

# UNIT - I

## **FUNDAMENTALS OF CRYSTALLOGRAPHY**

# What is Crystal structure?

- Crystal structure tells us about the arrangement and pattern of atoms/molecules within a material or mineral.
- It has been observed that only knowing what elements are in the mineral is not important, but it is also very important to know how those elements are stacked together??

# Crystallography

- **Crystallography** is the experimental science of determining the arrangement of atoms in crystalline solids.

Or in other words.....

Crystallography is a branch of science that examines crystals.

Its interest is mainly focused on their internal structure, not in their external shape.

**As a science, crystallography has produced 28 Nobel Prizes, more than any other scientific field.**

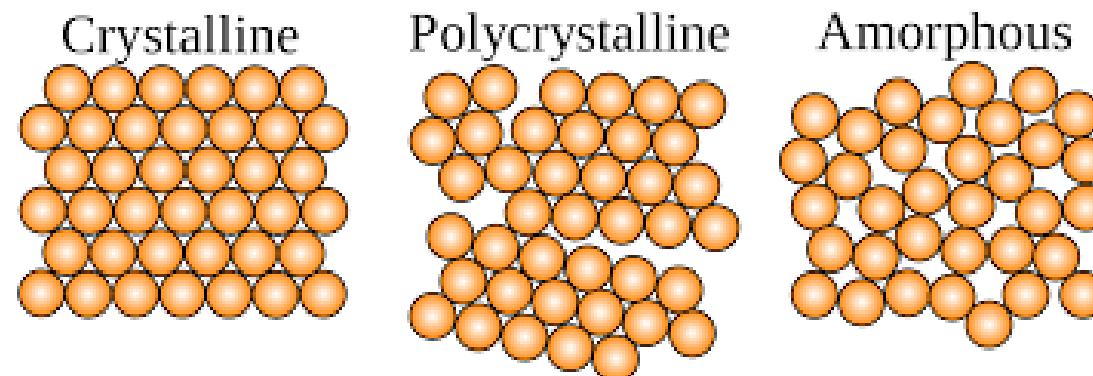
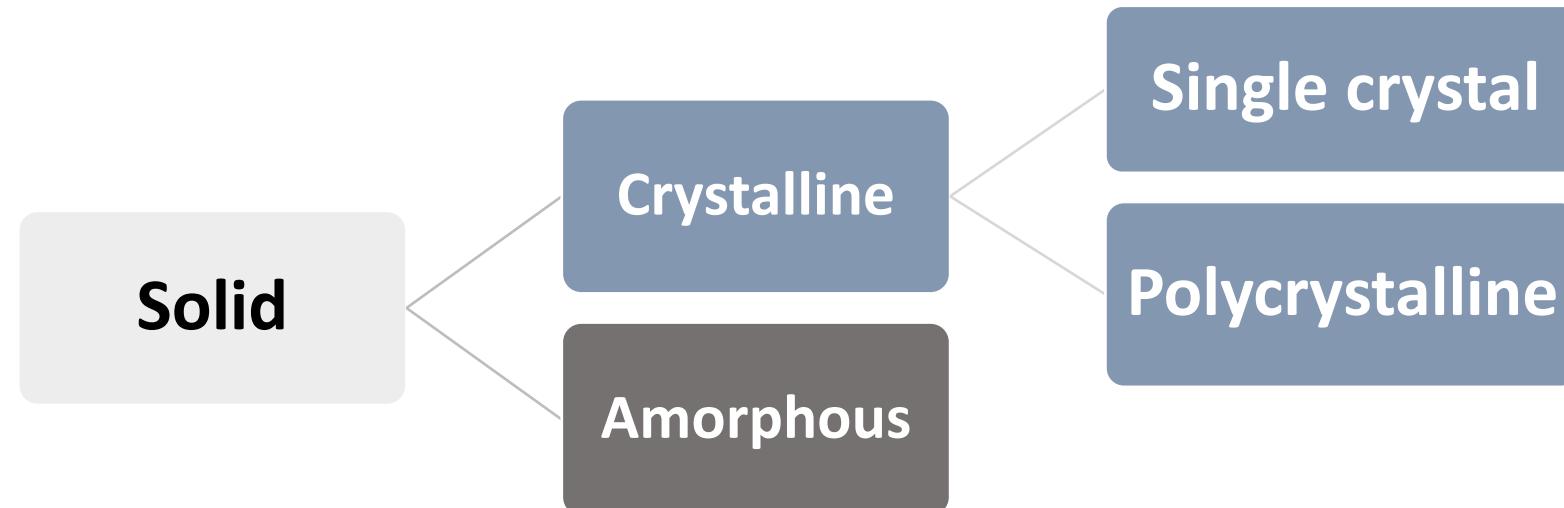
## Why we need to study Crystal structure??

- The atomic and/or molecular structure that is revealed by Crystallography comprises the most relevant information to understand the various properties of the materials, so that we can modify them for required applications.

## What is its use for IT/CSE students??

- Computer chips
- Quantum computers or supercomputers
- Computer science covers development of computers, development of software as well as the networking between computers using a variety of hardware technologies - **require a knowledge of material science - Computer chips, memory devices etc.**
- **Computer** chips, both for CPU and memory, are composed of semiconductor materials. Rate of heat generation in a semi-conductor (CPU) can be improved with proper choice of the material used.

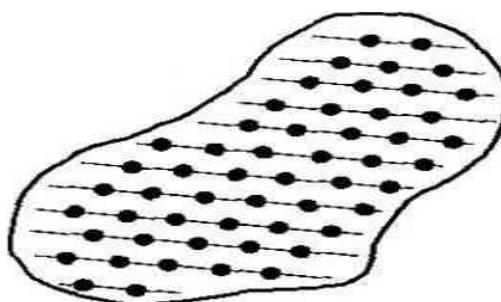
On the basis of order in which atoms are arranged in a solid, they are classified as:



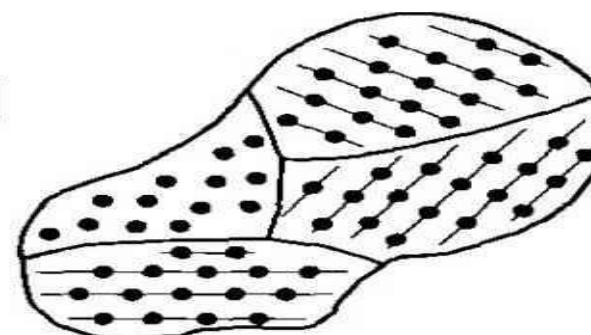
<b>Crystalline Solids</b>	<b>Amorphous solids</b>
They have a definite shape and geometrical form.	They do not have a definite geometrical shape.
They have a sharp (definite) melting point.	They melt over a wide range of temperatures.
They are rigid and incompressible.	They too are usually rigid and cannot be compressed to any appreciable extent. However graphite is soft because of its unusual structure.
They give a clean cleavage, i.e., break into pieces with plane surfaces.	They give irregular cleavage.
They have a definite heat of fusion.	They do not have a definite heat of fusion.
Anisotropic, i.e. their mechanical properties and electrical properties depend on the direction along which they are measured.	Isotropic, i.e. they have similar physical properties in all directions because the constituents are arranged in random manner.

# Crystalline materials

- **Single crystals**
- Rare occurrence
- Have a structure that repeats periodicity over its whole volume.
- Can be considered to be made up of a single grain
- anisotropic
- E.g. Diamond, rocksalt

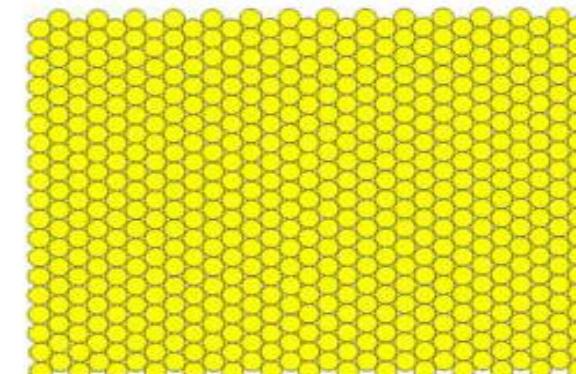


Single crystal

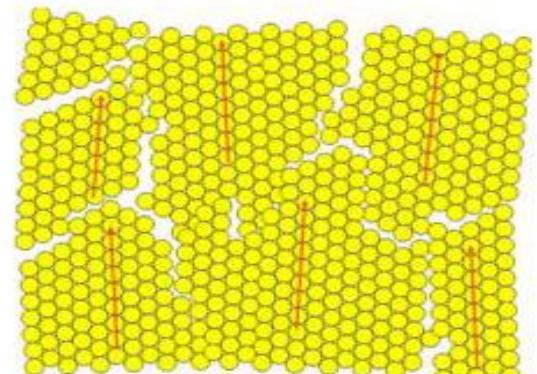


Polycrystalline solid

- **Polycrystalline**
- occurs in majority
- local periodicity
- comprised of many individual grains, each grain can be thought of a single crystal
- size of each grain  $\sim 10^3\text{-}10^4 \text{ \AA}$ .
- isotropic
- e.g. Metals



Single crystal structure in a solid



General crystal structure in a solid

# Types of Polycrystalline solids

Dr. Vanita Thakur

The atoms are bound together by electrostatic forces. Depending on the nature of bond between the neighboring atoms, the crystals can be classified as follows:

## **1. Ionic Crystals:** in these type of crystals,

- the atoms exist in the form of ions and are held together by ionic bonds.
- Have high melting point
- Are poor conductors.
- Interatomic forces are non-directional

e.g. table salt

## **2. Covalent Crystals:**

- Atoms are held together by covalent bonds.
- Electron is shared by neighboring atoms
- Have high melting point
- Do not conduct.
- Interatomic forces are directional

e.g. diamond

## **3. Metallic Crystals**

- Held together by electrostatic force between cations and delocalized electrons
- Electrons are loosely bound to nuclei
- High conductivity

e.g. Copper, gold

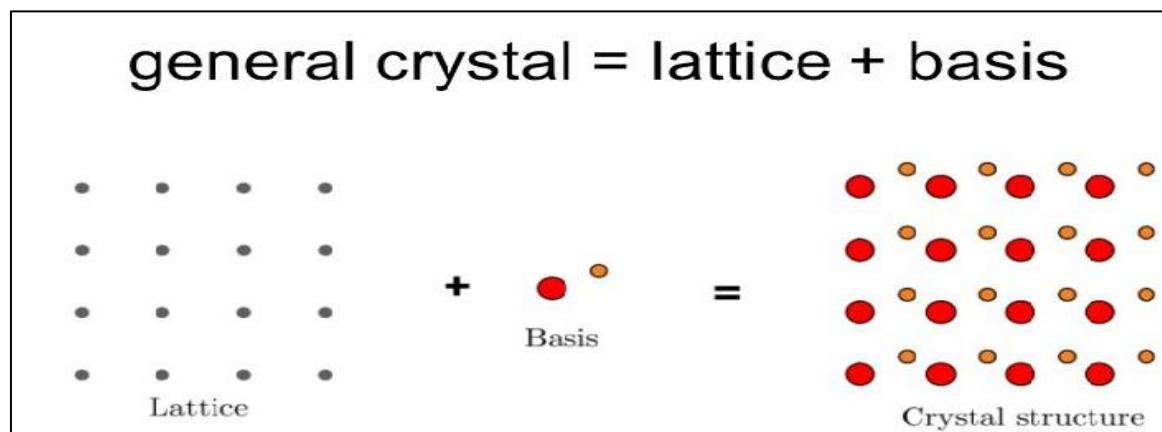
# Space lattice

Dr. Vanita Thakur

French mathematician, Bravais, gave the concept of lattice.

- *Lattice is an imaginary geometrical framework*
- **Def:** Lattice is a hypothetical regular and periodic arrangement of points in space. In which every point has surrounding identical to that of every other point. It is used to describe the structure of a crystal.
- Basis: A basis is a collection of atoms in particular fixed arrangement in space. A basis can be a single atom or group of atoms.

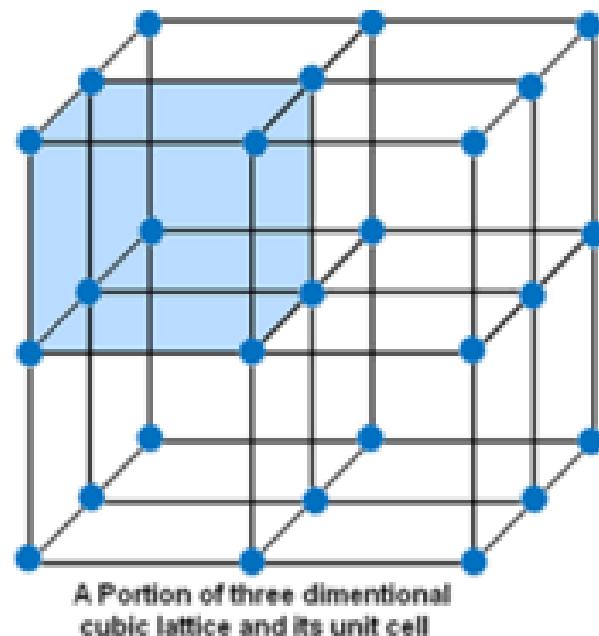
A lattice combined with basis gives rise to crystal structure.



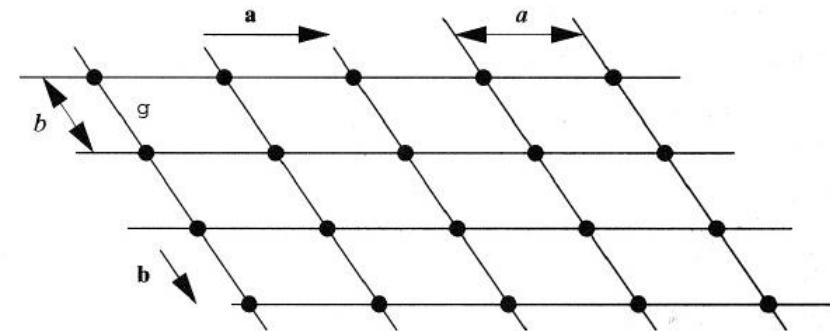
## One dimensional lattice

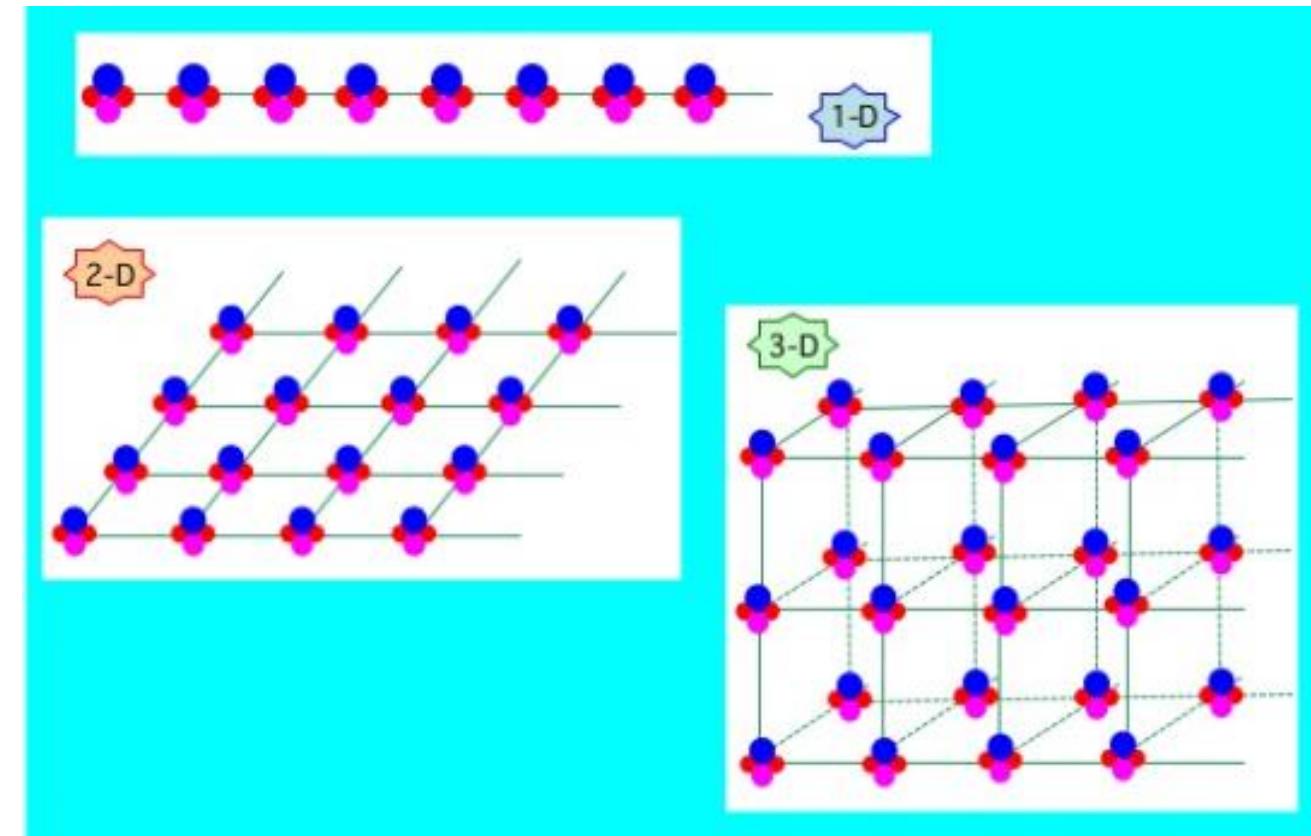
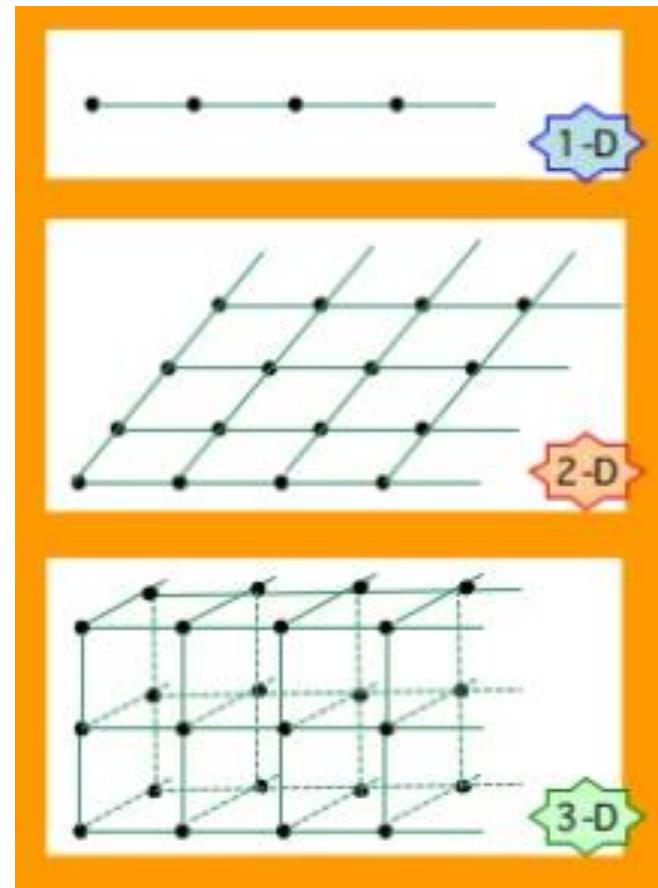


## Three dimensional lattice



## Two dimensional lattice



**Lattice****+ Basis****=****Crystal Structure**

# Unit cell

A unit cell is the smallest geometrical unit, which when repeated in space indefinitely, generates the space lattice. Hence, it is the smallest volume that carries the full description of the entire lattice.

