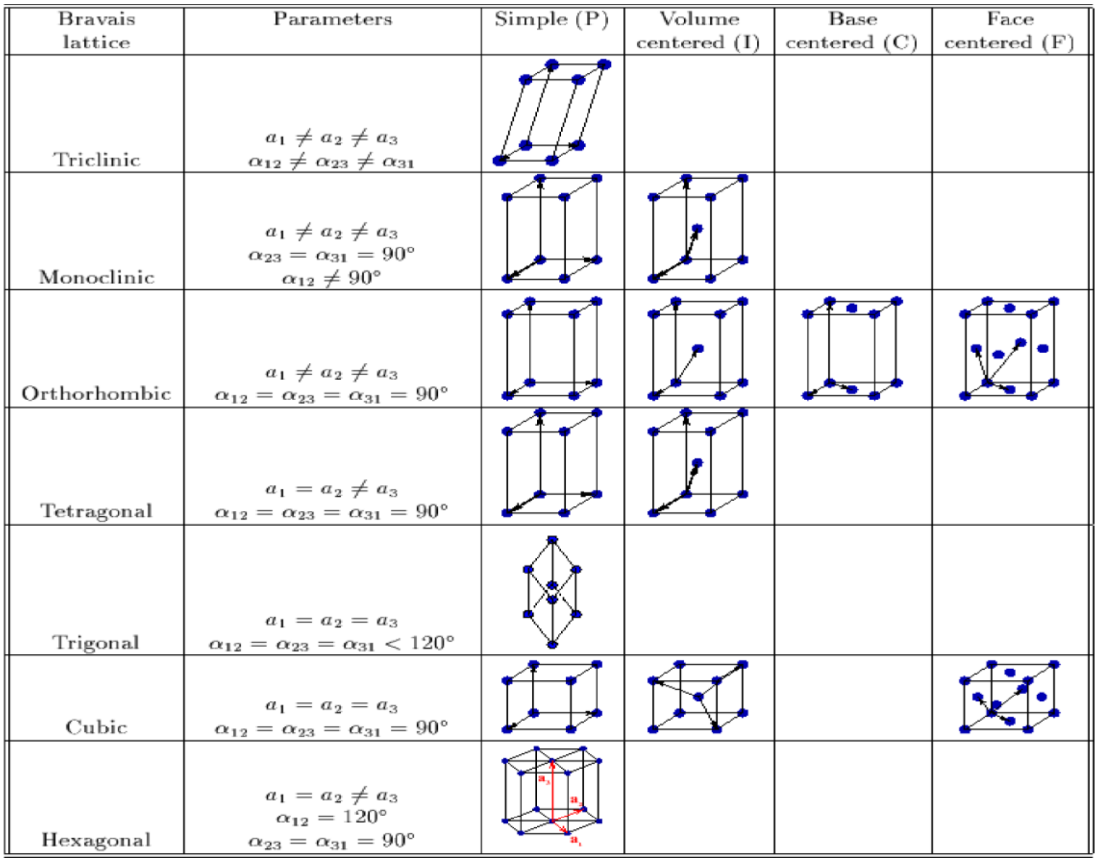
In three-dimensional space, there are 14 Bravais lattices. These are obtained by combining one of the seven lattice systems with one of the centering types. The centering types identify the locations of the lattice points in the unit cell as follows:

Primitive (P): lattice points on the cell corners only (sometimes called simple)

Base-centered (A, B, or C): lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered).

Body-centered (I): lattice points on the cell corners, with one additional point at the center of the cell

Face-centered (F): lattice points on the cell corners, with one additional point at the center of each of the faces of the cell.



Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Atomic Packing Factor (APF) Calculation for SC, BCC, and FCC

The Atomic Packing Factor (APF) is the fraction of volume occupied by atoms in a unit cell. It is given by:

$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

where:

- Volume of Atoms = Number of atoms per unit cell × Volume of one atom.
- Total Volume of Unit Cell = a^3 (where, ‘a’ is the lattice parameter).
- Atoms are assumed to be hard spheres with radius r.

1. **Simple Cubic (SC) Structure**

- Atoms per unit cell: 1
- Lattice parameter: $a=2r$
- Volume of one atom: $\frac{4}{3}\pi r^3$
- Total volume of atoms: $1\times\frac{4}{3}\pi r^3$
- Total unit cell volume: $a^3=(2r)^3=8r^3$

$$\text{APF} = \frac{\frac{4}{3}\pi r^3}{8r^3} = \frac{\pi}{6} \approx 0.52\ (52\%)$$

2. **Body-Centered Cubic (BCC) Structure**

- Atoms per unit cell: 2
- Lattice parameter: $a = \frac{4r}{\sqrt{3}}$
- The volume of one atom: $\frac{4}{3}\pi r^3$
- The total volume of atoms: $2 \times\frac{4}{3}\pi r^3$
- Total unit cell volume: $a^3 = (\frac{4r}{\sqrt{3}})^3$

$$\text{APF} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{8\pi r^3}{3 \times \frac{64r^3}{3\sqrt{3}}} = \frac{\pi\sqrt{3}}{8} \approx 0.68\ (68\%)$$

3. **Face-Centered Cubic (FCC) Structure**

- Atoms per unit cell: 4
- Lattice parameter: $a = \frac{4r}{\sqrt{2}}$
- Volume of one atom: $\frac{4}{3}\pi r^3$
- Total volume of atoms: $4 \times \frac{4}{3}\pi r^3$
- Total unit cell volume: $a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$

$$\text{APF} = \frac{4\times\frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{16\pi r^3}{3\times\frac{64r^3}{4\sqrt{2}}} = \frac{\pi}{3\sqrt{2}} \approx 0.74\ (74\%)$$

Lattice plane or Crystal Plane:

A crystal plane is an imaginary two-dimensional surface within a crystal lattice along which atoms are arranged in a repeating pattern. These planes are described using Miller indices (hkl), which define their orientation relative to the crystal axes. Crystal planes are crucial in determining material properties such as cleavage, slip, diffraction, and electronic behavior in solids.

Basic Properties of Crystal Planes:

1. **Defined by Lattice Points:** Crystal planes pass through specific atomic positions in a crystal.
2. **Miller Indices (*hkl*)**: A set of three integers that define a plane's orientation within the crystal lattice.
3. **Impact on Properties:** Crystal planes influence mechanical strength, cleavage, diffraction, and material slip**.**

Example of Crystal Planes:

- (100) Plane: Cuts the x-axis but is parallel to the y and z axes**.**
- (110) Plane: Cuts the x and y axes but is parallel to the z-axis**.**
- (111) Plane: Cuts all three axes equally.

Procedure for Finding Miller Indices

1. Identify Intercepts with Axes:
    - Determine where the plane intersects the crystal axes (x, y, and z).
    - Express these intercepts in terms of the lattice parameters a, b, c that is (x = pa, y = qb, z = rc) here p, q, r the intercepts.
    - If the plane is parallel to an axis, the intercept is considered ∞ (infinity).
2. Take the Reciprocals:
    - Convert the intercepts into their reciprocal values. i.e., (1/p :1/q :1/r)
3. Clear Fractions (Multiply by LCM):
    - If the reciprocals contain fractions, multiply by the lowest common multiple (LCM) to convert them into smallest integers.
4. Write as (*hkl*) Without Commas:
    - The final integers obtained are the Miller indices (*hkl*).
    - Represent them as (*hkl*) without commas.