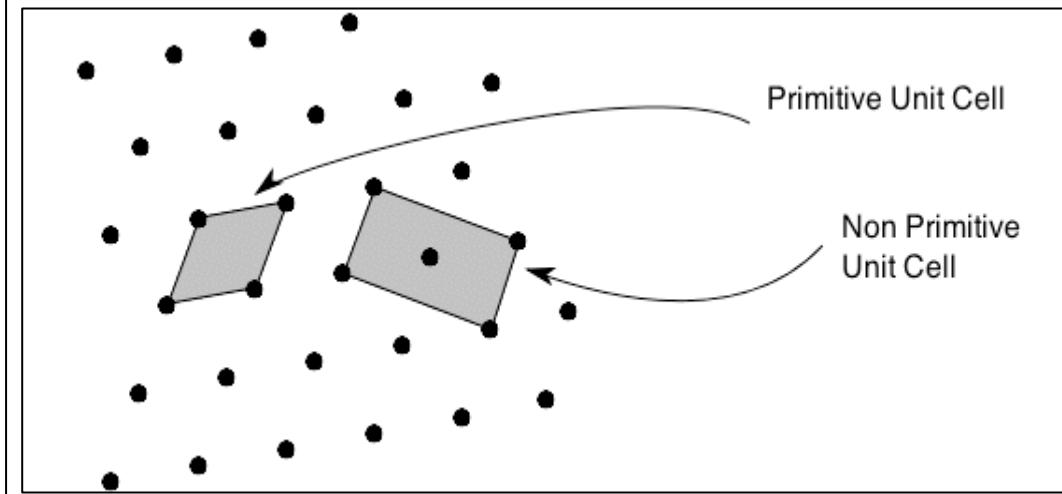
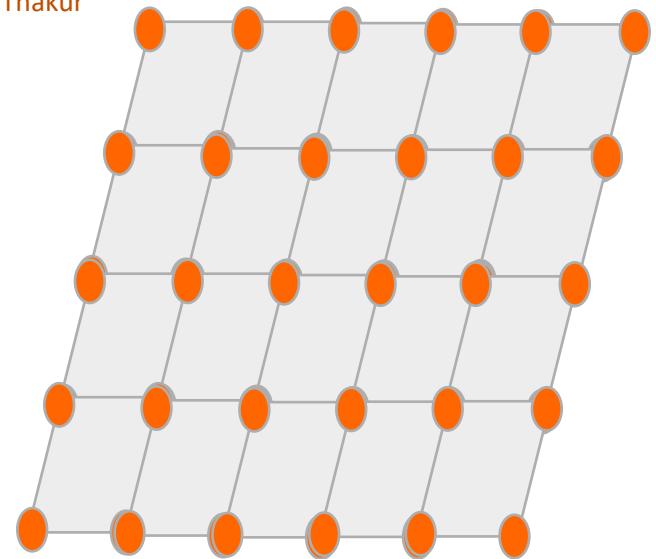
Types of unit cell:

1. **Primitive unit cell**- which has 1 lattice point per unit cell.

2. **Non-Primitive unit cell**- which has **2 or more lattice points** per unit cell.

3. **Wigner-Seitz Cell**-It is a special type of **primitive-cells** known as Wigner-Seitz cell. The **Wigner-Seitz cell** of a lattice point is defined as the volume that encloses all points in space which are closer to this particular lattice point than to any other.

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## Unit Cell (contd...)

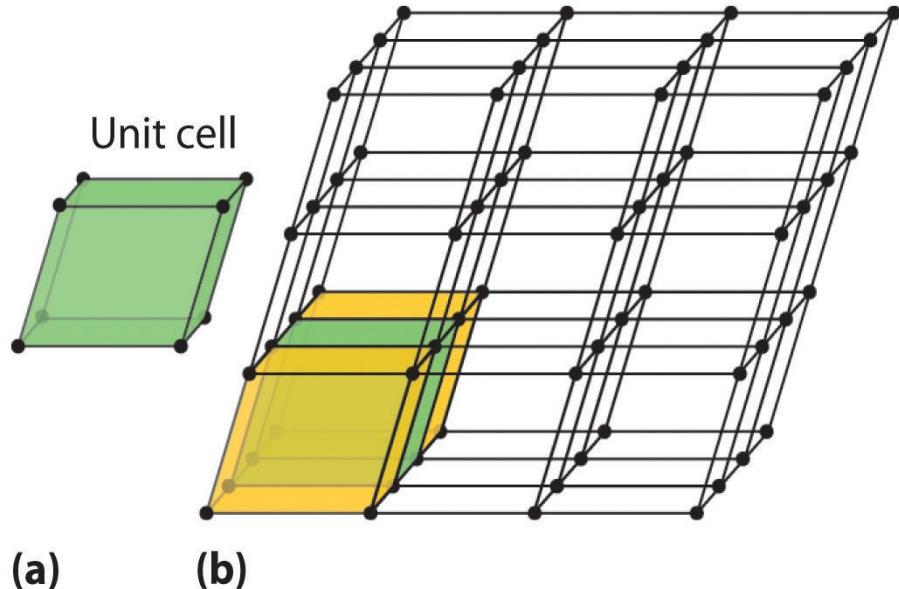
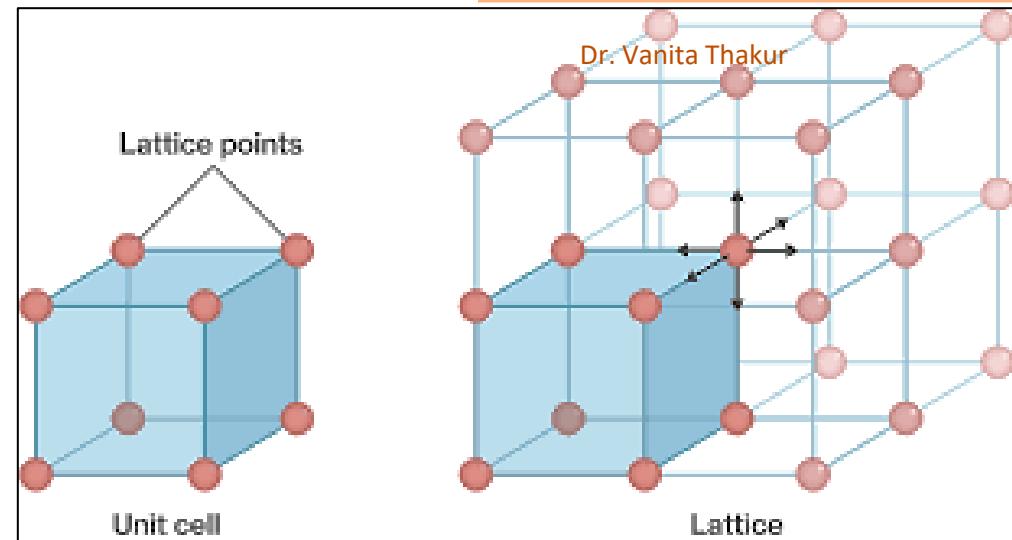
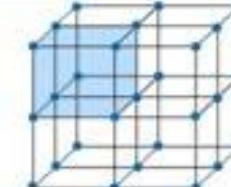
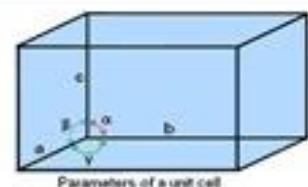
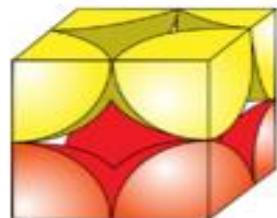
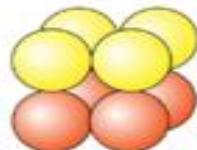
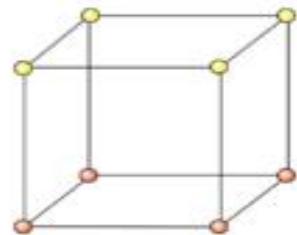


Fig. a shows- A unit cell in 3-dim  
Fig. b shows- resulting regular 3-dim lattice



Crystal lattice	Unit Cell
Orderly three dimensional arrangements of atoms in space is called crystal lattice. It is diagrammatic representation of constituent particles, such as atoms, ions or molecules of a solid.	The smallest unit of a crystal lattice is called unit cell. Repeated unit cells form crystal lattice.
 A portion of three dimensional lattice, lattice and its unit cell	 Parameters of a unit cell

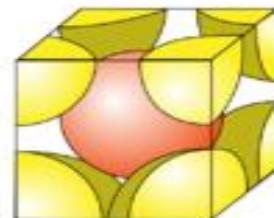
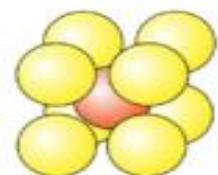
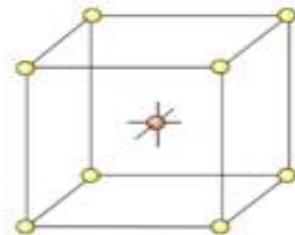
**Simple Cubic**

$$\text{Radius: } r = a/2$$

C.N. 6

$Z_{\text{eff}}$  1

P.F 52%

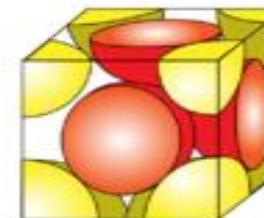
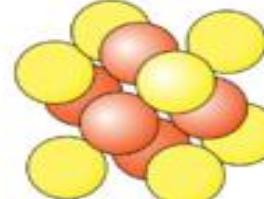
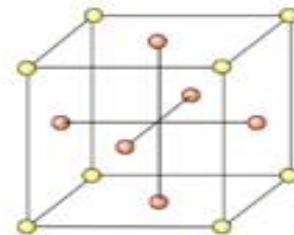
**Body-centered cubic**

$$r = \sqrt{3} a/4$$

8

2

68%

**Face-centered cubic**

$$r = \sqrt{2} a/4$$

12

4

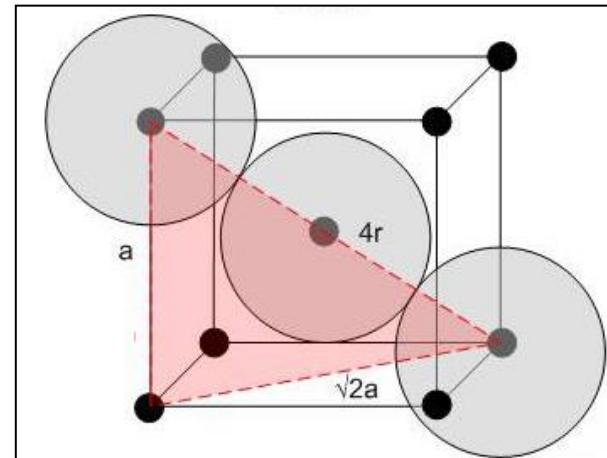
74%

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Where  $Z_{\text{eff}}$  is No. of atoms per unit cell.

P.F is Packing fraction, which is defined as the fraction of space occupied by atoms in a unit cell.

bcc



- In  $\Delta ABC$
- $$AC^2 = AB^2 + BC^2$$

**Atomic radius:**

BCC

$$AC^2 = a^2 + a^2$$

$$AC^2 = 2a^2$$

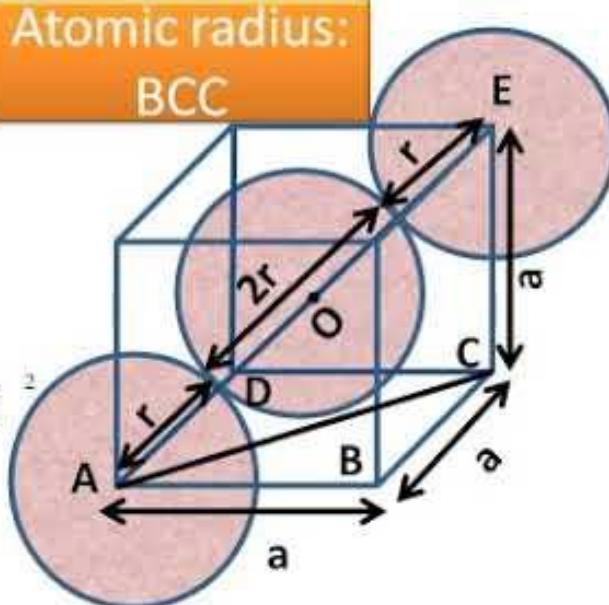
- In  $\Delta ACE$

$$AE^2 = AC^2 + CE^2$$

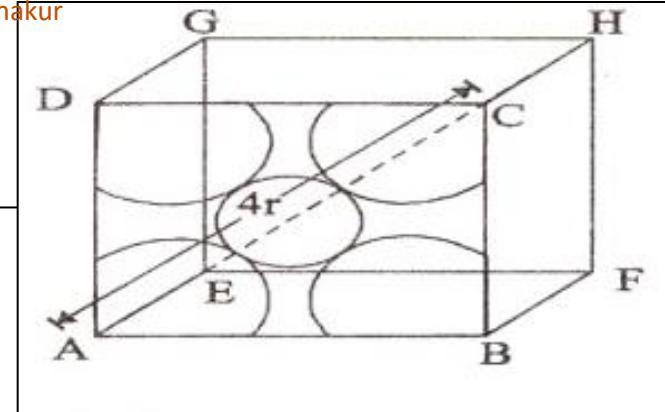
$$(4r)^2 = 2a^2 + a^2$$

$$16r^2 = 3a^2$$

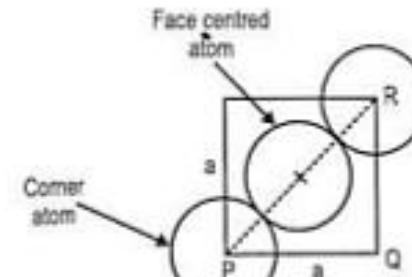
$$r = \frac{\sqrt{3}}{4}a$$



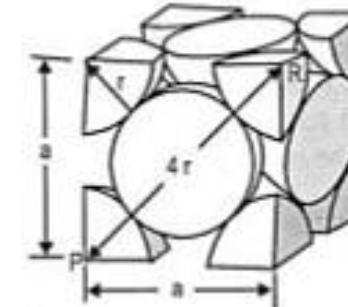
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• FCC



(a) Front view of unit cell



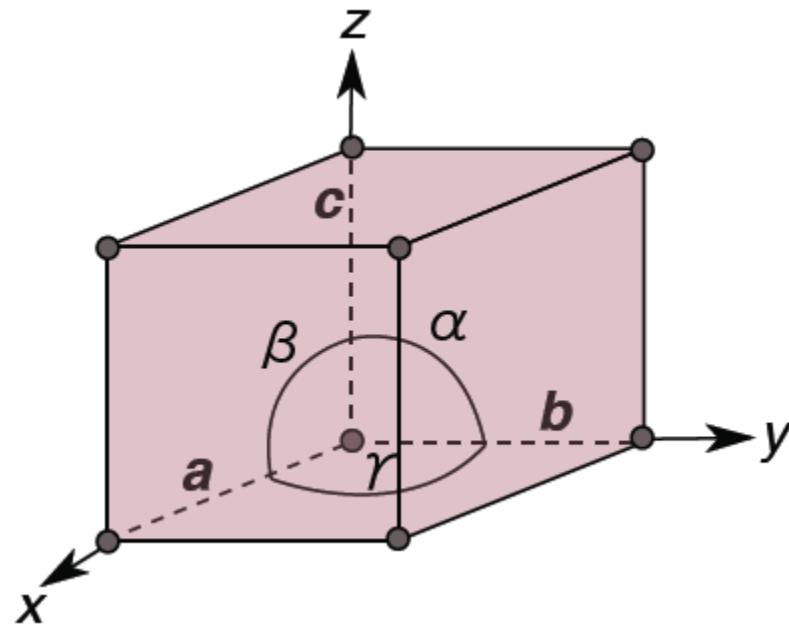
(b) Portion of atoms inside the FCC unit cell

From triangle PQR,  $PR^2 = PQ^2 + QR^2$

$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$a = \frac{4r}{\sqrt{2}}$$

# Lattice Parameters



$\text{OX, OY, OZ}$  are called Crystallographic axes.

Three sides of the unit cell  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  are called Primitives.

Angle between three crystallographic axes are called viz.  $\alpha$ ,  $\beta$ ,  $\gamma$ . Interfacial angles.

$\alpha \rightarrow$  angle between sides  $b$  and  $c$   
 $\beta \rightarrow$  angle between sides  $a$  and  $c$   
 $\gamma \rightarrow$  angle between sides  $a$  and  $b$

$(a, b, c)$  and  $(\alpha, \beta, \gamma)$  are collectively known as lattice parameters.

# Bravais Lattice

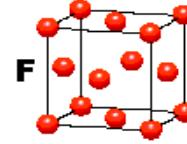
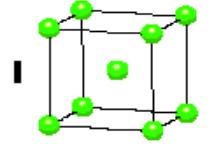
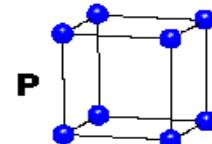
- There are **seven** fundamentally different types of unit cells, which vary in the relative edge lengths and the angles between them.
- There are **14 ways** of arranging identical points in 3-dim space, satisfying condition of periodicity, so that they are in every way equivalent to their surroundings.

**14 Bravais lattices = 7 primitives + 7 Non primitives**

# Bravais lattice (contd...)

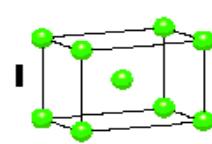
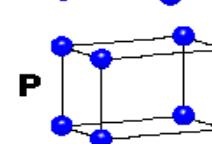
## CUBIC

$a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



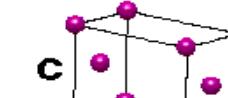
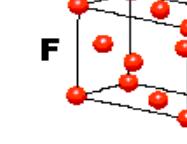
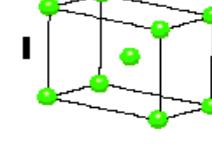
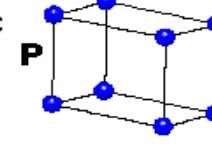
## TETRAGONAL

$a = b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



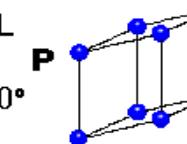
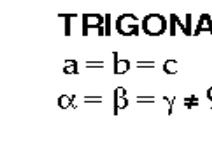
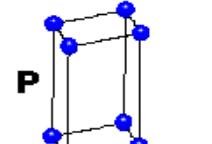
## ORTHORHOMBIC

$a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



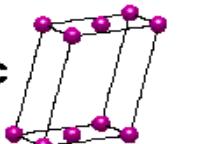
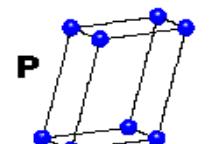
## HEXAGONAL

$a = b \neq c$   
 $\alpha = \beta = 90^\circ$   
 $\gamma = 120^\circ$



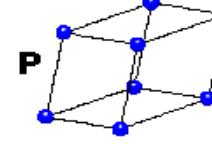
## MONOCLINIC

$a \neq b \neq c$   
 $\alpha = \gamma = 90^\circ$   
 $\beta \neq 120^\circ$



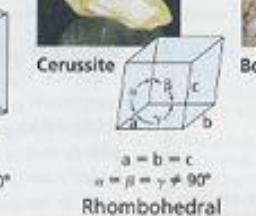
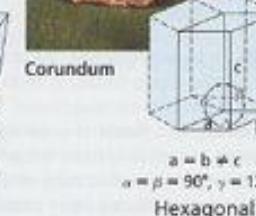
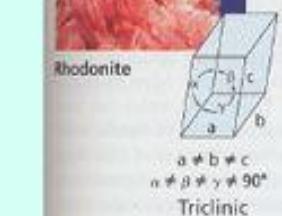
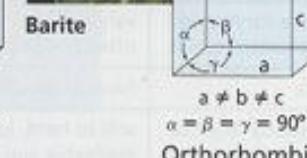
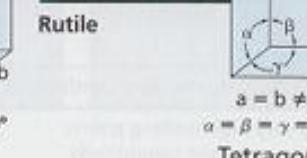
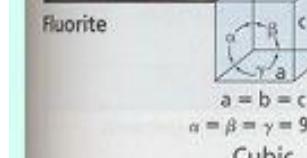
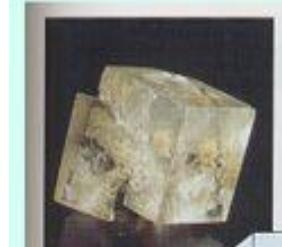
## TRICLINIC

$a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



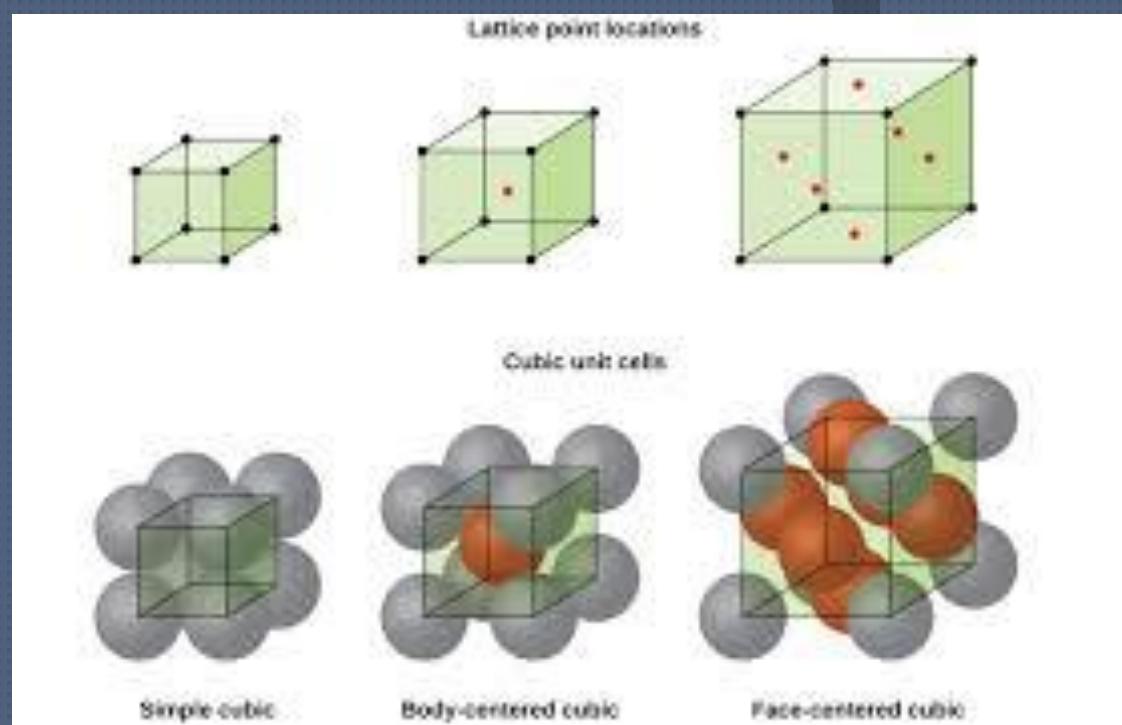
**4 Types of Unit Cell**  
**P**= Primitive  
**I**= Body-Centred  
**F**= Face-Centred  
**C**= Side-Centred  
+  
**7 Crystal Classes**  
**→ 14 Bravais Lattices**

## Seven Basic Crystal Systems



Crystals are classified into seven categories based on their overall shapes.