Interplanar distance/spacing

The interplanar distance (d) is the perpendicular distance between two successive parallel planes in a crystal lattice. It depends on the unit cell parameters (a, b, c) and the Miller indices (*h, k, l*) of the planes. The general formula gives it for all types of crystal systems:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

For a cubic crystal, where a = b = c, this simplifies to:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Interplanar distance is crucial in X-ray diffraction (Bragg's Law) for determining crystal structures.

Relation with Bragg's Law: When this relation is substituted into Bragg's equation (2d sin θ =nλ), we find that the first-order (n = 1) diffraction maxima in Bragg reflections are given by

$$\lambda = \frac{a}{\sqrt{h^2+k^2+l^2}}\ 2\sin\theta$$

If the wavelength λ of the radiation and the Bragg angle θ are known, then the equation above can be used to calculate the axial length of a side of a cubic crystal and the Miller indices of the set of planes involved in giving a particular maximum.

Mathematical Problems:

1. For a simple cubic crystal lattice parameter 2.04 Å. Calculate the spacing of the lattice plane (212.

Hints/Solution: For a cubic crystal, where a = b = c,

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Here, *h* = 2, *k* = 1, *l* = 2 and a = b = c = 2.04 Å

Therefore, $d_{212} = \frac{2.04}{\sqrt{2^2+1^2+2^2}} = \frac{2.04}{3} = 0.68\ \text{Å}$

2. Show that in a simple cubic lattice the separation between the successive lattice planes (100), (110), and (111) is the ratio 1: 0.71: 0.58.

Hints/Solution: For a cubic crystal, where a = b = c,

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$d_{100} = \frac{a}{\sqrt{1^2+0^2+0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2+1^2+0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$$

Therefore, $d_{100}: d_{110}: d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : 0.71 : 0.58$

Introduction of Symmetry: Many of the molecules we study possess symmetry, some have no symmetry, and some are highly symmetrical. Symmetry plays an important role in the structure and characteristics of molecules. Therefore, it would be appropriate to study the symmetry properties of molecules and to classify them based on geometric characteristics.

It is very important to understand the symmetry and point group of orbitals and molecules so that their behaviors under different circumstances are clearly understood. The point groups are based on the shapes of orbitals and structures of molecules. For example, the ‘s’ orbital is spherical and has a particular symmetry, while the ‘p’ orbital has a dumbbell shape and has a different symmetry. Similarly, the ‘d’ orbitals have different shapes and hence different symmetries. Methane has a tetrahedral shape, and its symmetry is T_d. In contrast, benzene is hexagonal planar, with a symmetry group of D6h. Water, on the other hand, is V-shaped, and its point group is $C_{2v.}$

The objective is to provide you with the information necessary for the interpretation of conventional crystal structure and diffraction data. It will then be demonstrated that from such data it is possible to construct a model of the crystal structure and specify the geometry of the bonding. Symmetry is also valuable for understanding the thermal, mechanical, optical, magnetic, and electrical properties of solids.

What is symmetry?

In a single sentence, symmetry can be defined as the spatial relationships between objects in a pattern.

Symmetry Operators:

A symmetry operator describes an imaginary action that can be used to develop a pattern. Operators change the position and orientation of an object in space. The seven symmetry operators are :

1. Translation.
2. Rotation
3. Reflection
4. Inversion (Centre of symmetry)
5. Roto-inversion (invention axis)
6. Glide (Translation + Reflection) and
7. Screw (Rotation + translation)

Symmetry elements:

Of course, we realize the symmetry in the objects when we look at them. However, we must express them scientifically. This could be done with the help of symmetry elements. These are nothing but some physical entities such as lines, planes, points, etc.

Are they present in objects or molecules?

The answer is 'no', these are imaginary.

Definition

Such as a symmetric element is a geometric entity, an act, or a plane on a point about which or through which a symmetry operation may be performed. The primary function of the symmetry element is to specify the reference point about which action occurs.

The first five symmetry elements that we consider are:

1. Translation vectors.
2. Rotation axes.
3. Mirror planes
4. Centers of symmetry (Inversion points).
5. Invention axes

Only five types of symmetry operations will leave the center of gravity of the molecule unchanged.

1. Rotation about a symmetry axis
2. Reflection of a molecule in a plane
3. Invention Through a point
4. Rotation - reflection
5. Identity operation

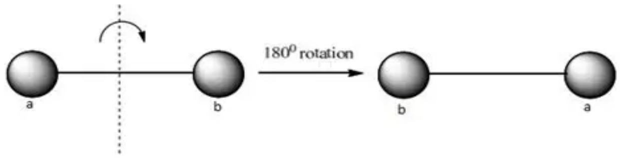
Symmetry operations and symmetry elements

SL No.	Symmetry operations	Symmetry elements	Symbol
I	n- fold rotation	n- fold rotation axis	C_n
II	Reflection	Mirror plane	σ
III	n-fold Rotation - Reflection	n-fold Rotation – Reflection axis	S_n
IV	Invention	Inversion centre or centre of symmetry	I or C_i
V	Identity	Identity element	I or E

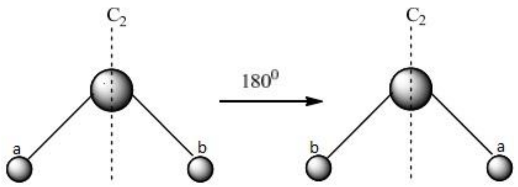
Symmetry operations: There are some mechanical operations, such as rotation, inversion, etc., performed about the symmetry elements so that indistinguishable structures are produced; they are said to be symmetry operations.

Axis of symmetry or proper rotational axis of symmetry (C_n): It is an imaginary line passing through an object or a molecule about which, when the object or molecule is rotated by a certain angle an indistinguishable structure is produced.

C_2 axis of rotation: When the below V-shaped molecule is rotated by 180^0 about the axis passing through the blue sphere, red and green spheres are interchanged. If the colors of the spheres are removed, the two structures are indistinguishable.



C_2 axis of rotation in a linear molecule



C_2 axis of rotation in water molecule

C_3 axis of rotation: The angle between any two spheres is equal to 120^0. Hence, rotation by 120^0 gives an indistinguishable structure. When the colors of the spheres are removed, the two structures cannot be distinguished.

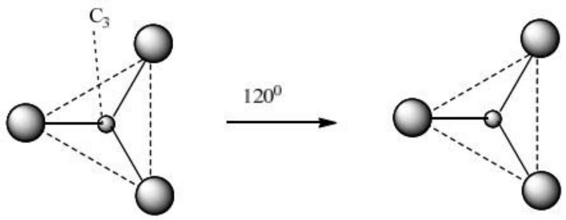


Fig 1 1.3.2: C_3 axis of rotation

C_4 axis of rotation: The two structures cannot be distinguished if the letters are removed.

C_6 axis of rotation: 60^0 rotation about the axis perpendicular to the proper gives an indistinguishable structure, once the colors of the spheres are removed.

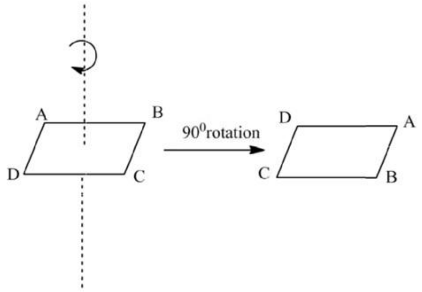
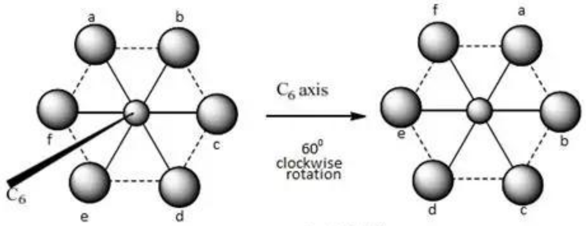


Fig 1 1.3.1: C_4 axis of rotation



C_6 axis of rotation

Order of axis: This imaginary line, i.e., the axis of symmetry, is represented as C_n. Where 'n' is known as the order of the axis. This tells how many times we have to rotate the object to reach the initial structure, i.e., one full rotation. Or, it tells the angle ($360^0/n$) by which we have to rotate the molecule to get the indistinguishable structure.

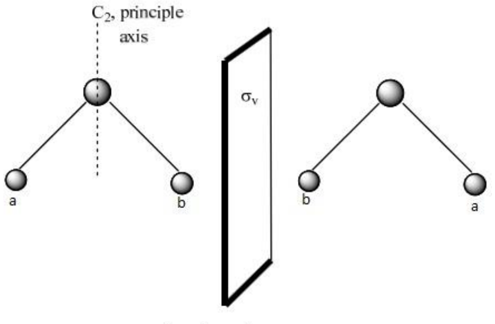
- ❖ C_2 axis of symmetry, $360^0/2=180^{0,}$ i.e., 180^0 rotation will give an indistinguishable structure.
- ❖ C_3 axis of symmetry, $360^0/3=120^{0,}$ i.e., 120^0 rotation will give an indistinguishable structure.
- ❖ C_4 axis of symmetry, $360^0/4=90^{0,}$ i.e., 90^0 rotation will give an indistinguishable structure.
- ❖ C_6 axis of symmetry, $360^0/6=60^{0,}$ i.e., 60^0 rotation will give an indistinguishable structure.

The principal axis of symmetry: That axis for which the 'n' value is maximum is called the principal axis of symmetry.

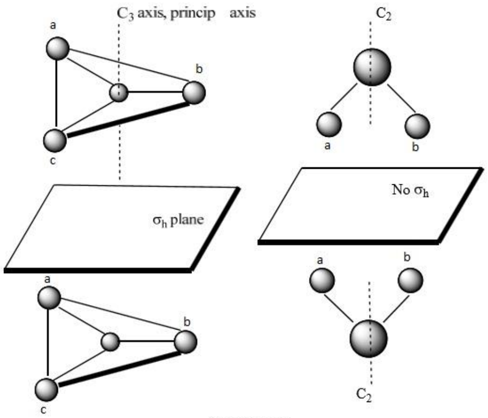
Plane of symmetry: It is an imaginary plane cutting the molecule or object into two halves, which are mirror images.

- ➢ The plane of symmetry is divided into two categories
  1. Vertical mirror plane (σ_v)
  2. Horizontal mirror (σ_h)

- **Vertical mirror plane (σ_v):** This is the mirror plane parallel to the principle axis of symmetry.



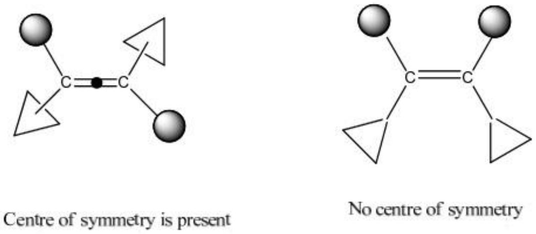
σ_v plane of symmetry



σ_h plane of symmetry

Horizontal mirror (σ_h): When the mirror plane is perpendicular to the principle axix, it is called horizontal mirror plane symmetry.

Centre of symmetry: A unit cell has a centre of symmetry
if there is a point at which the unit cell remains invariant.
When the mathematical transform **r** = -**r** is performed on it.
This a point in the unit cell such that, if there is an atom at
vector position **r**, there is an equivalent atom located at – **r.**

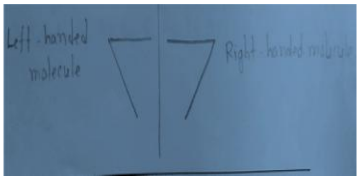


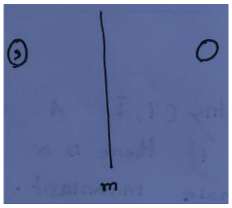
Centre of symmetry is present

No centre of symmetry

Centre of symmetry

Mirror plane (m): This is a plane in the unit cell such that when a mirror reflection in this plane is performed, the cell remains invariant. In the adjacent fig., at one side of the mirror, the shape of the molecule is right-handed, and at the opposite side of the mirror, the shape of the molecule is left-handed.





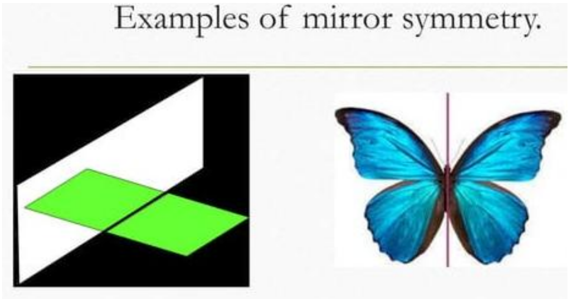
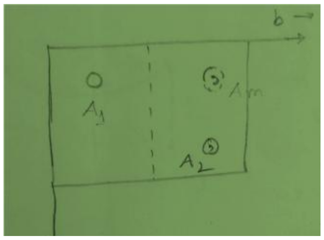


Fig. Reflection operator. The normal of the mirror is parallel to X, and the positive x-direction is to the right. A comma specifies the left-handed replica

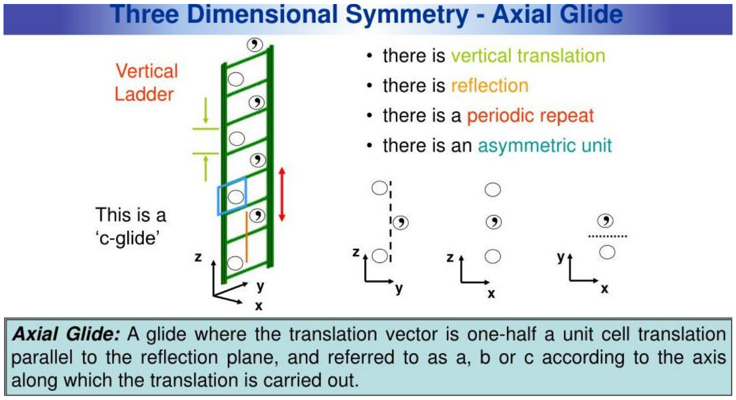
.

Glide plane (a, b, c, n, d)



The glide plane symmetry element operates by a combination of mirror reflection and a translation. The description of this symmetry element is specified by reference to these vectors ***a, b,*** and ***c*** , which define the edges of the unit cell.