# Cubic Lattice



Dr. Vanita Thakur

**CRYSTAL LATTICE simple cubic**

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$

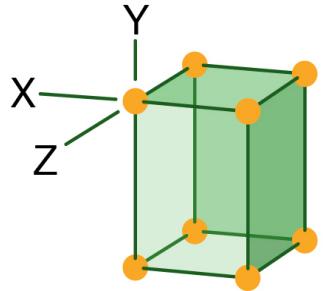
**CRYSTAL LATTICE body-centered cubic**

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$

**CRYSTAL LATTICE face-centered cubic**

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$

## Tetragonal crystal system



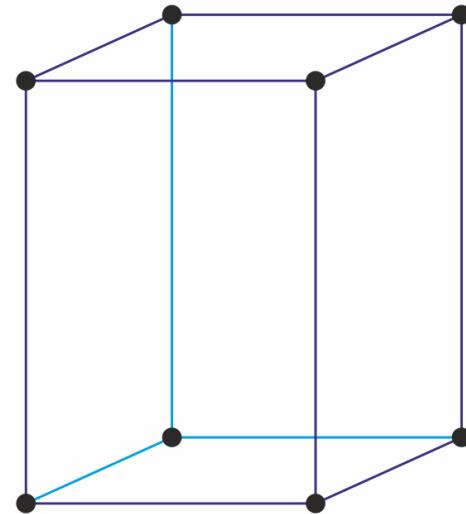
Two of the three axes are equal in length, and all three axes are perpendicular to one another.

Its one variant is:

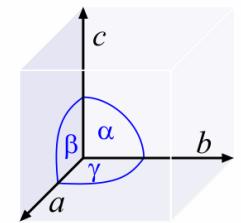
### Body-centred tetragonal

lattice point in the middle of the unit cell

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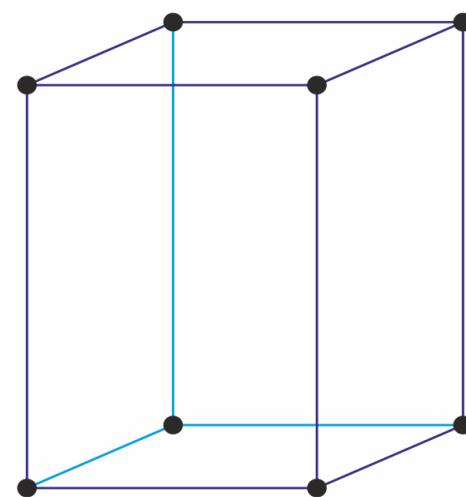


CRYSTAL LATTICE  
simple tetragonal

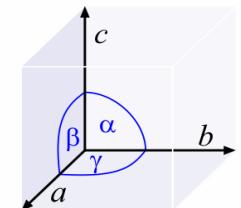


$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$



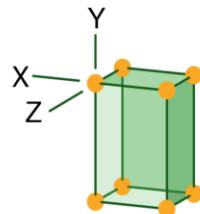
CRYSTAL LATTICE  
simple tetragonal



$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

## Orthorhombic crystal system



All three axes are unequal in length, and all are perpendicular to one another.

Its three variants are:

### Body-centred orthorhombic

lattice point in the middle of the unit cell

### Base-centred orthorhombic

lattice points in the middle of each of the two ends

### Face-centred orthorhombic

lattice points in the middle of each side

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## ■ Orthorhombic:

### Number of Bravais lattices

**simple**

**body-centered**

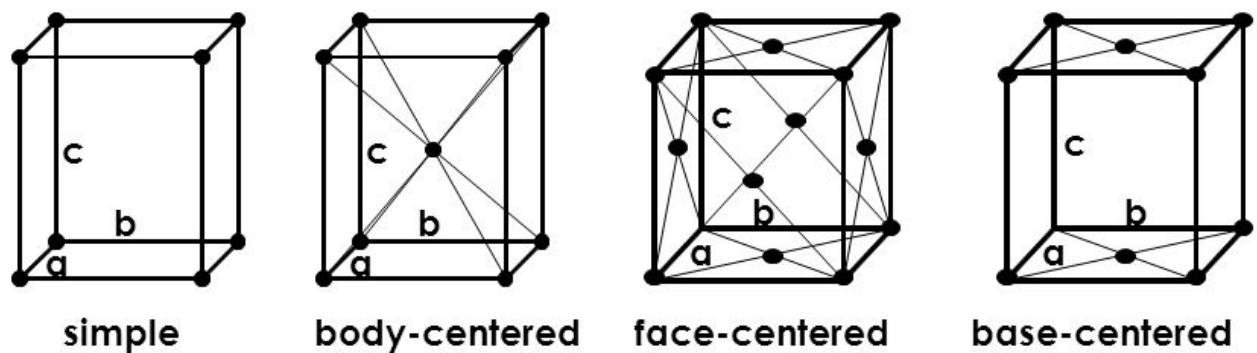
**face-centered**

**base-centered**

### Conditions

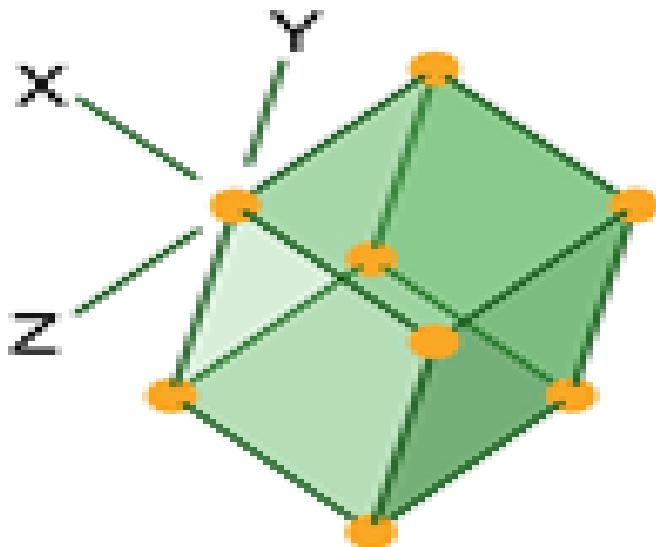
$a_1 \neq a_2 \neq a_3$

$\alpha = \beta = \gamma = 90^\circ$

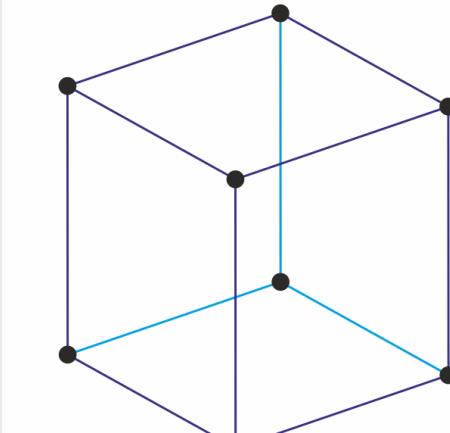


## Rhombohedral (or trigonal)\*

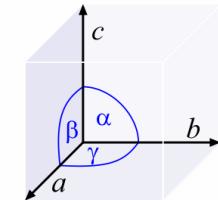
All three axes are of equal length, and none of the axes is perpendicular to another, but the crystal faces all have the same size and shape.



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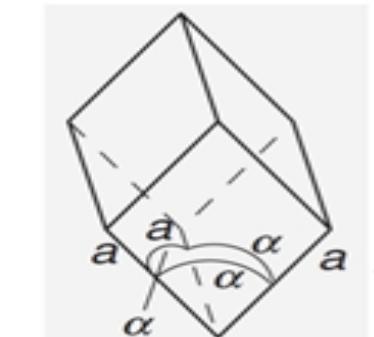
CRYSTAL LATTICE  
rhombohedral



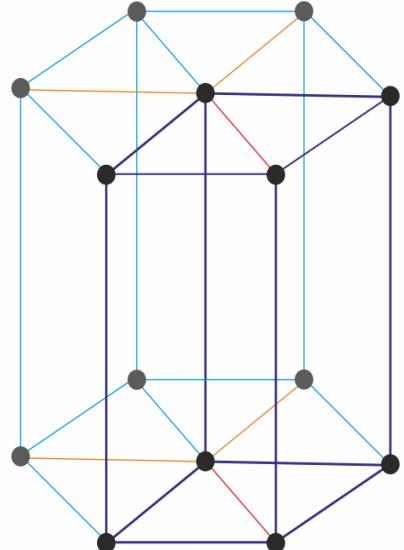
$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

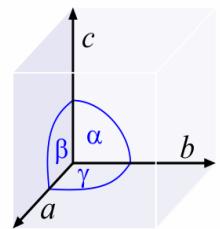
$$a = b = c \\ \alpha = \beta = \gamma \neq 90^\circ$$



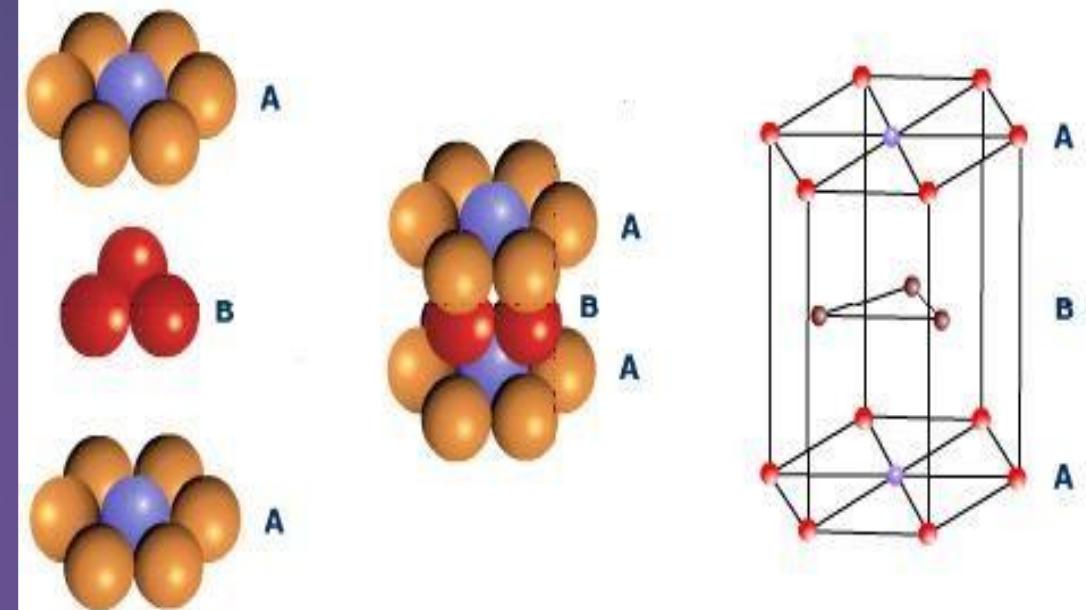
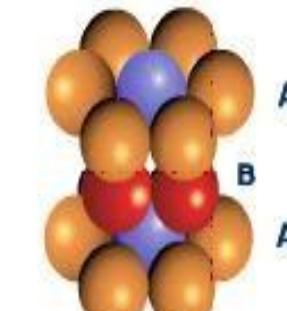
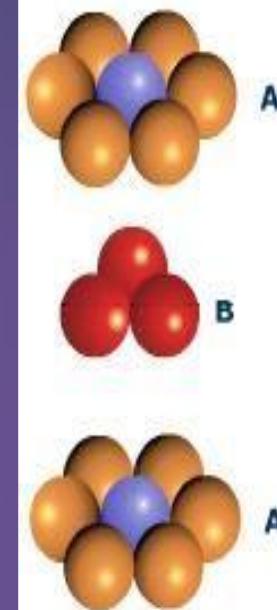
Example:  $\text{CaCO}_3$ ,  
 $(6.36\text{\AA}, 6.36\text{\AA}, 6.36\text{\AA}, 46.1^\circ, 46.1^\circ, 46.1^\circ)$



CRYSTAL LATTICE  
hexagonal

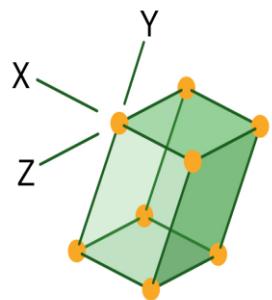


$$a = b \neq c \\ \alpha = \beta = 90^\circ \quad \gamma = 120^\circ$$



# Hexagonal Lattice

## Monoclinic crystal system



All three axes are unequal in length, and two axes are perpendicular to each other.

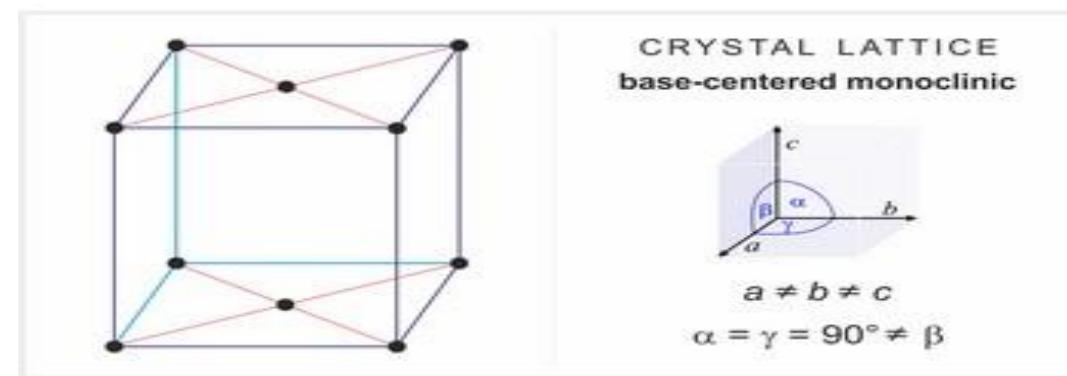
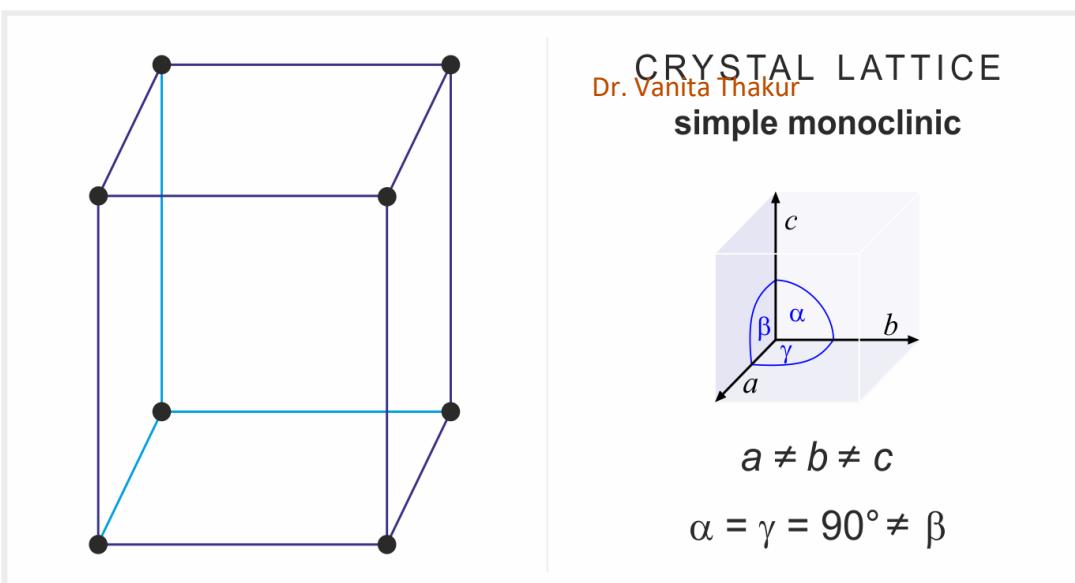
Its one variant is:

$$a \neq b \neq c$$

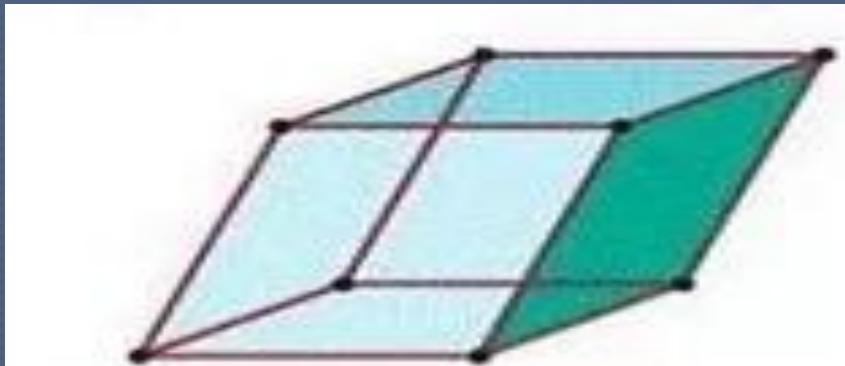
### Base-centred monoclinic

lattice points in the middle of each of the two ends

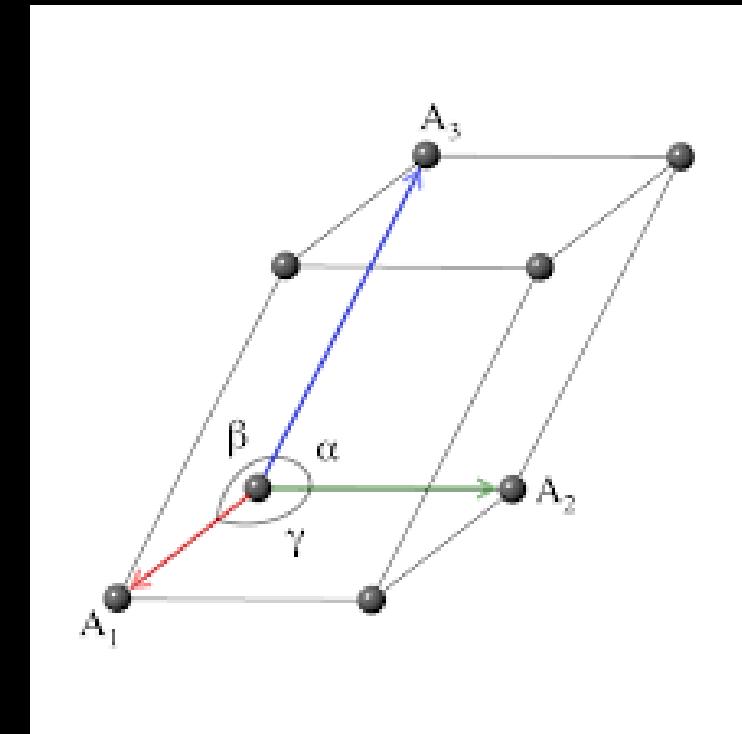
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# Triclinic