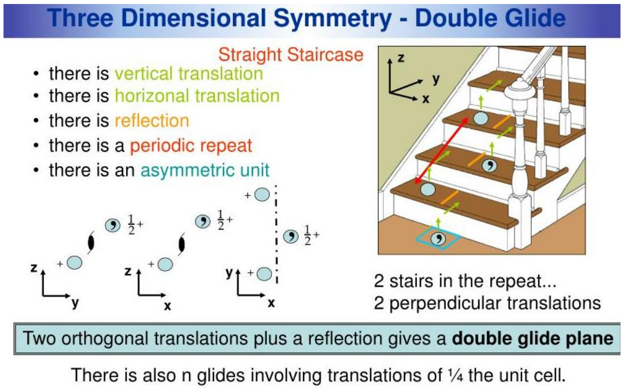
In this fig. for an 'a-glide' plane perpendicular to the b-direction, the point A_1 is first reflected through the point A_m and then displaced by a/2 to the point A_2.



Three Dimensional Symmetry - Axial Glide

- there is vertical translation
- there is reflection
- there is a periodic repeat
- there is an asymmetric unit

Axial Glide: A glide where the translation vector is one-half a unit cell translation parallel to the reflection plane, and referred to as a, b or c according to the axis along which the translation is carried out.



Three Dimensional Symmetry - Double Glide

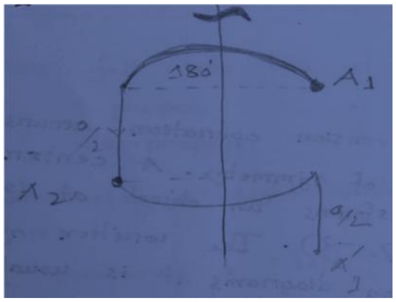
- there is vertical translation
- there is horizonal translation
- there is reflection
- there is a periodic repeat
- there is an asymmetric unit

2 stairs in the repeat...
2 perpendicular translations

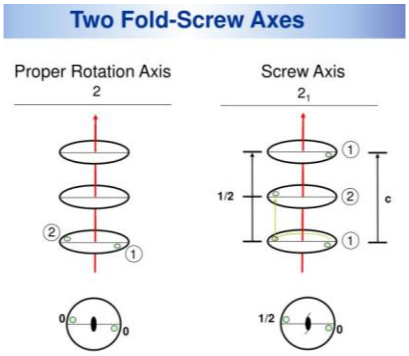
Two orthogonal translations plus a reflection gives a **double glide plane**

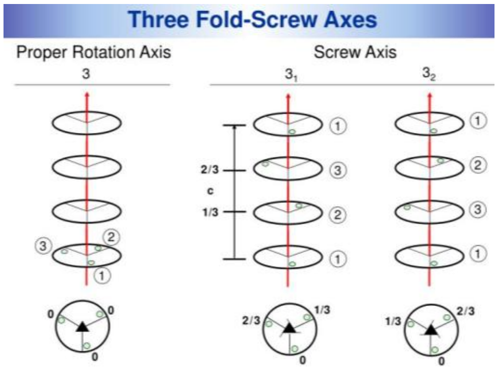
There is also n glides involving translations of ¼ the unit cell.

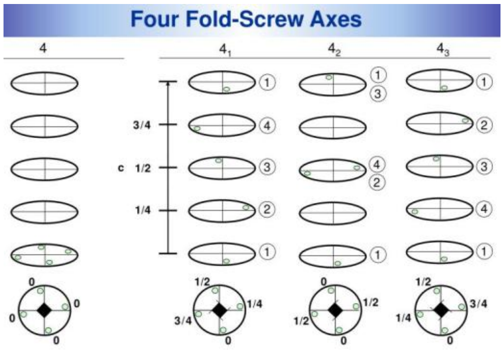
Screw axes (2_1; 3_13_2; $4_14_24_3$; $6_16_26_36_46_5$)

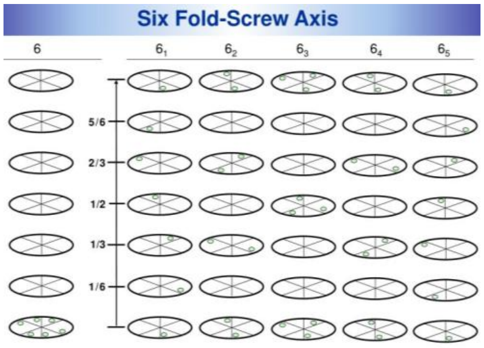


The screw axes symmetry elements operate by a combination of rotation and translation. It is denoted by 2_1; 3_13_2; $4_14_24_3$; $6_16_26_36_46_5$. The behavior of a 2_1 axis parallel to *a*-axis is shown in the following figure. The point A_1 is first rotated by an angle π around the axis and then displaced by a/2 to give a point A_2. The same operation repeated on A_2 gives A_1, which is equivalent to point A_1 in the next cell.







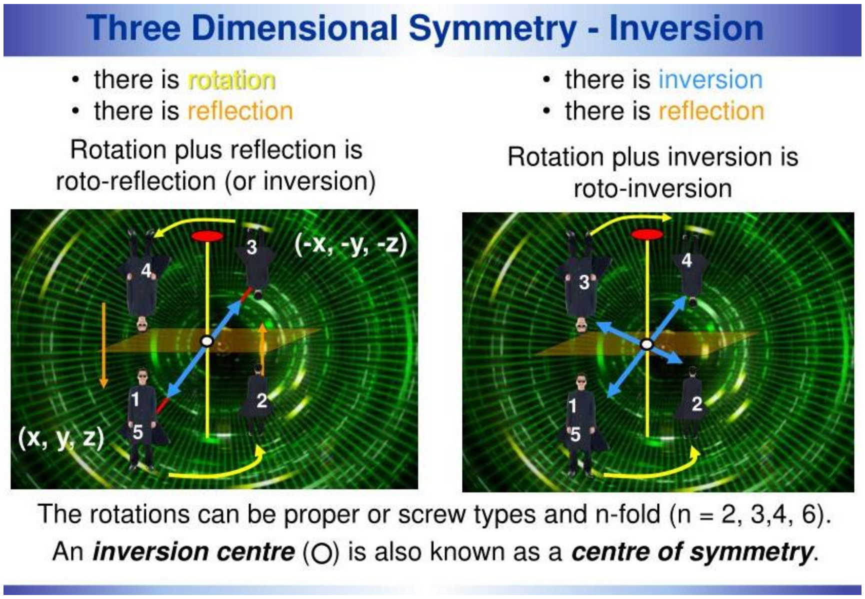


Inversion

The inversion operation occurs through an element called a center of symmetry. A center of symmetry at the origin transforms an object at (x,y,z) to the position(-x,-y,-z). The written symbol is an ‘i’ or ‘I’ and on diagrams it is usually indicate by a small, open circle, like the mirror, inversion also creates a left-handed replica.

Roto-inversion

The roto-inversion opposites an object in a pattern about its axis and then inverts the object through a center of symmetry on the axis.



Three Dimensional Symmetry - Inversion

- there is rotation
- there is reflection

Rotation plus reflection is roto-reflection (or inversion)

- there is inversion
- there is reflection

Rotation plus inversion is roto-inversion

The rotations can be proper or screw types and n-fold (n = 2, 3,4, 6). An ***inversion centre*** (○) is also known as a ***centre of symmetry***.

Point group: Chemists classify molecules according to their symmetry. The collection of symmetry elements present in a molecule forms a ‘group’ typically called a point group.

Why is it called a ‘point group’?

Because all the symmetry elements (points, lines, and planes) will intersect at a single point.

A point group is a group of symmetry operations, all of which leave at least one point unmoved. A crystallographic point group is a point group that maps a point lattice onto itself in three-dimensional rotations.

Equivalent points: The equivalent points are those points that can be produced by various symmetry operations applied to a unit cell.

Point group (m): For a crystal system, the point group ‘m’ implies that the system has a mirror plane perpendicular to the axis of rotation.

Mirror Plane 2/m: For a crystal system, the point group 2/m implies that the system has a mirror plane perpendicular to the 2-fold rotation axes.

Point group

- A point group operation in a lattice is defined as the collection of symmetry operations that when applied about a lattice point, leave the lattice invariant.
- Point group symmetry does not consider translation.
- A point group does not give the lattice type.
- Included symmetry elements are rotations, mirror planes, the center of symmetry, and rotary inversion.
- In space lattice, there are 32 different possible self-consistent combinations of 3D symmetry elements passing through a point.
- Up to three symbols or a combination of symbols can be used to describe a point group.
- Examples: 222, m, 2/m

Nomenclature

i. m is used in preference to the system has a mirror plane perpendicular to the axis of rotation.
ii. A mirror plane normal to a symmetry axis is indicated by X/m, where X is 2,3,4 or 6.
iii. Where there are two distinct sets of mirrors parallel to a symmetry axes mm is used.
iv. Up to three symbols or a combination of symbols can be used to describe a point group. ***Examples*** 3m, 23, 432, and 6/mmm are all point groups. The order is important.

There are 32 crystallographic point groups divided into seven crystal systems.

1	Triclinic	2	**1**, -1
2	Monoclinic	3	**2**, m, m/2
3	Orthorhombic	3	222, mm2, mmm
4	Tetragonal	7	**4**, -4, 4/m, 422, 4mm, -42m, 4/mmm
5	Trigonal	5	**3**, -3, 32, 3m, -3m
6	Hexagonal	7	**6**, -6, 6/m, 622, 6mm, -6m2, 6/mmm
7	Cubic	5	23, m-3, 432, -43m, m-3m

Space group

- Symmetry elements possible for a unit cell can be combined in a group and is called the space group of the unit cell.
- A space group symmetry is a combination of the translational symmetry of a lattice together with other symmetry elements such as rotation and screw axis.
- In a space lattice, there are 230 space groups.
- Example: C_m, P_{nma}
- Any space group, C_m, is based on a c-face-centered cell and has a mirror plane.
- A space group completely describes the symmetry of a crystal.
- 230 space group = 14 Bravais lattice + 32 points groups + screw axes + Glide planes.

The first three letters identify the centering of the lattice.

a) P- Primitive

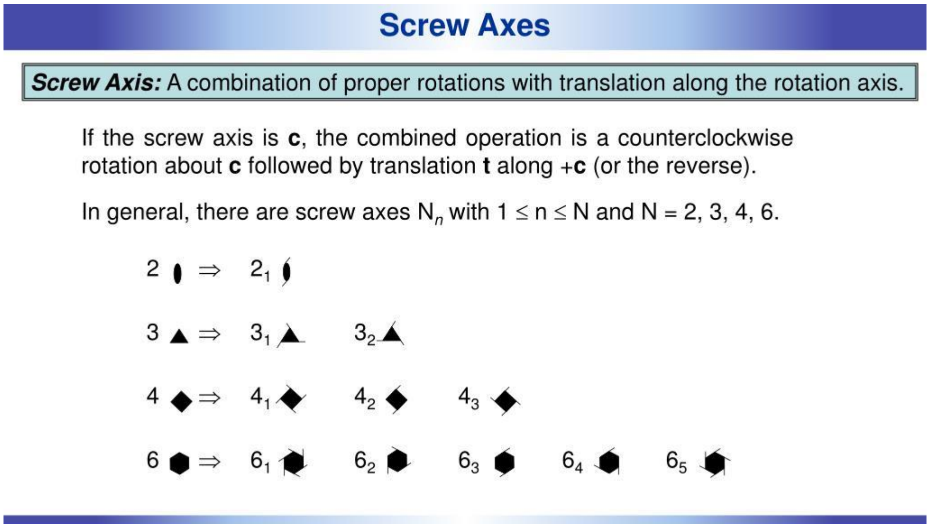
b) I – Body centered
c) B – B-face centered
d) F – Face centered
e) C – C-face centered

Space group = $\mathbf{P_{nma}}$

The space group symbol indicates **a primitive lattice** with

- An n-glide plane perpendicular to the x-axis.
- A mirror plane perpendicular to the y-axis.
- A glide plane perpendicular to the z-axis. mmm – point group.

Graphical symbol of symmetry operation:

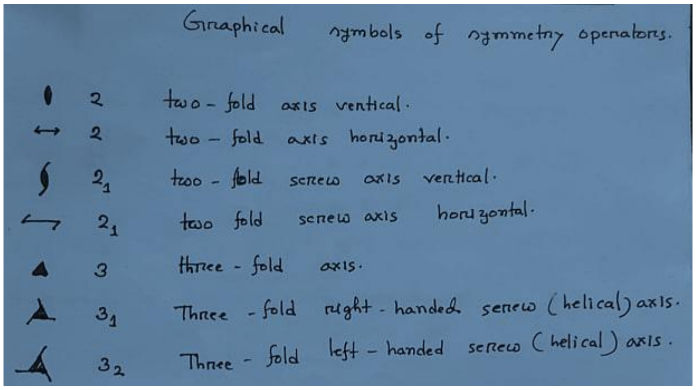


Screw Axes

Screw Axis: A combination of proper rotations with translation along the rotation axis.

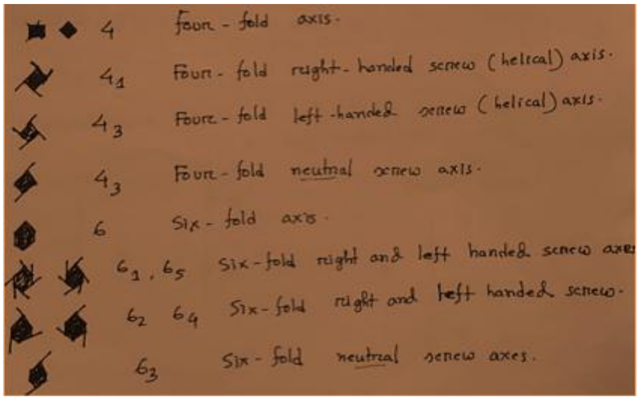
If the screw axis is **c**, the combined operation is a counterclockwise rotation about **c** followed by translation **t** along +**c** (or the reverse).

In general, there are screw axes N_n with $1 \le n \le N$ and N = 2, 3, 4, 6.