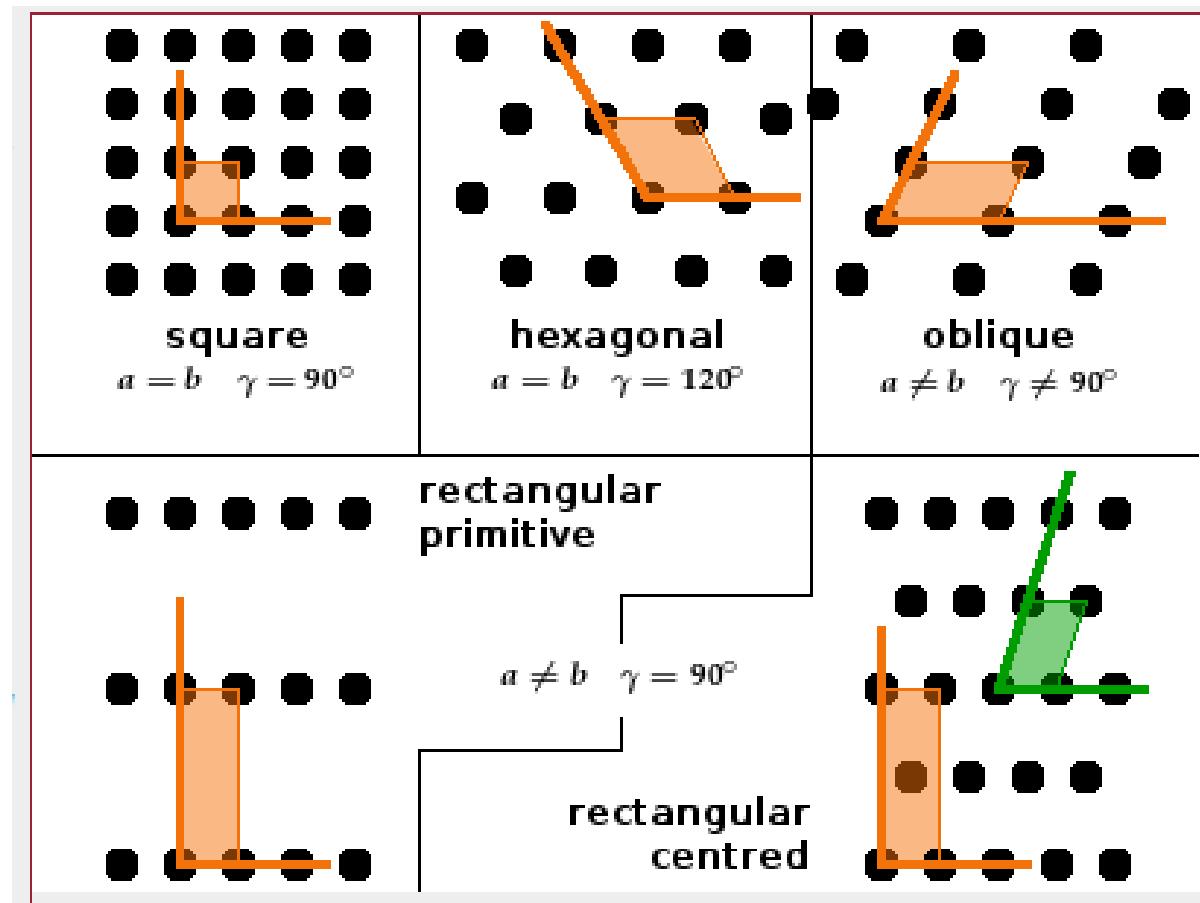


**Triclinic**  
 $a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



Name	Number of Bravais lattices	Conditions © Bart Van Zeghem 2007	Primitive	Base-centered	Body-centered	Face-centered
Triclinic	1	$a_1 \neq a_2 \neq a_3, \alpha \neq \beta \neq \gamma$	✓			
Monoclinic	2	$a_1 \neq a_2 \neq a_3, \alpha = \beta = 90^\circ \neq \gamma$	✓	✓		
Orthorhombic	4	$a_1 \neq a_2 \neq a_3, \alpha = \beta = \gamma = 90^\circ$	✓	✓	✓	✓
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$	✓		✓	
Cubic	3	$a_1 = a_2 = a_3, \alpha = \beta = \gamma = 90^\circ$	✓		✓	✓
Trigonal	1	$a_1 = a_2 = a_3, \alpha = \beta = \gamma < 120^\circ \neq 90^\circ$	✓			
Hexagonal	1	$a_1 = a_2 \neq a_3, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	✓			

# Bravais lattices in two dimensions



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Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2, \alpha = 90^\circ$
Rectangular	2	$a_1 \neq a_2, \alpha = 90^\circ$
Hexagonal	1	$a_1 = a_2, \alpha = 120^\circ$
Oblique	1	$a_1 \neq a_2, \alpha \neq 120^\circ, \alpha \neq 90^\circ$

# Miller Planes



# Miller Indices (hkl)

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- Many physical properties of crystalline solids are anisotropic i.e. depend upon directions within the crystal. Therefore, there was need to specify planes in the crystal.
- For this purpose, a British mineralogist W.H. Miller (in 1839) devised a system known as Miller indices.
- Miller indices are group of three numbers that indicates the orientation of a plane or set of parallel planes of atoms in a crystal.

## Determination of Miller Indices

- Determine the intercepts of the face along the crystallographic axes, in terms of unit cell dimensions.
- Take the reciprocals.
- Clear fractions.
- Reduce to lowest terms.

Lets see an example in next slide....

# Procedure for finding Miller indices:

## Step 1:

Find the intercepts of the plane along the axes x, y, z which are 4, 2, 3.

## Step 2:

Take reciprocals of the intercepts.

$$1/4, 1/2, 1/3$$

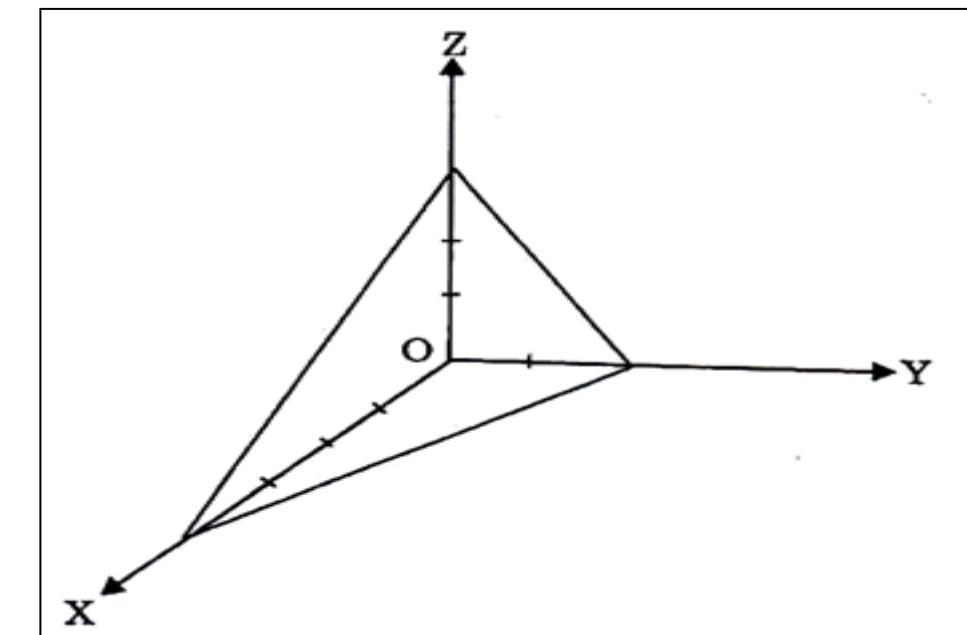
## Step 3:

Convert into smallest integers in the same ratio.

$$3 \ 6 \ 4$$

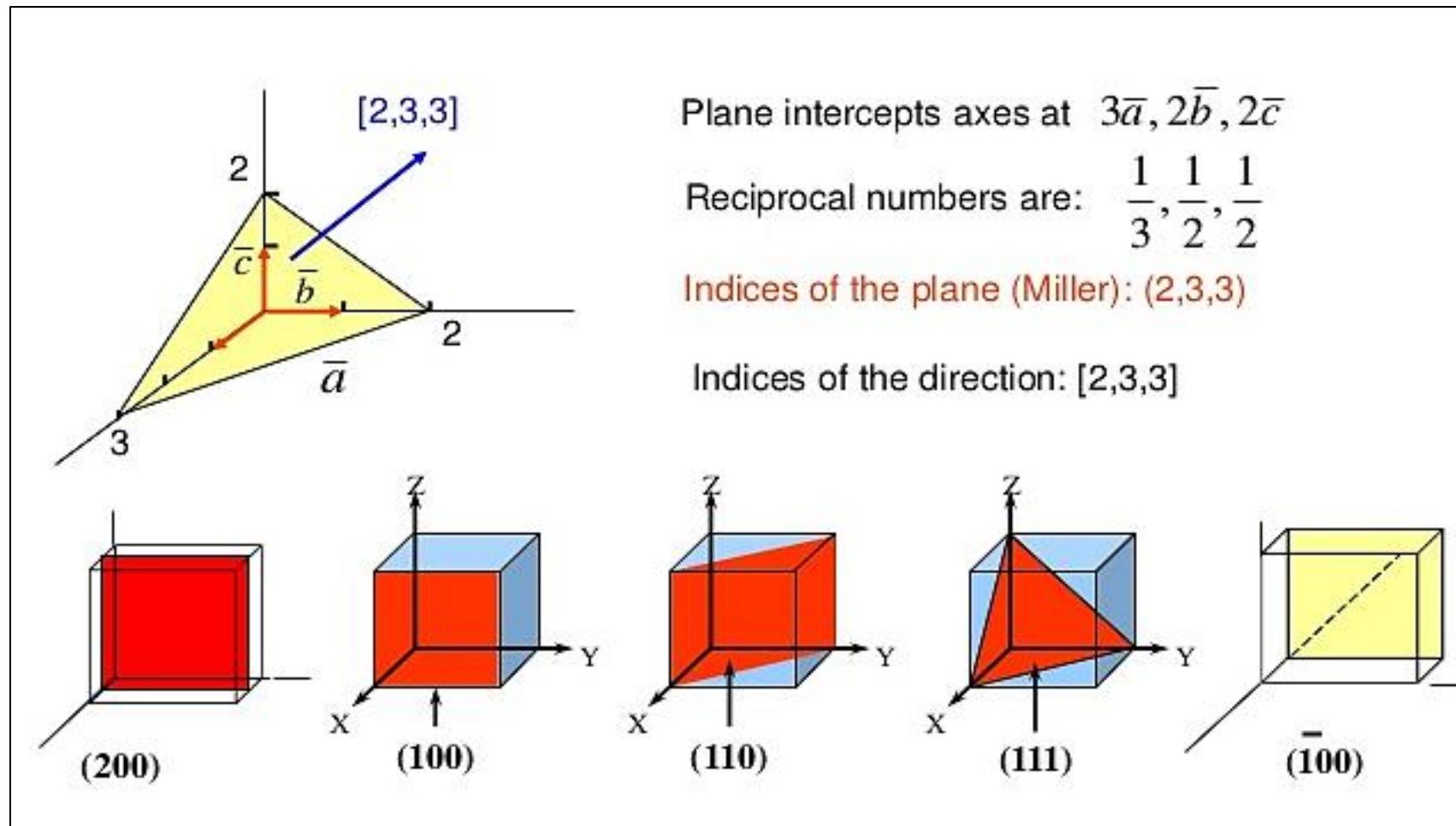
## Step 4:

Enclose in parentheses. ... (3 6 4)

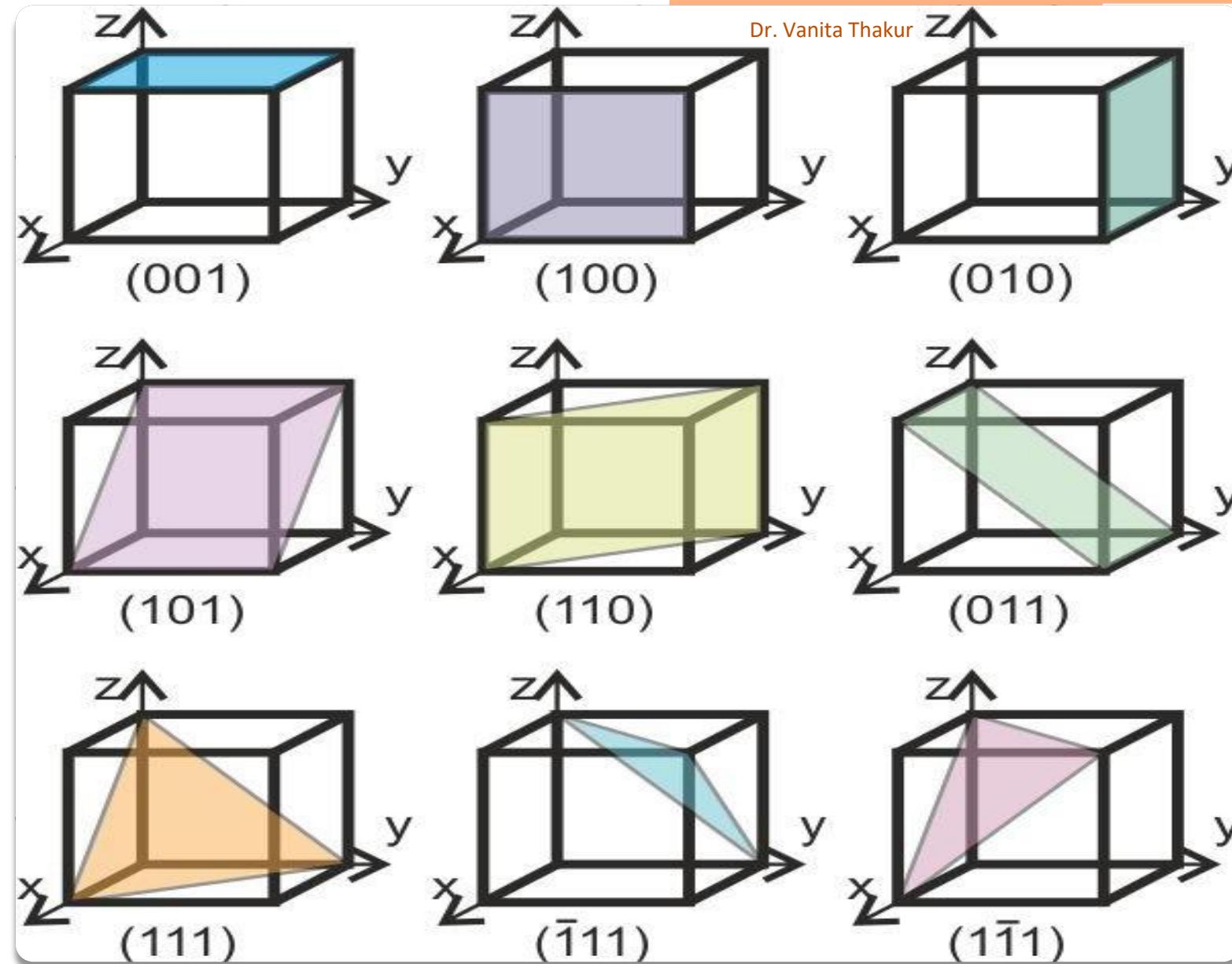


# Another Example:

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# Different Planes



# Points to remember:

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- The **directions** in space are represented by square brackets [x y z].
- The **indices of a plane** are represented by a small bracket, (h, k l).
- Commas are not used. (1 1 0) is read as “One-one-zero” and not “one hundred ten”.
- Negative indices are represented by putting a bar over digit, e.g. ( $\bar{1}\bar{1}0$ ).
- When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas for clarity, e.g. (3, 11, 12).
- Family of planes is represented with curly brackets { } e.g.  
**(100), (010), (001), ( $\bar{1}00$ ), ( $0\bar{1}0$ ), ( $00\bar{1}$ ) are grouped as {100}**

Similarly, the directions are grouped as <100>

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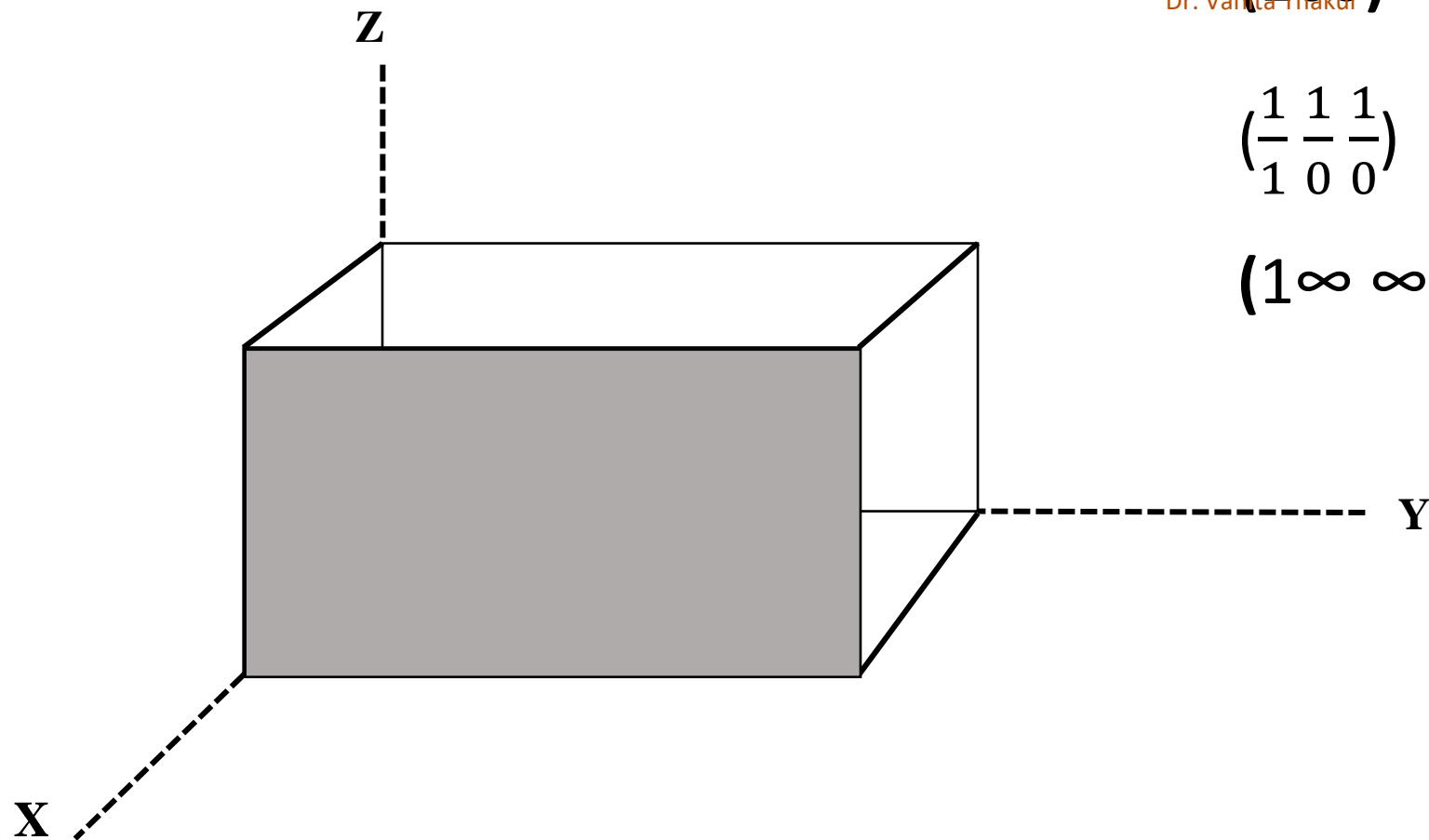
**Let's Learn How To Draw These  
Planes**

(100)

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$$\left( \frac{1}{1} \frac{1}{0} \frac{1}{0} \right)$$

$$(1\infty\infty)$$

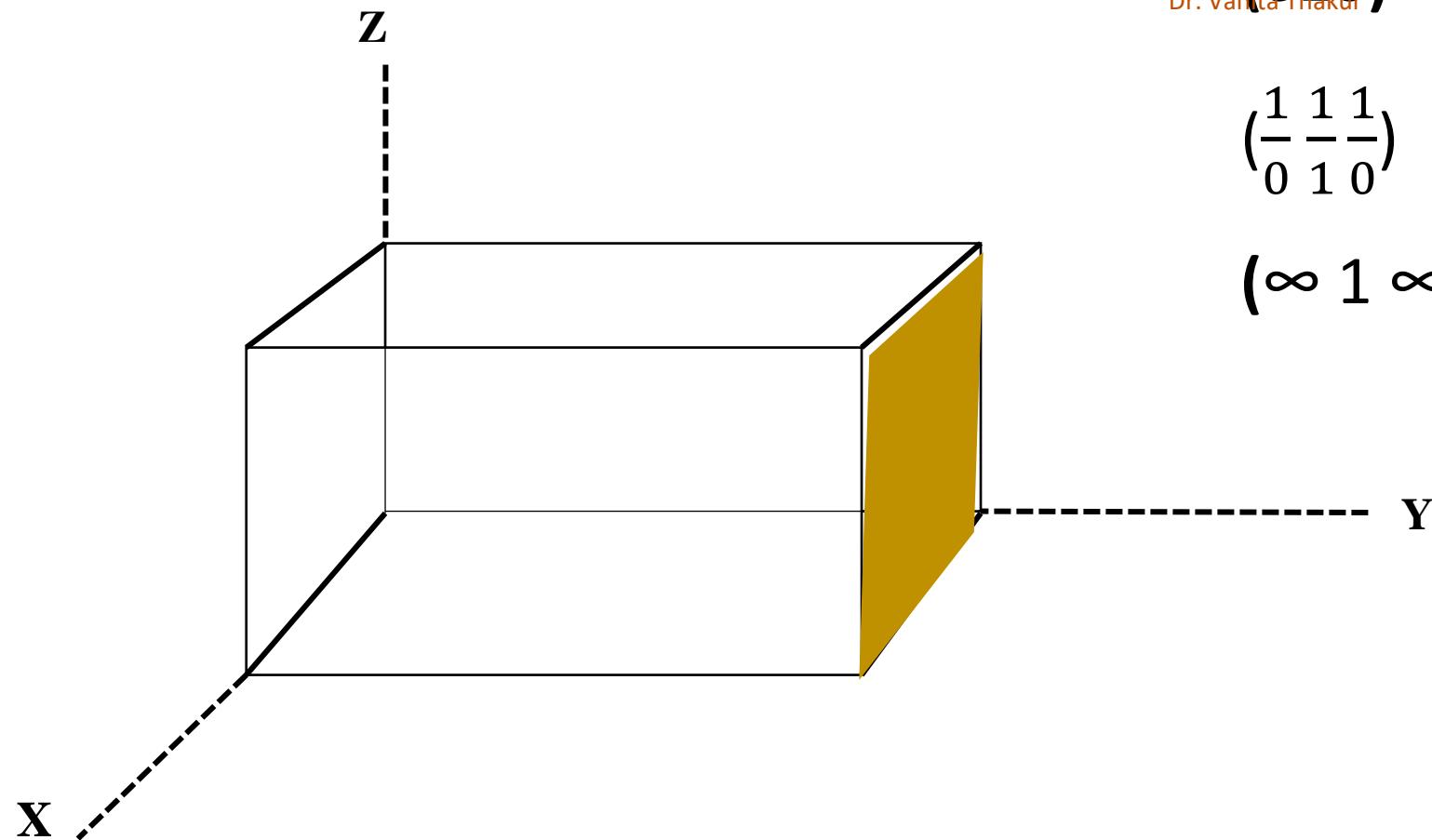


**(010)**

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$$\left( \frac{1}{0} \frac{1}{1} \frac{1}{0} \right)$$

$$(\infty 1 \infty)$$

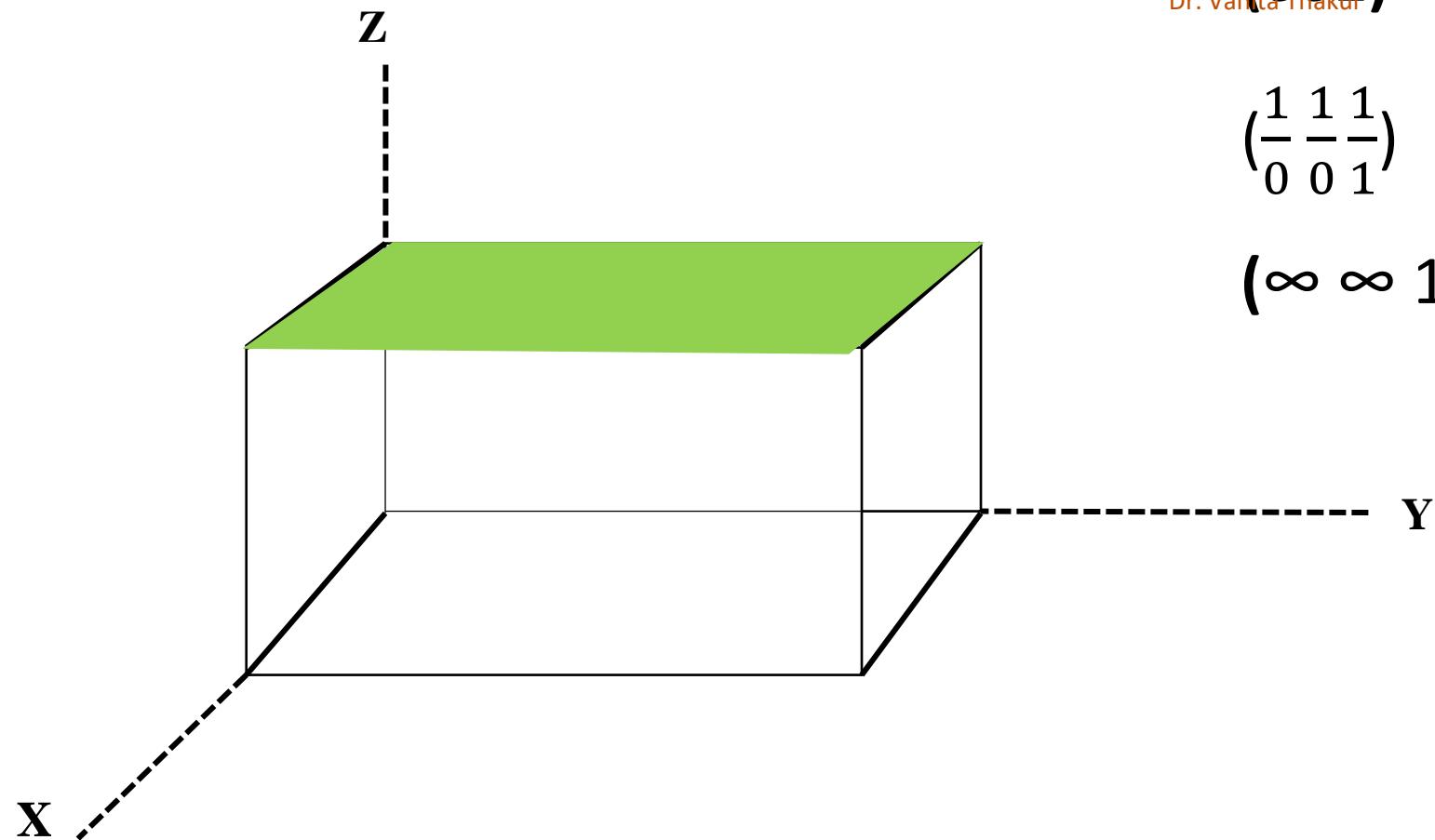


**(001)**

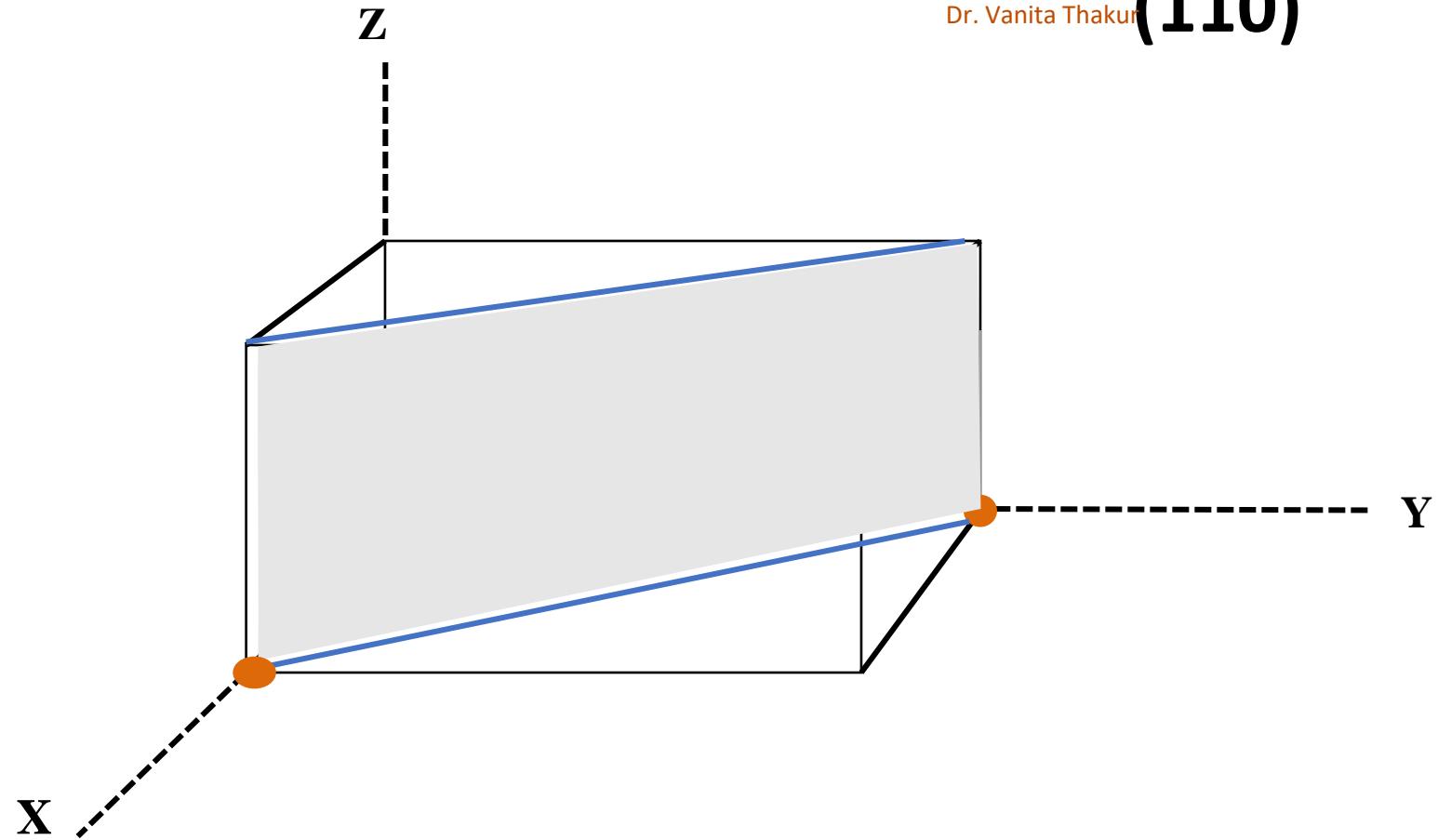
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$$\left(\frac{1}{0} \frac{1}{0} \frac{1}{1}\right)$$

$$(\infty \infty 1)$$

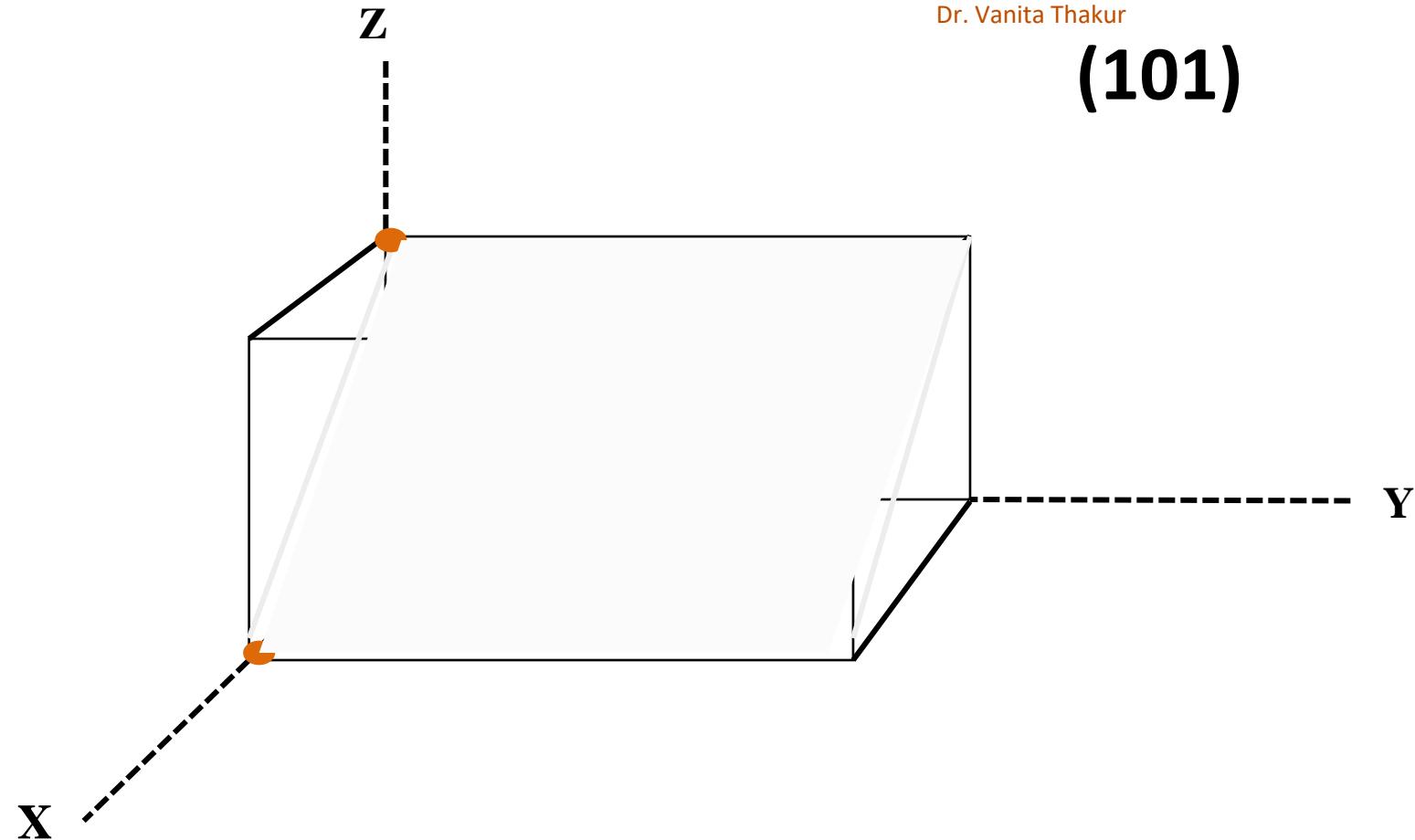


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**(110)**



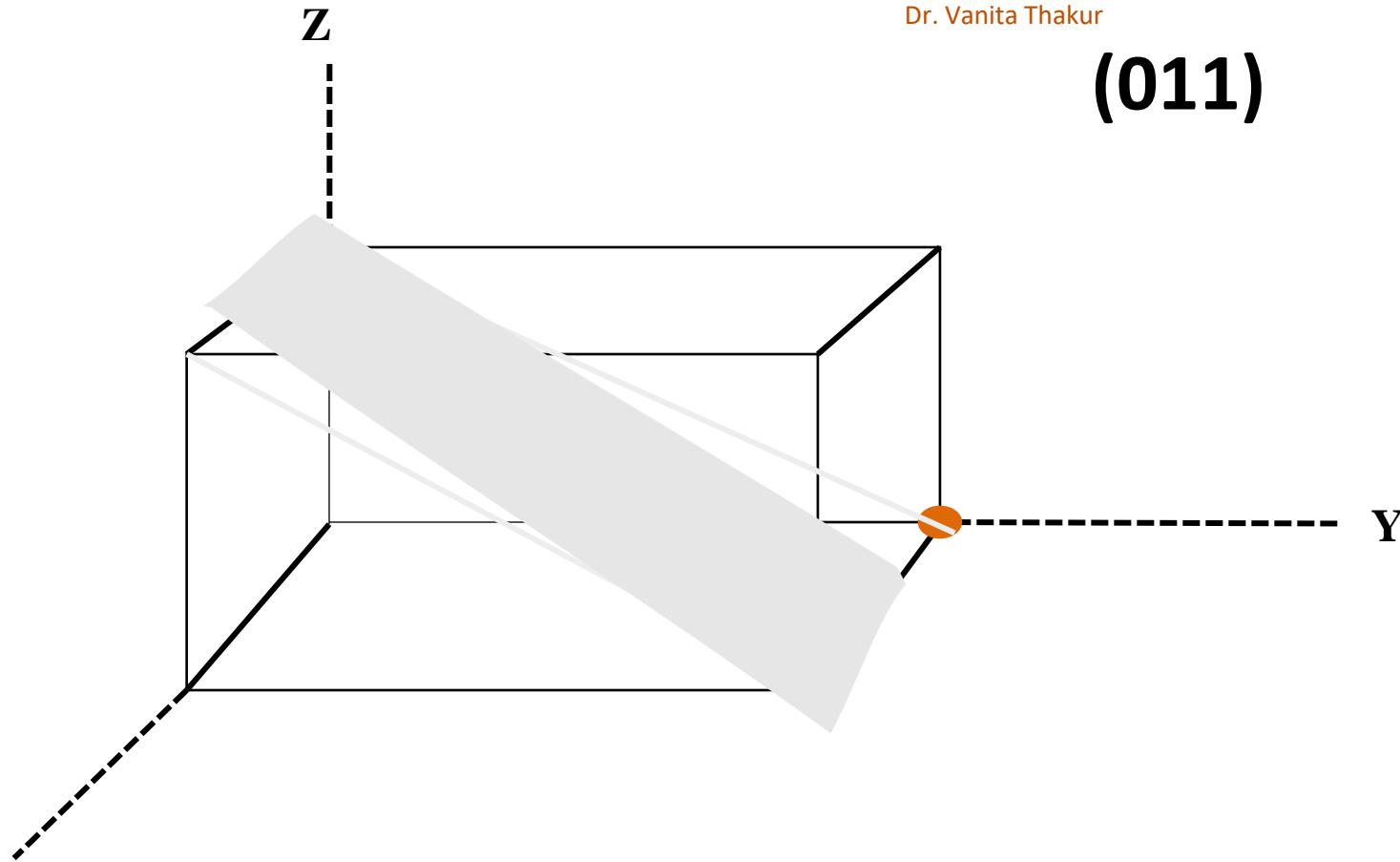
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**(101)**