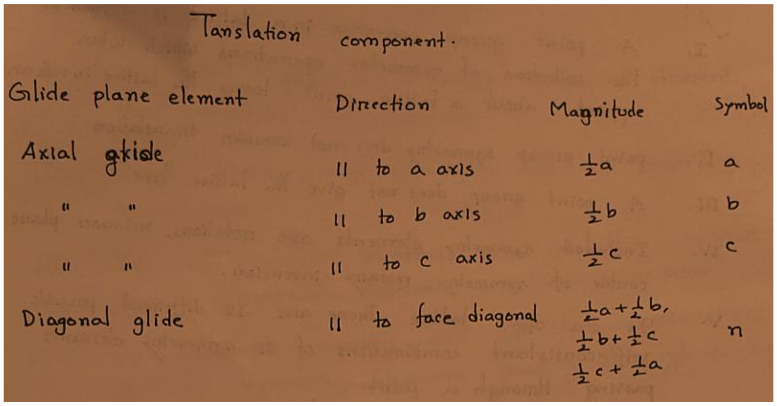
Graphical symbols of symmetry operators.

2	two - fold axis vertical.
2	two - fold axis horizontal.
2_1	two - fold screw axis vertical.
2_1	two fold screw axis horizontal.
3	three - fold axis.
3_1	Three - fold right - handed screw (helical) axis.
3_2	Three - fold left - handed screw (helical) axis.

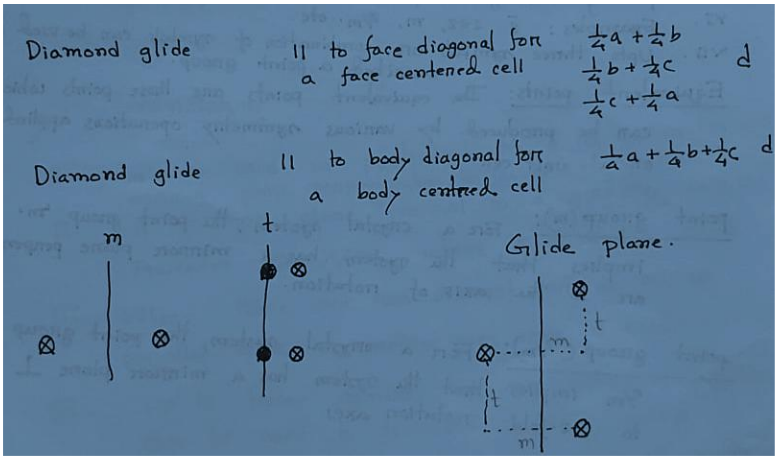


4	four - fold axis.
4_1	Four - fold right - handed screw (helical) axis.
4_3	Four - fold left - handed screw (helical) axis.
4_3	Four - fold neutral screw axis.
6	Six - fold axis.
6_1, 6_5	Six - fold right and left handed screw axes
6_2 6_4	Six - fold right and left handed screw.
6_3	Six - fold neutral screw axes.

The translation components are:

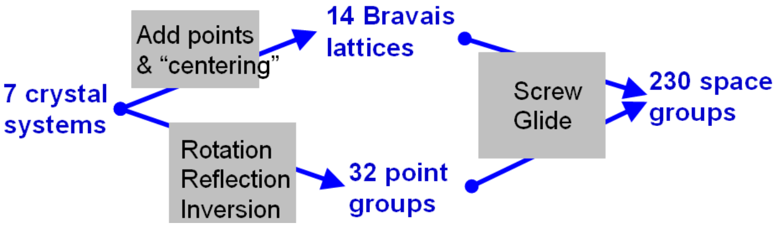


	Tanslation component.		
Glide plane element	Direction	Magnitude	Symbol
Axial glide	∥ to a axis	$\frac{1}{2}a$	a
" "	∥ to b axis	$\frac{1}{2}b$	b
" "	∥ to c axis	$\frac{1}{2}c$	c
Diagonal glide	∥ to face diagonal	$\frac{1}{2}a+\frac{1}{2}b$, $\frac{1}{2}b+\frac{1}{2}c$ $\frac{1}{2}c+\frac{1}{2}a$	n



Diamond glide	∥ to face diagonal for a face centered cell	$\frac{1}{4}a+\frac{1}{4}b$ $\frac{1}{4}b+\frac{1}{4}c$ $\frac{1}{4}c+\frac{1}{4}a$	d
Diamond glide	∥ to body diagonal for a body centred cell	$\frac{1}{4}a+\frac{1}{4}b+\frac{1}{4}c$	d

Schematically shows the relationship between the 7-crystal systems, 14 Bravais lattices, 32 point groups and 230 space groups.



Diffraction of X-rays by a crystal:

X-rays, like other electromagnetic waves, interact with the electron cloud of the atoms. Because of their shorter wavelengths, X-rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction effects. X-ray diffraction (XRD) is a technique used to study the structure of crystalline materials. It works by directing X-rays at a sample and measuring the angles and intensities of the diffracted beams. The diffraction pattern provides information about the crystal structure, phase composition, and atomic arrangement. When X-rays enter into a crystal, each atom acts as a diffraction center, and the crystal as a whole acts like a three-dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystals.

Some types of diffraction other than X-ray diffraction are-

- Neutron Diffraction
- Electron Diffraction

Laue equation

We know that when a beam of X-rays with wavelength λ strikes a row of equally spaced atoms, each atom becomes a source of scattering of waves in all directions which reinforces in certain directions to produce various orders of diffraction spots. The condition of reinforcement is the path difference between the rays diffracted by two adjacent atoms in the row, which must be an integral multiple of the wavelength.

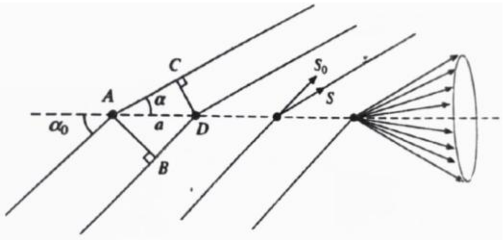


Fig.1 Diffraction of x-rays by one row of atoms.

For simplicity, let us consider a one-dimensional row of atoms with interatomic distance a (Fig.1). Suppose that AB is the incident plane wavefront making an angle α_0 with a row of atoms, and CD is the diffracted Plane wavefront leaving at an angle α with the same row of atoms. Then the path difference between the two consecutive rays is

$$\Delta = (AC - BD) = a\,(\cos\alpha - \cos\alpha_0)$$

and a diffracted beam is observed only if

$$a\,(\cos\alpha - \cos\alpha_0) = e\lambda \qquad (1)$$

where e = 0, 1,2,..is any integer giving the order of diffraction.

This equation will be satisfied by all the diffracted beams lying on the concentric cone with respect to the line of atoms and has the semi-apex angle α (Fig.1). Thus, for any given angle of incidence, there will be a series of concentric cones surrounding the row of atoms, where each cone represents various orders of diffraction. The direction of the primary beam is indicated by the downward arrow, while the higher orders of diffraction are indicated by the numbers (Fig.2)

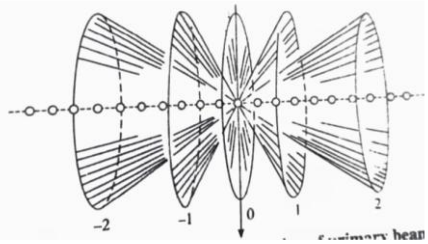


Fig. 2. Diffraction cones around a row of atoms. Direction of the primary beam is indicated by the arrow. Numbers indicate the order of diffraction.