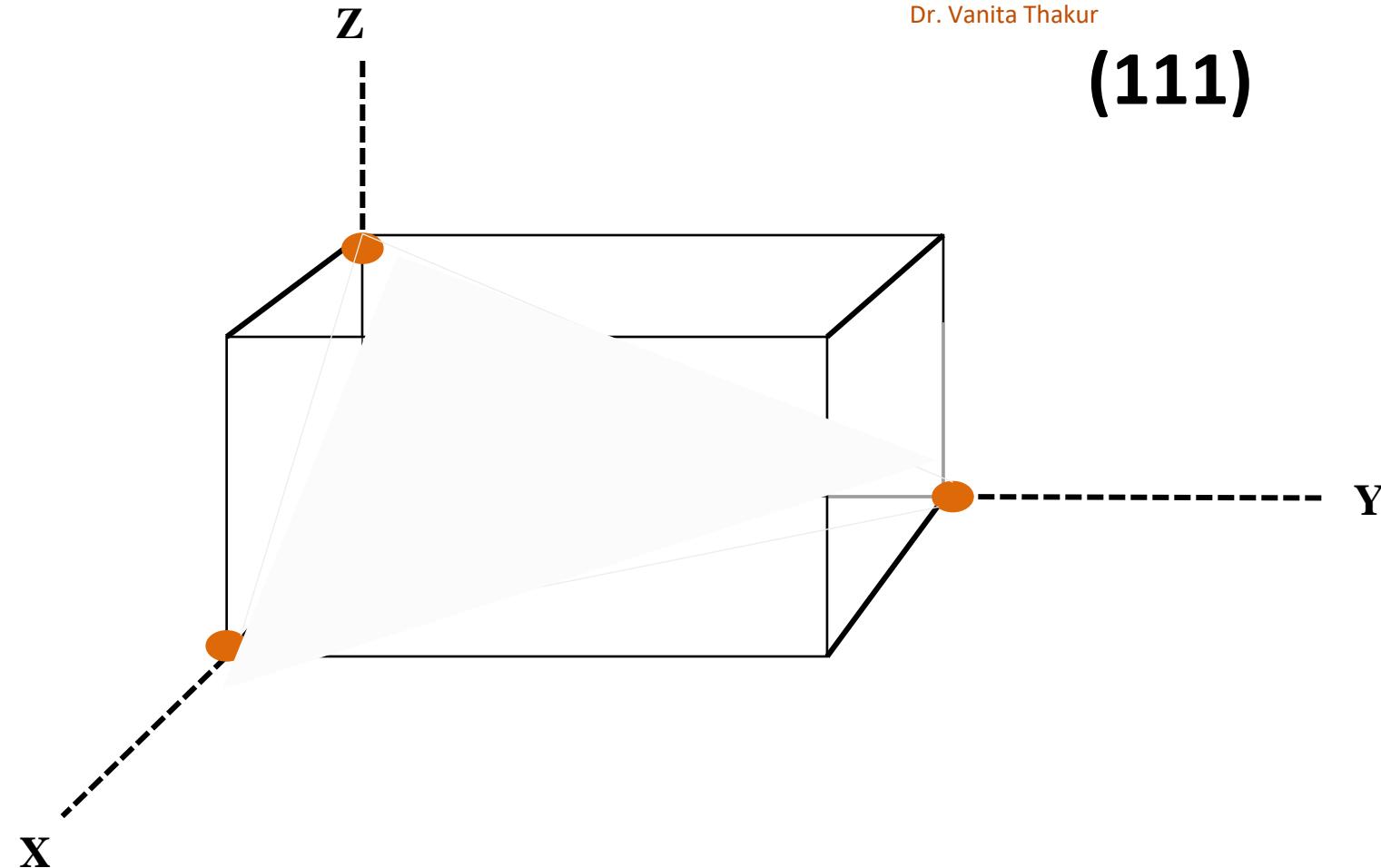
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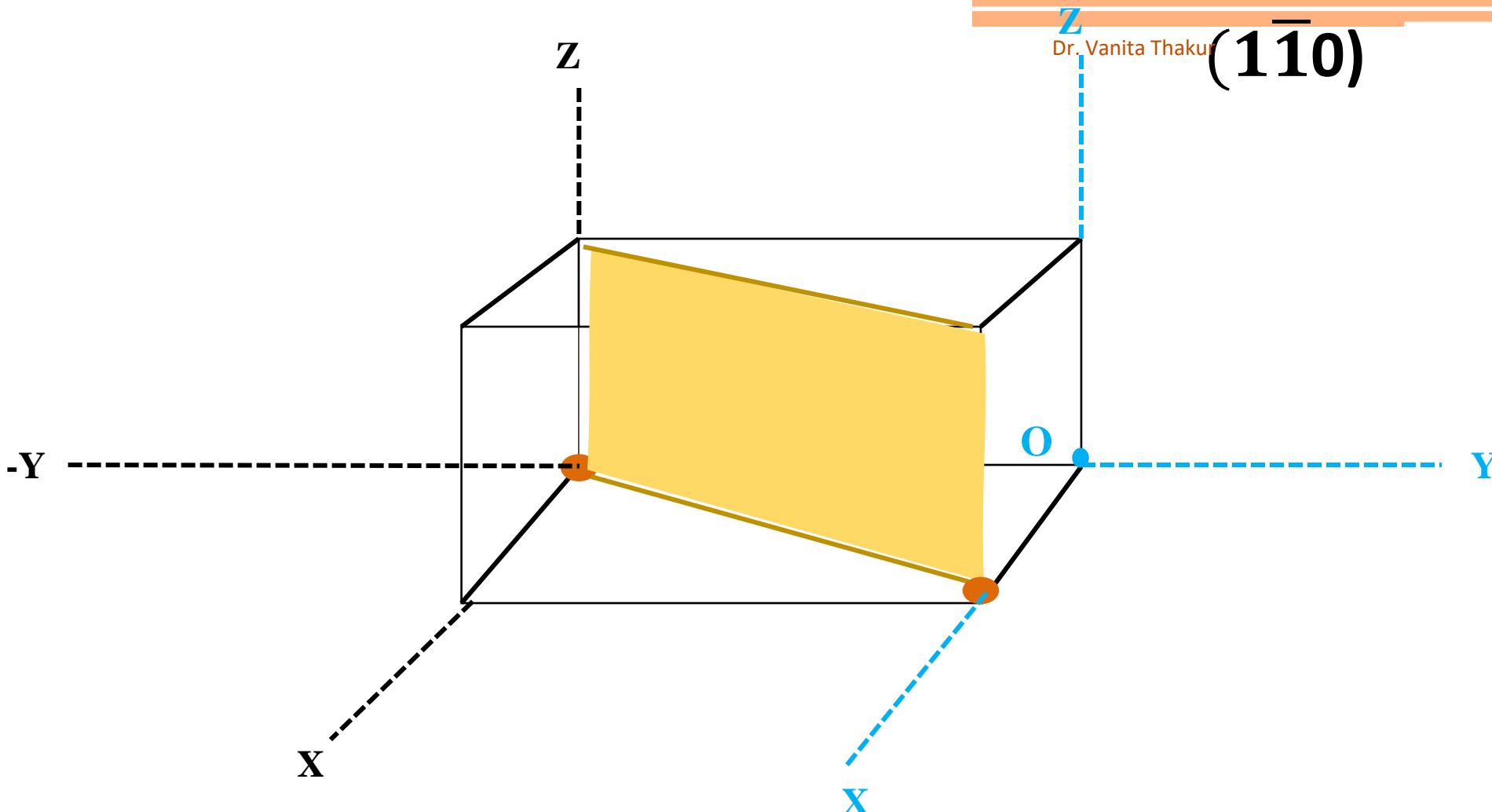
**(011)**



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**(111)**





Z

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(1 $\bar{1}$ 0)

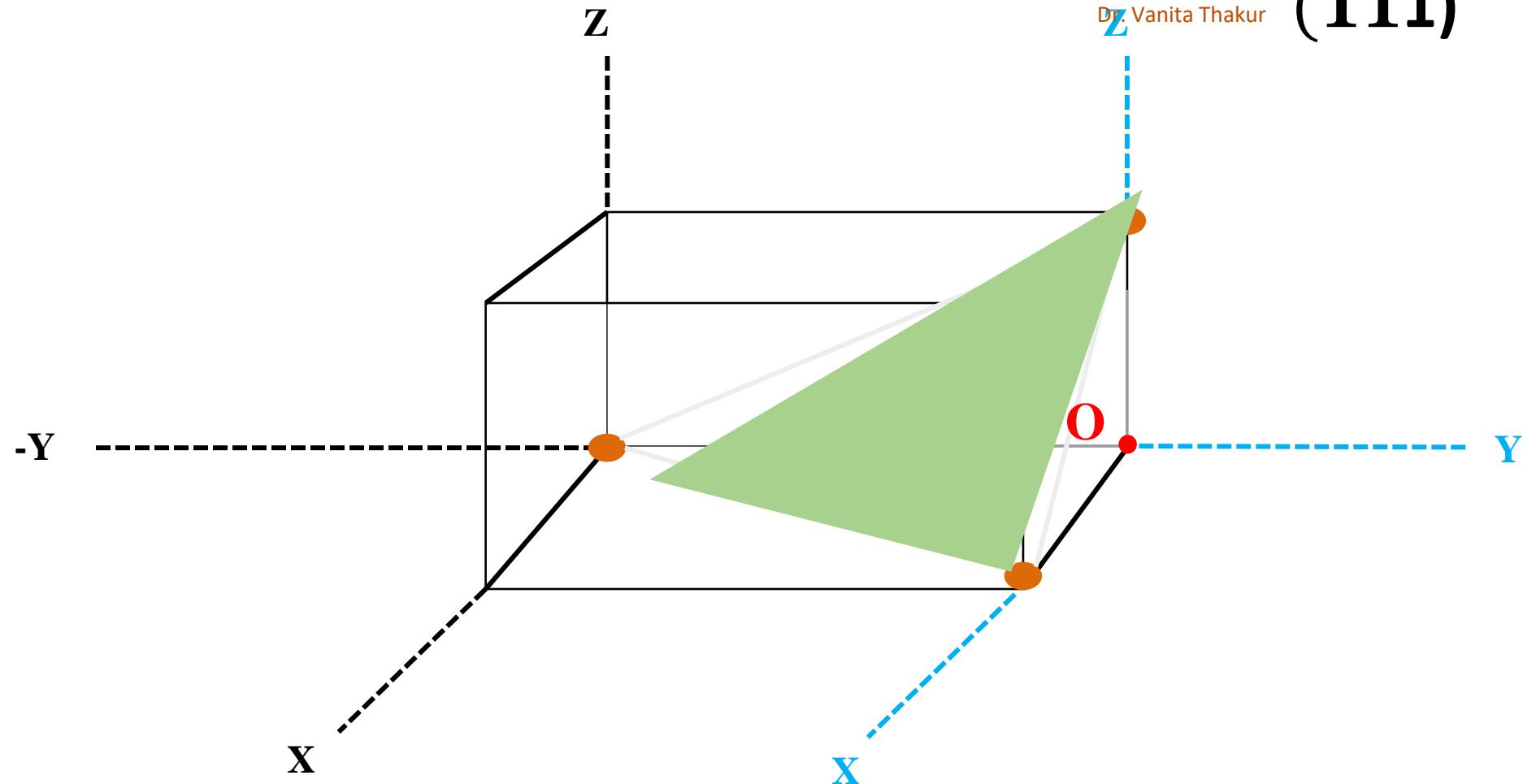
-Y

X

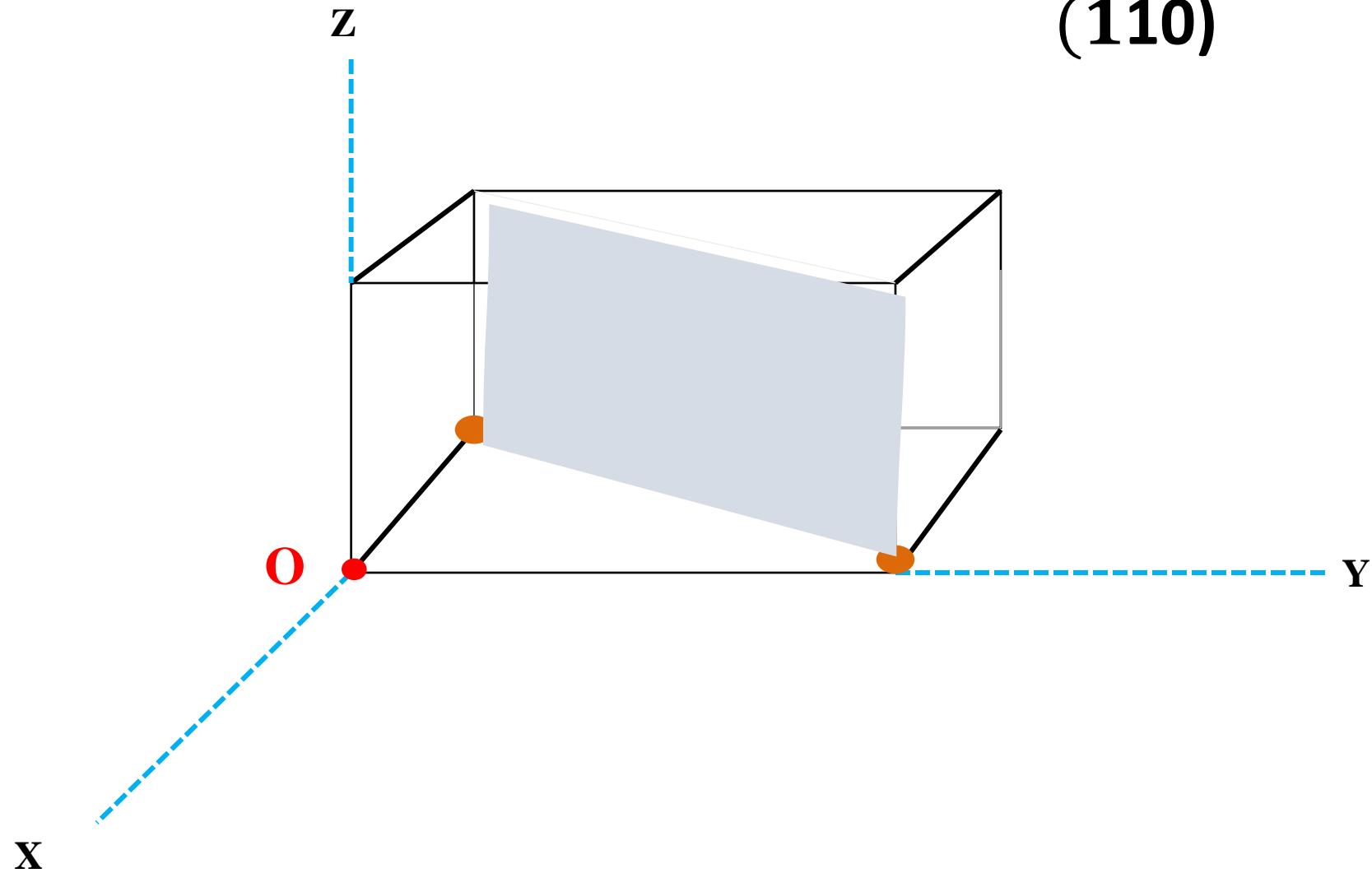
O

Y

X



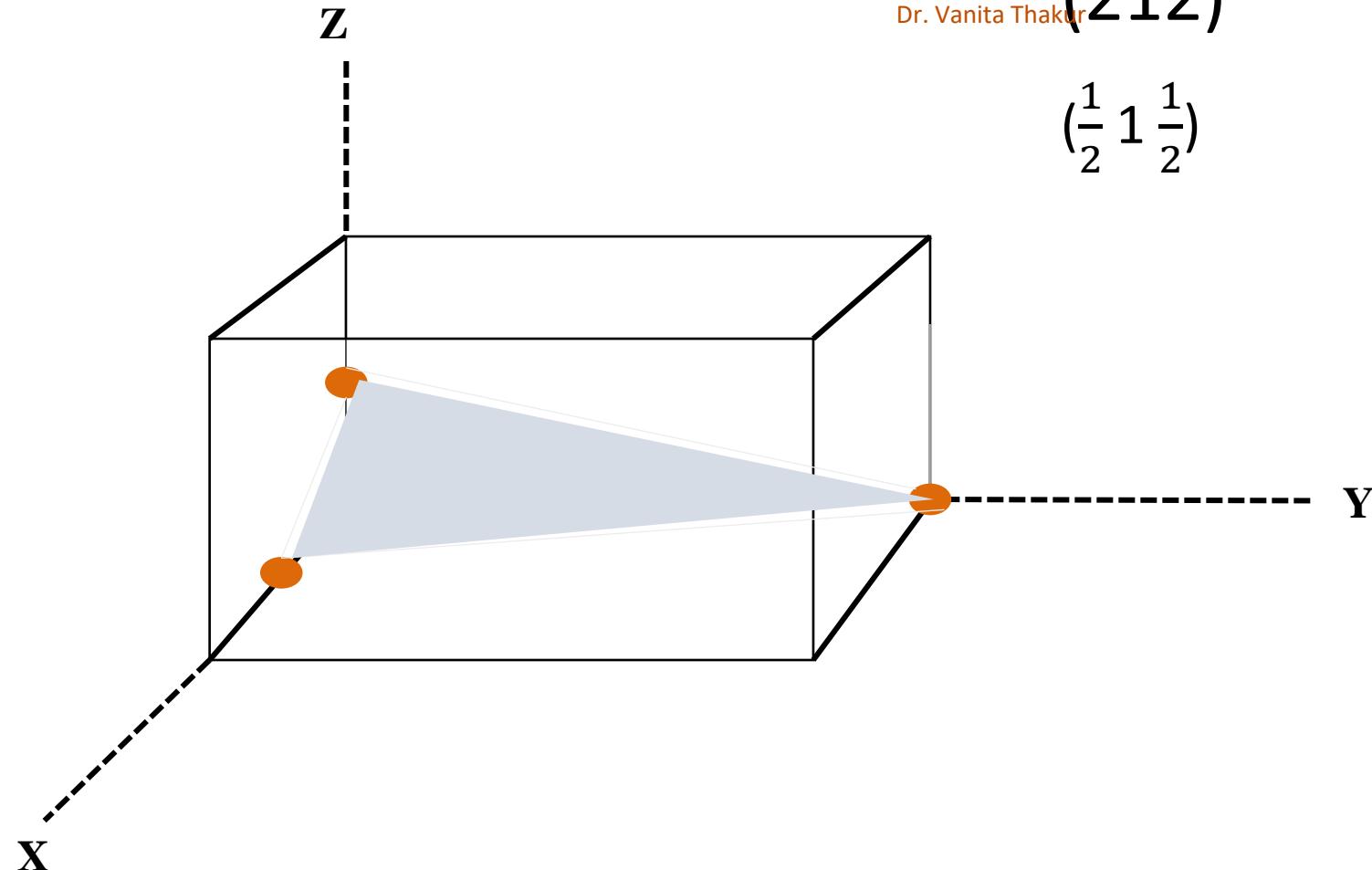
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**(110)**



(212)

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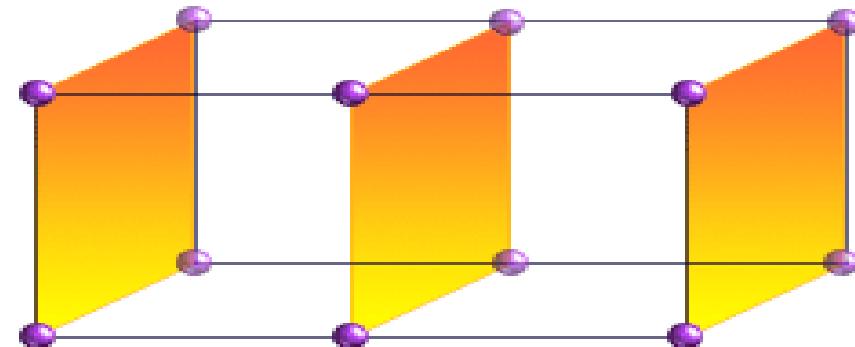
$$\left(\frac{1}{2} \ 1 \ \frac{1}{2}\right)$$



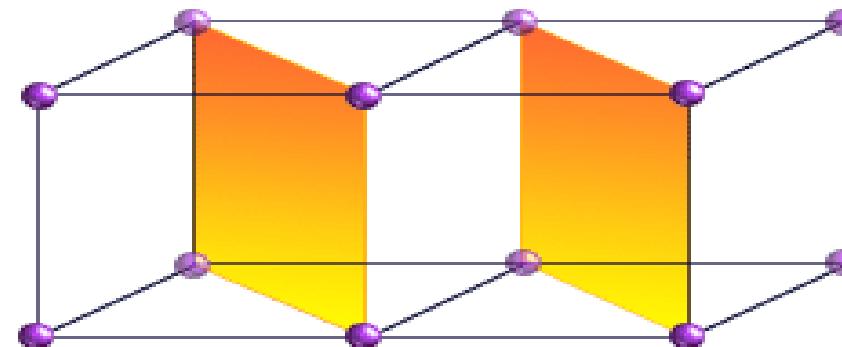
# Important Features of Miller Indices:

1. A plane parallel to one of the coordinate axes has an intercept of infinity and therefore, the Miller index for that axis is zero.
2. Miller indices do not only define particular plane but a set of parallel planes.
3. All the parallel equidistant planes have the same Miller indices. Thus, the Miller indices define a set of parallel planes i.e. (211) and (422) are the same, it is the ratio of indices which is only of importance.
4. If  $(h k l)$  are the Miller indices of a plane, then the plane cuts the axes into  $a/h$ ,  $b/k$  and  $c/l$  segments respectively.
5. The distance  $d$  between adjacent planes of the indices  $(h k l)$  is given by-  
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
where  $a$  is the edge of the cube.