If we assume S_0 and S as the unit vectors, respectively in the directions of the incident and diffracted beam and "a" is the translation vector along the x-axis, then in vector notation the eq. 1 can be written as

$$a.\,(S - S_0) = e\lambda \qquad (1a)$$

In a two-dimensional plane lattice with an interatomic spacing "a" in one direction and "b" in another, for intense diffracted beams to occur, the two equations of the type (18 or 19) must be satisfied simultaneously:

$$\begin{aligned} a\,(\cos\alpha - \cos\alpha_0) &= a.\,(S - S_0) = e\lambda \\ b\,(\cos\beta - \cos\beta_0) &= b.(S - S_0) = f\lambda \qquad \text{(Equation 2)} \end{aligned}$$

where β_0, β, and f respectively have the same meaning for the b-rows of atoms as α_0, α, and e for the a-rows of atoms.

Finally, as we know a crystal is a three-dimensional periodic arrangement of atoms, thus the diffraction occurs from a simple space lattice with a unit cell defined by the primitive translations a, b, c the following three equations must be satisfied simultaneously:

$$\begin{aligned} a\,(\cos\alpha - \cos\alpha_0) &= a\,.\,(S - S_0) = e\lambda \\ b\,(\cos\beta - \cos\beta_0) &= b.\,(S - S_0) = f\lambda \\ c\,(\cos\gamma - \cos\gamma_0) &= c.\,(S - S_0) = g\lambda \qquad \text{(Equation 3)} \end{aligned}$$

where γ_0, γ, and g respectively have the same meaning for the c-rows of atoms as (α_0, α, e) and (β_0, β,,f) for a- or b-rows of atoms. These three equations together are called Laue equations.

Bragg's Law:

To visualize x-ray diffraction, let us consider a crystal of equidistant parallel planes of atoms with the interplanar spacing as **d**. Further, consider a monochromatic X-ray beam of wavelength **λ** having a common wave front, falls at an angle **θ** on these planes (Fig. 1). Each atom scatters the X-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase (i.e. in certain directions only) where they interfere constructively. In all other directions, there is destructive interference.

Consider two of the incoming X-rays **OE** and **O'A** inclined at an angle **θ** with the topmost plane of the crystal and are scattered in the directions **AP** and **EP'**, also at an angle **θ** with that plane. Since the path lengths of the rays **OEP'** and **O'AP** are the same, they arrive at **P** and **P'**, respectively in phase with each other and again form a common wavefront.

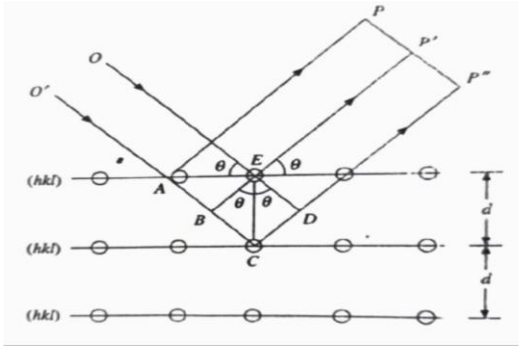


Fig.1. Diffraction of X-rays by crystal planes

This is the condition for scattering in phase by one (top) plane of the crystal. To see the effect of an adjacent plane, let us consider the incoming beam O'E and scattered ray C'P'. If EB and ED are parallel to the incident and scattered wavefront respectively, then the total path O'C'P' is longer than the path OEP' (or O'AP) by an amount:

$$\Delta = BCD = 2BC$$

By construction. And, from the right angle triangle EBC, we have $BC = d \sin\theta$, so that the path difference:

$$\Delta = 2d \sin\theta$$

If the two consecutive planes scatter in phase with each other, then we know that the path difference Δ must be equal to an integral multiple of wavelength, i.e.

$$\Delta = n\lambda$$

where n = 0, 1, 2, ... gives the order of reflection. Thus, the condition for in-phase scattering by a set of equidistant parallel planes in a crystal is given by:

$$2d \sin\theta = n\lambda \text{ ……………………………..1}$$

Equation 1 is the well-known **Bragg’s law**.

The diffracted beams thus fulfill the geometry of a reflection but arise only for certain discrete values of θ for which Bragg’s law is fulfilled.

We know that the maximum value of $\sin\theta = 1$. Using this in equation 1, we obtain:

$$(n\lambda) / (2d) \le 1$$

This indicates that **λ must not be greater than twice the interplanar spacing**, otherwise no diffraction will occur.

Example: Determine the angle through which an X-ray of wavelength 0.440 Å be reflected from the cube face of a rock salt crystal (d = 2.814 Å).

Solution: Given $\lambda = 0.440$ Å, $d = 2.814$ Å. Using Bragg’s law, angles for various orders of reflections (i.e. θ_1 for $n = 1$, θ_2 for $n = 2$, etc.) can be determined.

We know that:

$$\sin\theta = (n\lambda) / (2d)$$

Therefore, $\theta_1 = \sin^{-1} (\lambda / 2d) = \sin^{-1} (0.440 / 5.628) = \sin^{-1} (0.0782) = 4° 29'$

Similarly,

$$\theta_2 = \sin^{-1} (2 \times 0.0782) = 8° 59'$$
$$\theta_3 = \sin^{-1} (3 \times 0.0782) = 13° 34'$$
$$\theta_4 = \sin^{-1} (4 \times 0.0782) = 18° 13'$$
$$\theta_5 = \sin^{-1} (5 \times 0.0782) = 23°$$

Hence, the reflected beam will be observed at the following angles: 4° 29', 8° 59', 13° 34', 18° 13', and 23°, etc.

Experimental diffraction methods:

There are essentially three methods:

i. The rotating-crystal method,
ii. the Laue method, and
iii. The powder method.

Regardless of the method used, the quantities measured are essentially the same.

The rotating-crystal method

This method is used for analysis of the structure of a single crystal. The experimental arrangement is shown in Fig. 1. The crystal is usually about 1 mm in diameter and is mounted on a spindle that can be rotated. A photographic film is placed on the inner side of a cylinder concentric with the axis of rotation. A monochromatic incident beam of wavelength λ is collimated and made to impinge on the crystal. The specimen is then rotated, if necessary, until a diffraction condition is obtained, that is, λ and θ satisfy Bragg's law. When this occurs, a diffracted beam (or beams) emerges from the crystal and is recorded as a spot on the film.

By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of the unit cell as well as the arrangement of atoms inside the cell.

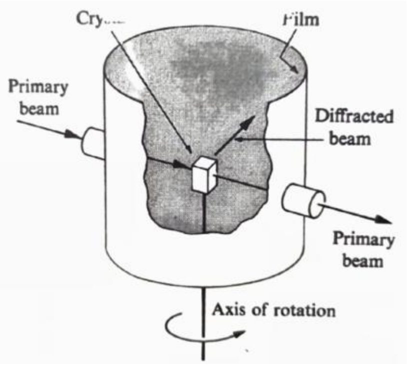


Fig. 1. Schematic diagram of X-ray diffraction by the rotating-crystal method.

The Laue method

This method can be used to rapidly determine the symmetry and orientation of a single crystal. The experimental arrangement is shown in Fig. 2. A white X-ray beam i.e. with a spectrum of continuous wavelength is made to fall on the crystal, which has a fixed orientation relative to the incident beam. Flat films are placed in front of and behind the specimen. Since λ covers a continuous range, the crystal selects that particular wavelength which satisfies Bragg's law at the present orientation, and a diffracted beam emerges at the corresponding angle. The diffracted beam is then recorded as a spot on the film. However, since the wavelength corresponding to a spot is not measured, one cannot determine the actual values of the interplanar spacing — only their ratios. Therefore one can determine the shape but not the absolute size of the unit cell. A typical Laue photograph is shown in Fig. 3. Note that if the direction of the beam is an axis of symmetry of the crystal, then the diffraction pattern should exhibit this symmetry. Figure 3 shows the 6-fold symmetry of the symmetry axis in Mg, which has a hexagonal structure.

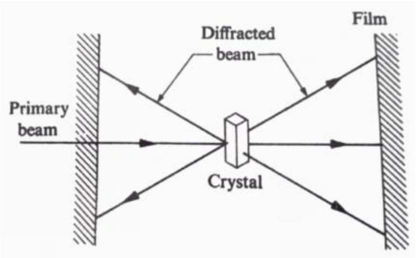


Fig.2 Experimental arrangement of Laue method.

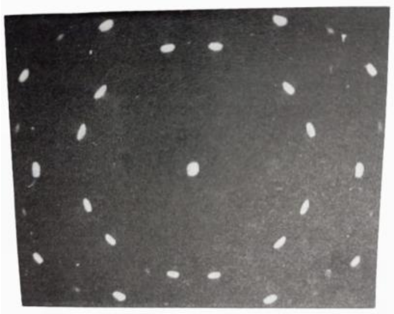


Fig. 3. Laue pattern for an Mg crystal, with the x-ray beam parallel to the 6 –fold symmetry axis.

The powder method

This method is used to determine the crystal structure even if the specimen is not a single crystal. The sample may be made up of fine-grained powder packed into a cylindrical glass tube, or it may be polycrystalline, in which case it is made up of a large number of small crystallites oriented more or less randomly. A monochromatic beam impinges on the specimen, and the diffracted beams are recorded on a cylindrical film surrounding it.

Due to the presence of numerous randomly oriented crystallites, there are always some that align correctly with the incident monochromatic beam to satisfy Bragg's law. As a result, a diffracted beam is produced at a specific angle. Since both the λ and θ are measurable, the interplanar spacing of the crystal can be determined. This principle enables the study of crystal structures using X-ray diffraction techniques.

Fig.4. The x-ray powder diffraction pattern for Cu.

Other sets of planes lead to other diffracted beams corresponding to different planar spacing for the same wavelength. Thus one can determine the lattice parameters quite accurately, particularly if the crystal structure is already known. Note also that, since the specimen is symmetric under rotation around the incident beam as an axis, the diffracted beam corresponding to each scattering angle 2θ fans out along a cone whose axis lies along the incident beam.

The reciprocal lattice

A crystal lattice may be considered an assembly of various sets of equidistant parallel planes. Instead, it is conceptually easier to visualize them in terms of their normal as one-dimensional lines. Such a description has been the basis of several crystallographic projections, viz. gnomonic, stereographic, etc. However, these projections display only the orientation of the planes for the crystallographic axes and not the interplanar spacings. We shall now discuss a projection that displays both.

Consider any given space lattice (or a real crystal lattice) and apply the following:

1. From a common origin draw a normal to each crystal plane.

2. Set the length of each normal equal to or 2π times the reciprocal of the interplanar spacing dy. ;

3. Mark a point at the end of each normal which represents the crystal plane.

A collection of points obtained in this way corresponding to various crystal planes form a lattice array and is known as reciprocal lattice. The reciprocal lattice points preserve all characteristics of the planes they represent. The direction from the origin preserves the orientation of the plane, and the distance of the point from the origin preserves the interplanar spacing of the planes it represents. The concept of the reciprocal lattice plays a very important role in the field of X-ray crystallography, lattice vibration electronic band structure, and, all of solid-state physics, this concept was first given by P.P. Ewald (192T) and application was made by J.D. Bernal (1972).

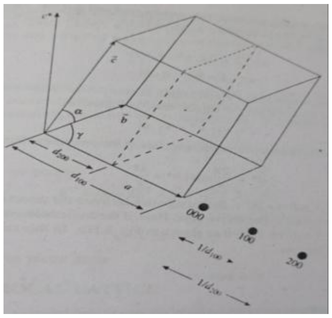


Fig.1. Relationship between crystal planes and their reciprocal lattice points

In a three-dimensional case, consider a direct crystal lattice whose unit cell is defined by the vectors **a, b,** and **c** (Fig. 1). If the area of the ***bc*-plane** is ***A***, then the volume of the unit cell ***V*** is given by

$$V = \text{Area of } bc\text{-plane} \times \text{height} = A \times d_{100}$$

so that

$$a* = 2\pi/\mathrm{d}_{100} = \frac{2\pi A}{V}$$

Now, from vector algebra we know that the area of the bc-plane $A = bc \sin \alpha = b \times c$, and the volume of a primitive unit cell , $V = a \cdot b \times c$. Therefore,

$$a^* = 2\pi/d_{100} = 2\pi \frac{b \times c}{a.(b \times c)}$$

$$\text{Similarly,} \qquad b^* = 2\pi/d_{010} = 2\pi \frac{c \times a}{a.(b \times c)} \text{ and } c^* = 2\pi/d_{001} = 2\pi \frac{a \times b}{a.(b \times c)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

With the help of above equations, several useful information can be obtained. First, see the result of the dot product of these reciprocal lattice vectors with their respective counterparts,

$$a^* \cdot a = 2\pi \frac{b \times c}{a.(b \times c)} \cdot a = 2\pi \ldots\ldots\ldots\ldots\ldots (2)$$

Similarly, we can obtain $b^* \cdot b = 2\pi$ and $c^* \cdot c = 2\pi$. On the other hand, taking the dot product of these vectors with the other vectors of the real lattice, we find

$$a^* \cdot b = 2\pi \frac{b \times c}{a.(b \times c)} \cdot \mathrm{b} \text{ and } a^* \cdot c = 2\pi \frac{b \times c}{a.(b \times c)} \cdot c$$

Since $b \times c$ is a vector which is perpendicular to both b and c, therefore, $b \times c \cdot b = 0$ and $b \times c \cdot c = 0$. This gives

$$a^* \cdot b = 0,\ a^* \cdot c = 0$$

Similarly, we can verify that

$$b^* \cdot c = 0,\ \ b^* \cdot a = 0$$

$$c^* \cdot a = 0,\ c^* \cdot b = 0$$

These important results tell us the following:

a^* is normal to b and c

b^* is normal to c and a

c^* is normal to a and b

Now using the reciprocal lattice vectors a^*, b^*, and c^*, a reciprocal lattice can be constructed. With the help of equation 1, the reciprocal lattice vector in general can be written as

$$\mathbf{G} = \sigma_{hkl} = ha^* + kb^* + lc^*$$

That is to reach any reciprocal lattice point *hkl*, one has to move *h* units along a^*, *k* units along b^*, and *l* units along c^*.

References:

1. *Introduction to Solid State Physics by C. Kittel*
2. *Solid State Physics by R.L. Singhal*
3. *Solid State Physics structure and properties of materials by M.A. Wahab*
4. *Solid State Physics by A.J. Dekker*
5. *Elementary Solid State Physics by M. Ali. Omar*
6. *Physics for Engineers by Giasuddin*