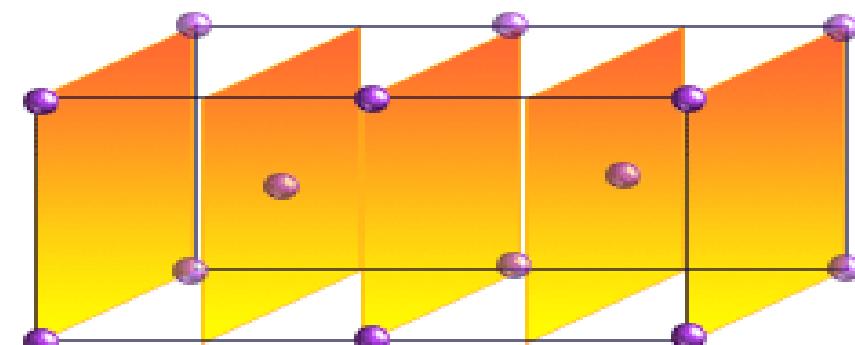
## Lattice Planes in Cubic Crystal



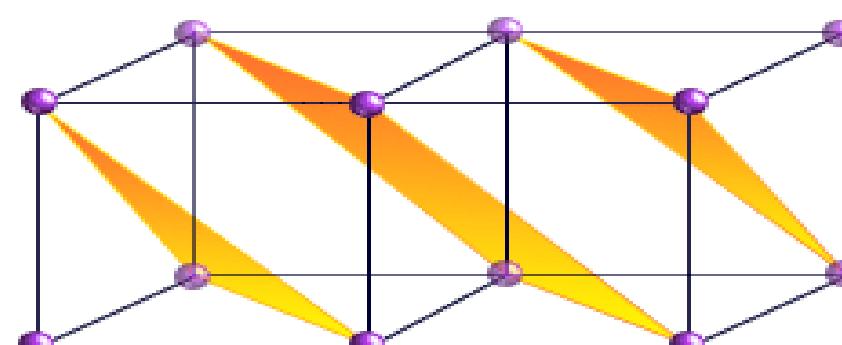
(1 0 0) Planes



(1 1 0) Planes



(2 0 0) Planes



(1 1 1) Planes

# Interplanar spacing

distance  $d \rightarrow$  b/w successive lattice planes is known as interplanar spacing.

Consider the fig. shown.

If this plane is rep. by M.I.  $(hkl)$   
then co-ords. of A, B & C will be  
 $\left(\frac{a}{h}, 0, 0\right), \left(0, \frac{b}{k}, 0\right) + \left(0, 0, \frac{c}{l}\right)$

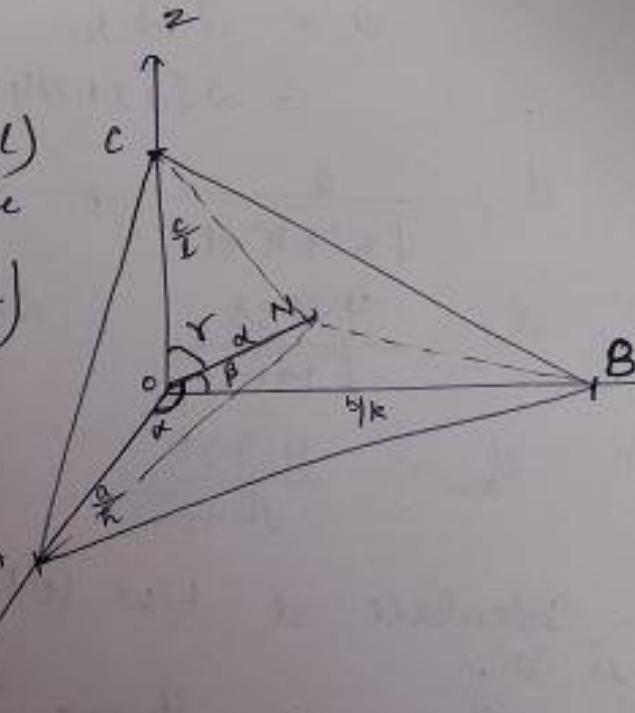
Let  $ON = d \rightarrow$  dist b/w two planes.

&  $\alpha, \beta + r \rightarrow$  angles made  
by  $ON$  with  $ox, oy + oz$

$$\cos^2\alpha + \cos^2\beta + \cos^2r = 1 \quad (\text{law of direction cosines})$$

from fig.

$$\cos\alpha = \frac{QN}{OA} = \frac{d}{ah}$$



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from fig.  $\cos\alpha = \frac{ON}{OA} = \frac{d}{a/h}$

~~PR.E.3~~

$$\cos\beta = \frac{ON}{OB} = \frac{d}{b/k}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{d}{c/l}$$

Subs. in ①

$$\frac{d^2}{a^2/h^2} + \frac{d^2}{b^2/k^2} + \frac{d^2}{c^2/l^2} = 1$$

$$d^2 \left[ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] = 1$$

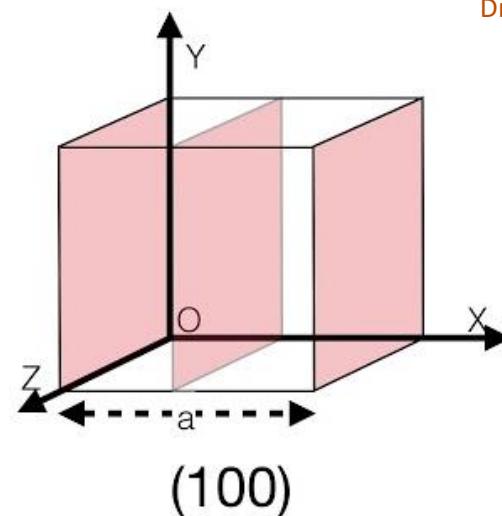
$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

for cubic system,  $a = b = c$

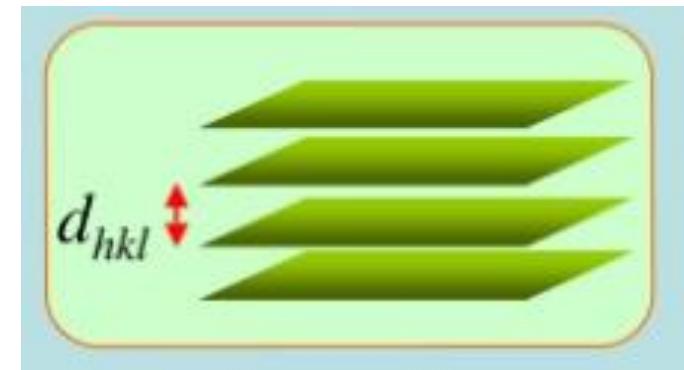
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

# Interplanar Spacing

$$d = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$



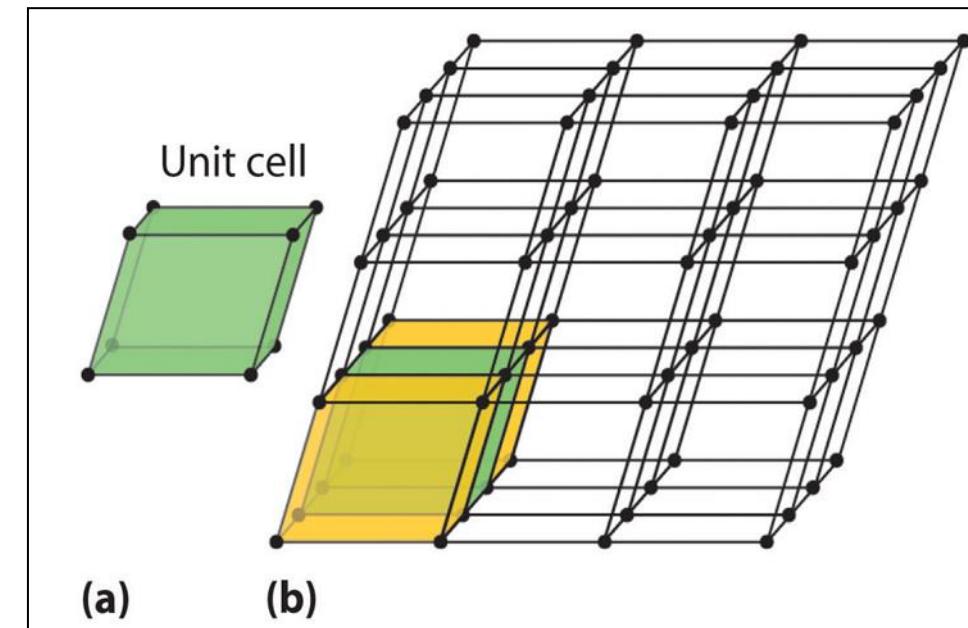
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Since for cubic system,  $a = b = c$

Therefore, interplanar spacing for cubic system is given by:

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



Lattice parameters of  $\text{Bi}_2\text{Fe}_4\text{O}_9$ :  $a=0.794 \text{ nm}$ ,  $b=0.844 \text{ nm}$ ,  $c=0.601 \text{ nm}$

Find the value of

$$d_{(141)}$$

$$d_{(330)}$$

**Answer:**

$$d_{(141)} = 0.1931 \text{ nm}$$

$$d_{(330)} = 0.1928 \text{ nm}$$

Copper, fcc,  $a = 3.61 \text{ \AA}$

Find the value of

$$d_{200}$$

$$d_{220}$$

$$d_{111}$$

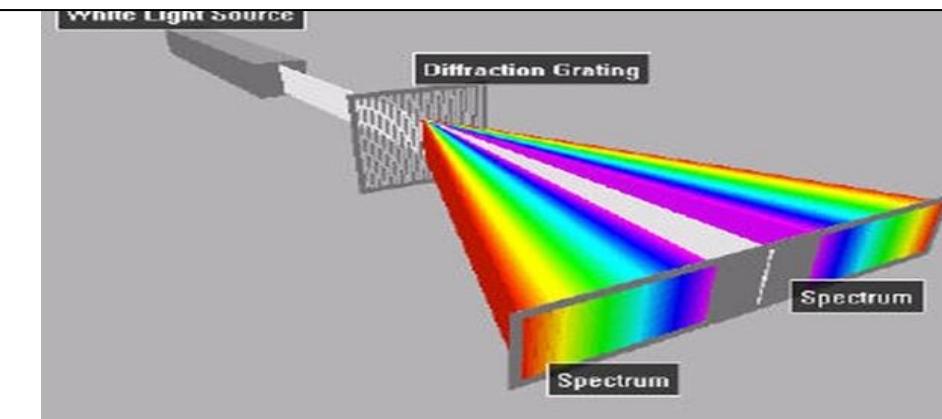
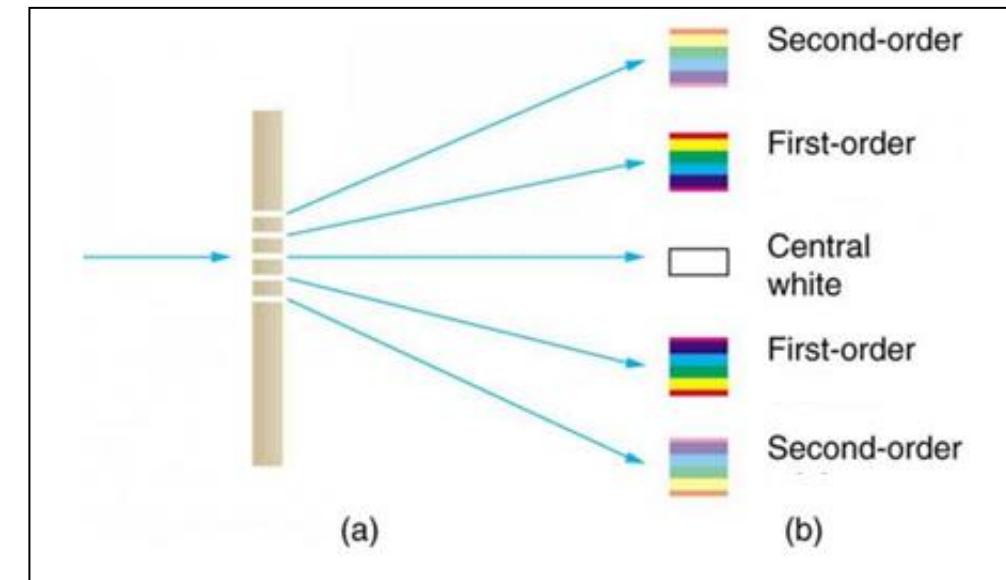
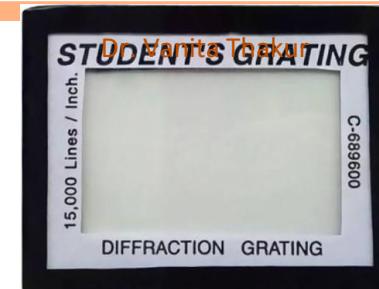
$$d_{200} = \frac{a}{2} = 1.805 \text{ \AA}$$

$$d_{220} = \frac{a}{2\sqrt{2}} = 1.276 \text{ \AA}$$

$$d_{111} = \frac{a}{\sqrt{3}} = 2.084 \text{ \AA}$$

# Diffraction

- **Diffraction is defined as the bending of light around corners or obstacles whose dimensions are comparable to the wavelength  $\lambda$  of light.**
- **A diffraction grating** is an optical component with a periodic structure that splits and diffracts light into several beams travelling in different directions.
- The diffraction grating used in laboratories has 1500 lines per inch.
- When light passes through these narrow slits, diffraction occurs.



- The dimensions of atoms and the interatomic spacing in a crystal are of the order of 2 to 5  $\text{\AA}^\circ$  which is of the order of wavelength of X-rays.
- In view of this Max van Laue predicted in 1912 that a crystal acts as a natural 3-dim. grating for X-rays, where regular periodic lines of atoms serve the role of parallel ruled lines .
- Laue was awarded Noble prize in 1914.

## Why visible light cannot be used to study the crystal structure?

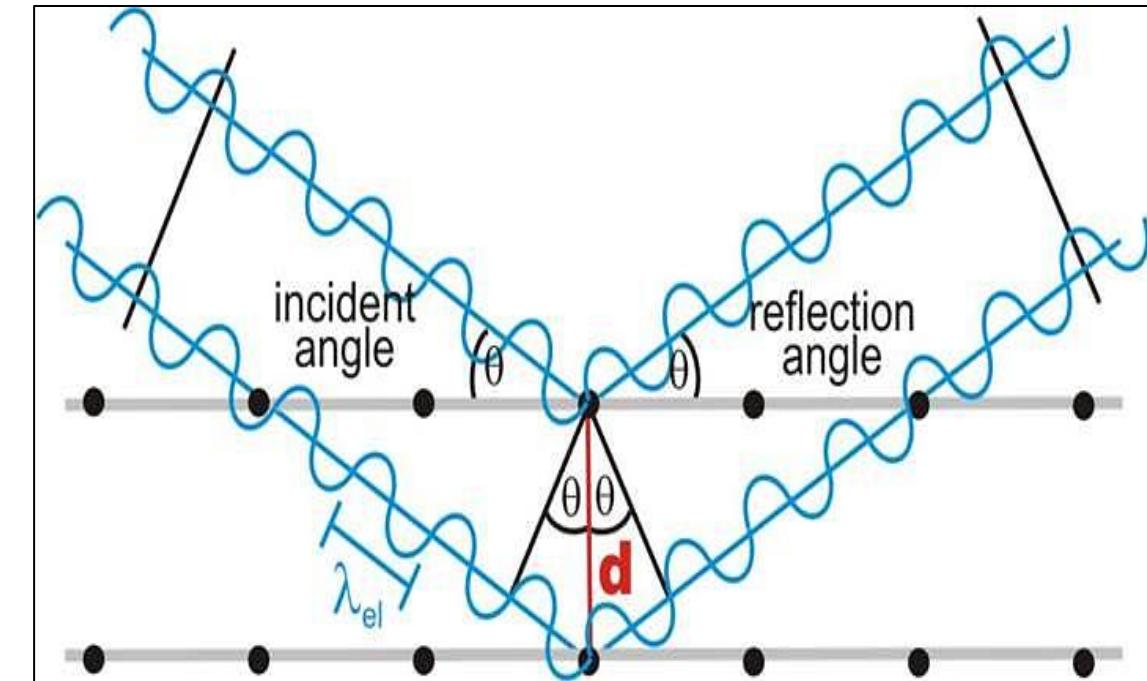
For diffraction the wavelength of light used should be matched with the inter atomic distance. So we cannot use the visible light as its wavelength is 400 nm to 700 nm. X-rays are having wavelength of around an Angstroms which is same as the inter atomic distance of the crystal.

# Bragg's law

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- In 1912, Bragg discovered that the X-rays can be regularly reflected by the successive atomic planes in the crystal. They are also known as Bragg's planes.
- Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings, are incident upon a crystalline sample, scattered by the atoms in the system and undergo constructive interference in accordance to Bragg's law.
- Bragg's law is a simple mathematical relationship that serves as a condition for Bragg reflection to occur.

$$m\lambda = 2d \sin \theta,$$



- When Bragg's law is satisfied, reflected rays are in phase and interfere constructively.

Path difference between reflected rays BC and EF is given by

$$\Delta = GE + EH \quad (1)$$

From fig. shown  $\angle ABG = \Theta + \alpha = 90^\circ \quad (2)$

$BE \perp MN$

Therefore,  $\angle MBE = \alpha + \angle GBE = 90^\circ \quad (3)$

$$90^\circ - \Theta + \angle GBE = 90^\circ$$

$$\angle GBE = \Theta$$

II ly,

$$\angle EBH = \Theta$$

In  $\triangle GBE$

$$\sin \Theta = \frac{GB}{BE},$$

$$so \quad GE = d \sin \Theta$$

II ly In  $\triangle EBH$ ,

$$EH = d \sin \Theta$$

Put above values in eqn. (1) we get

$$\Delta = 2d \sin \Theta$$

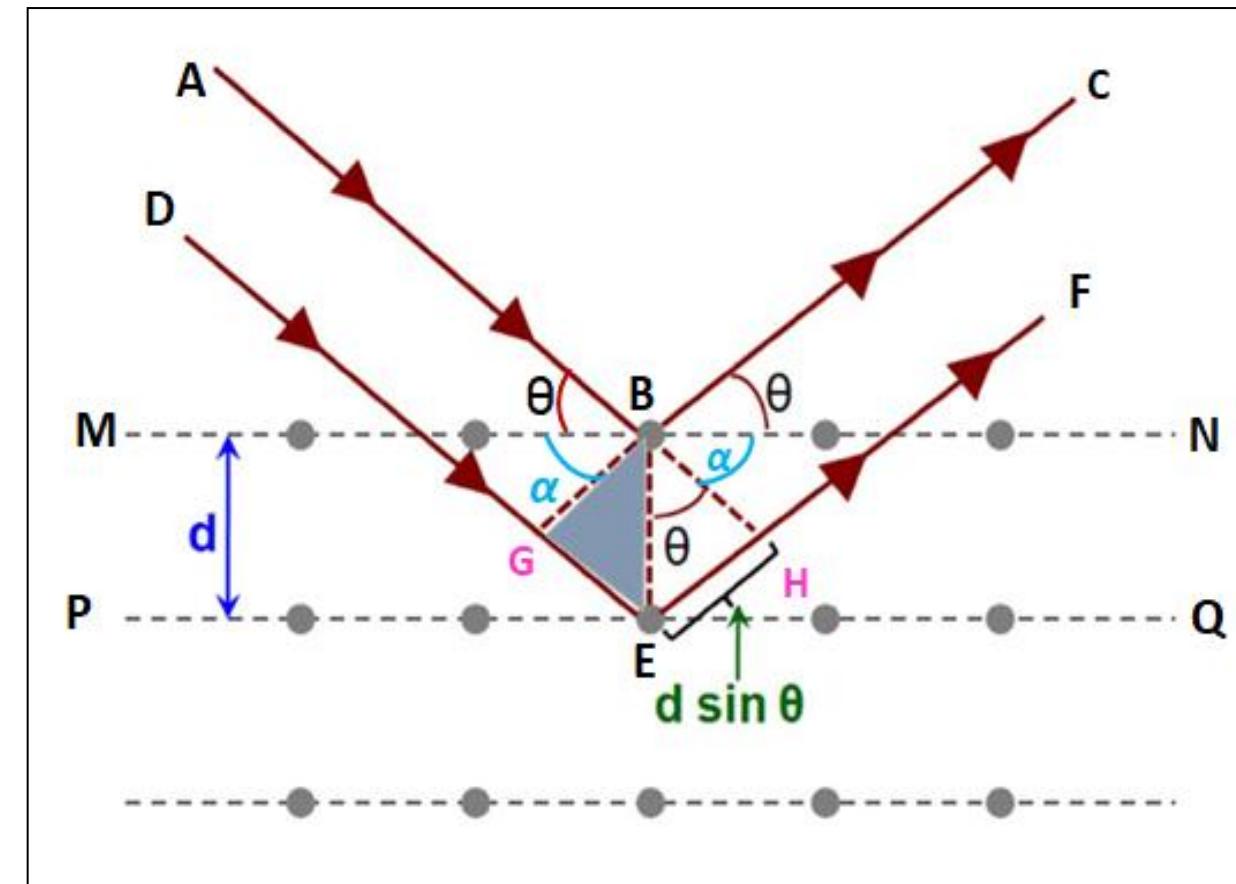
Rays BC and EF will interfere constructively only when

$$\Delta = m \lambda, \quad \text{where } m = 1, 2, 3, \dots$$

Therefore,

$$2d \sin \Theta = m \lambda$$

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This equation means that reinforcement of reflected waves will take place only at certain values of  $\Theta$ ,  $\lambda$  and  $d$ . In these directions resultant wave has maximum amplitude and produces bright spot on photographic plate.

$$2d \sin \Theta = m \lambda$$

Where

- $m$  is an integer determined by the order given,
- $\lambda$  is the wavelength of x-rays,
- $\Theta$  is the angle between the incident ray and the scattering planes.

Above equation is known as Bragg's law.

$$\Theta = \sin^{-1} \left( \frac{m\lambda}{2d} \right)$$

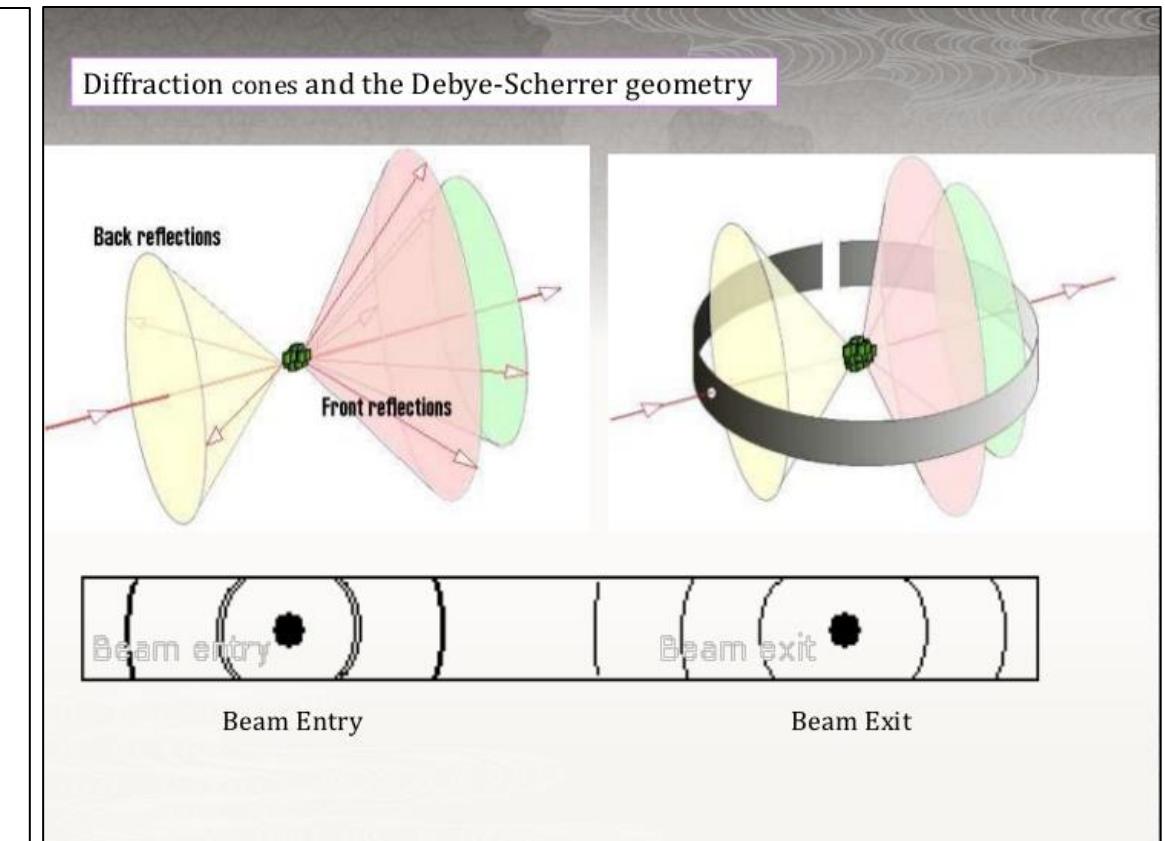
- ✓ For fixed  $\lambda$ ,  $\Theta$  depends on  $d$ .
- ✓  $m$  denotes order of reflection. Highest possible order is determined by the condition that  $\sin \Theta$  can't exceed 1.
- ✓ If  $\Theta$  is determined experimentally, and  $\lambda$  is known, then  $d$  can be determined using Bragg's law.

# Debye-Scherrer Method

(named after P. Debye and the German physicist P. Scherrer, who proposed this method in 1916)

- Debye-Scherrer Method is a method for studying the structure of crystalline solid in powder form using X-ray Diffraction (powdered-crystal method).
- This method is mostly useful for samples that are difficult to obtain in single crystal form.
- Debye-Scherrer camera is a cylindrical camera whose width is smaller as compared to its diameter.
- Material to be studied is taken in the form of a fine powder in a small capillary tube and is placed at the centre of drum.

- A narrow parallel beam of monochromatic X rays, upon falling onto a polycrystalline sample and being reflected by The crystallites that make up the sample, produces a number of coaxial ( i.e. having one common axis) diffraction cones.
- This method is used to determine the accurate value of lattice parameters (a, b and c).
- For every set of crystal planes, one or more crystals will be in such orientation to satisfy the Bragg's condition and hence capable of diffraction.
- The powder diffracts the X-rays in accordance with Bragg's law to produce cones of diffracted beams. These cones intersect the photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



- When film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.
- If  $x \rightarrow$  is the distance at which diffracted beam strikes the film from centre 'O'

then  $2\theta = \frac{180^0 x}{\pi R}$

Where  $R$  is radius of the drum.

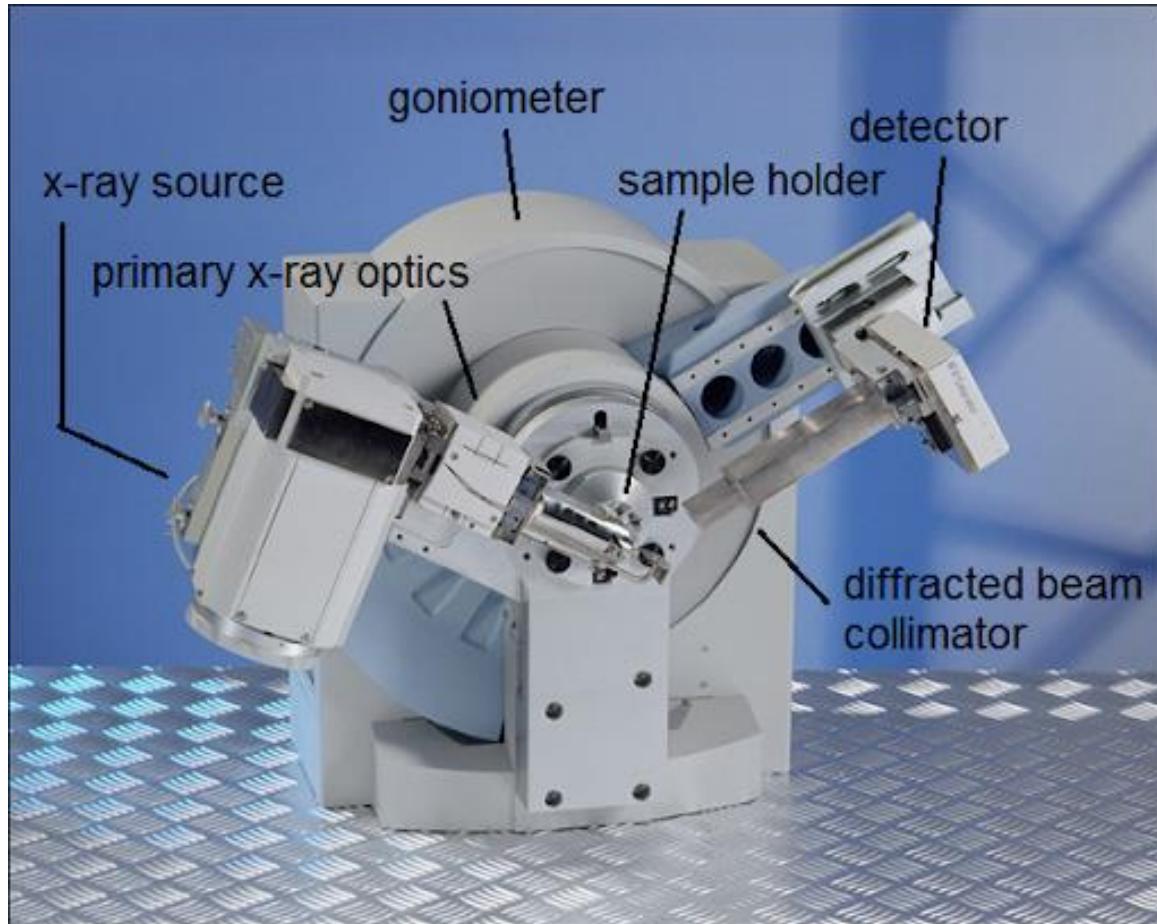


Or  $\theta = \frac{90^0 x}{\pi R}$

Let  $x_1, x_2, x_3, \dots$  be the distances between symmetrical arcs on the stretched photographic film.  
Then,

$$\theta_1 = \frac{90^0 x_1}{\pi R}, \theta_2 = \frac{90^0 x_2}{\pi R}, \theta_3 = \frac{90^0 x_3}{\pi R}, \dots$$

Using these values of  $\theta$  in Bragg's equation, the interplanar spacing ( $d$ ) can be calculated.



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# Applications of XRD

**Applications of X-ray diffraction includes**

- **characterization of crystalline materials**
  - **determination of lattice parameters**
  - **measurement of sample purity**
  - **To identify crystalline phases and orientation**
  - **Determination of grain size in polycrystalline materials**
  - **To determine atomic arrangement.**

# Diamond Cubic structure

Cubic (more common)  
Hexagonal

The diamond lattice (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal. It can be regarded as a face centered cubic lattice with the two-point basis:

Crystal structure: Diamond

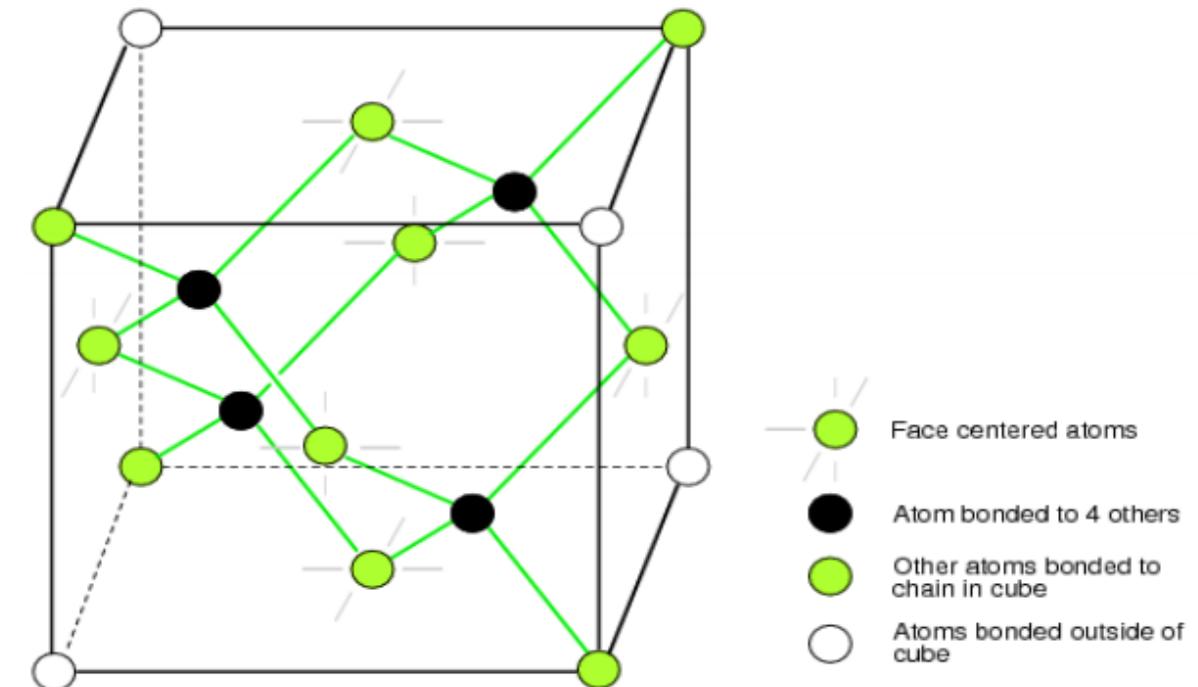
Bravais lattice: face centered cubic (basis of 2-C atoms)

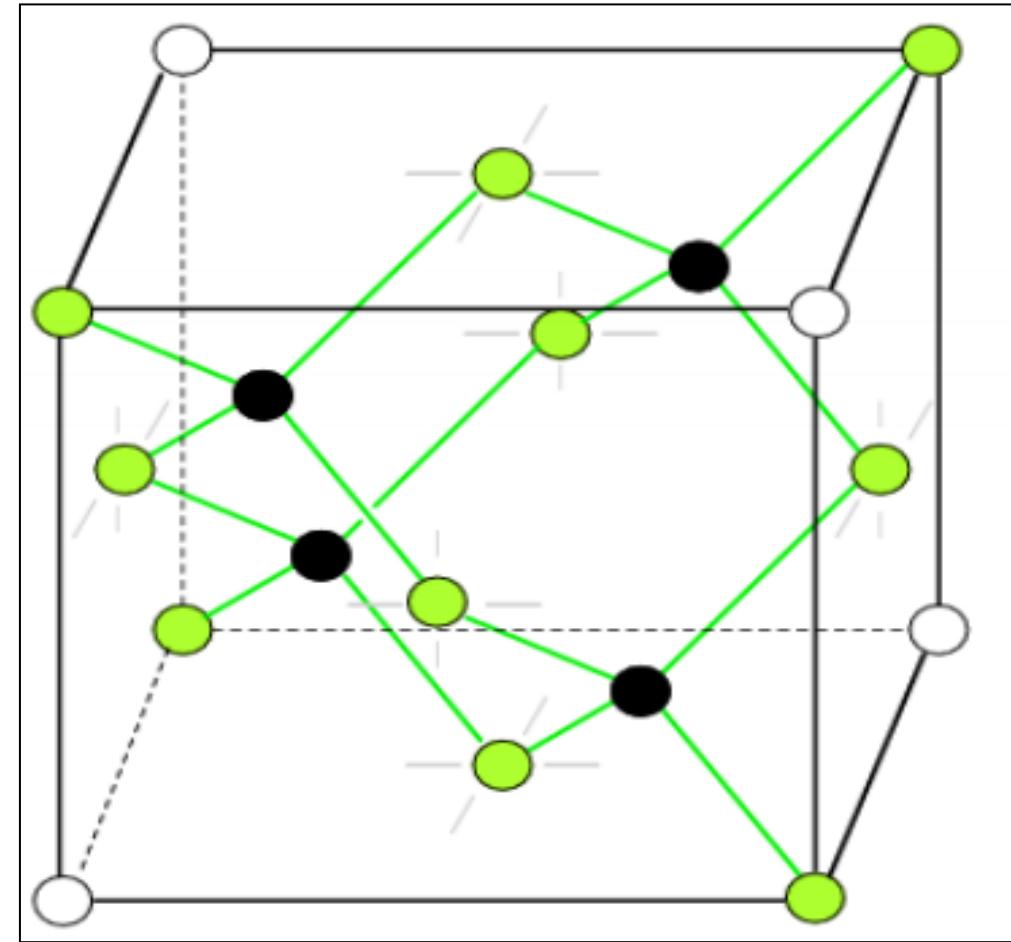
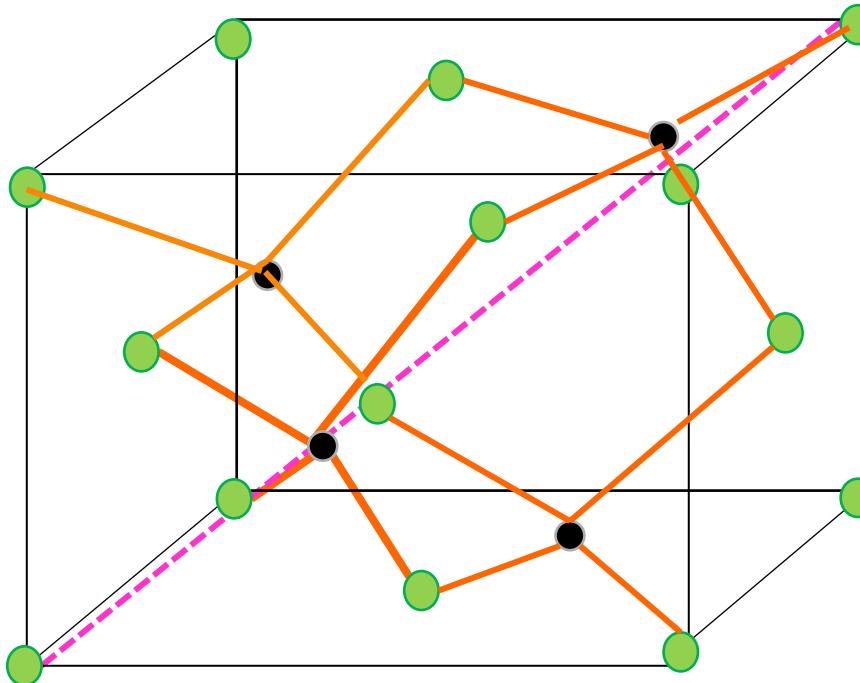
Coordination No. = 4

$$\text{Radius } r = \frac{\sqrt{3}}{8}a$$

P.F = 34% (loosely packed structure)

Diamond Unit Cell



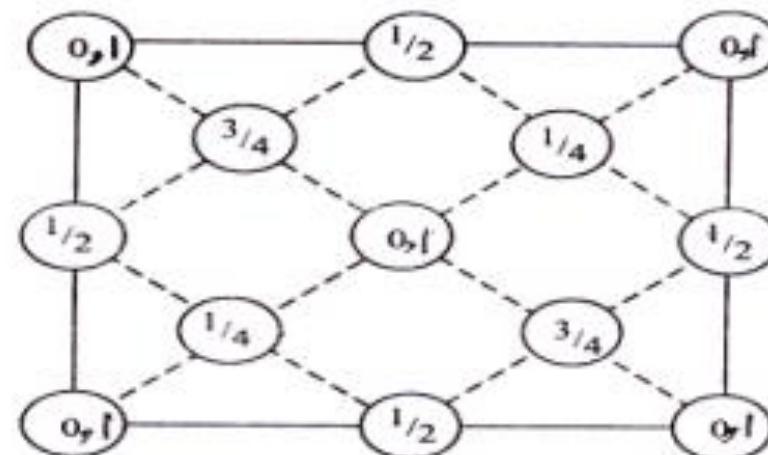
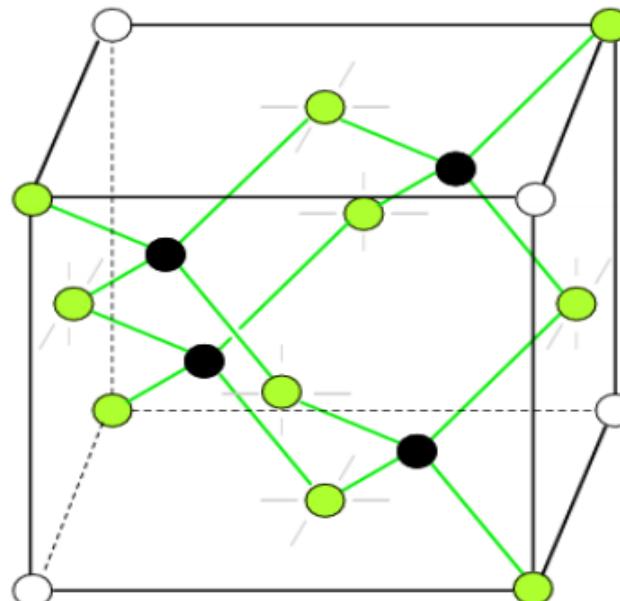


- ✓ The conventional unit cell is a cube with sides of  $a$ .
- ✓ There are 8 atoms in the conventional unit cell.
- ✓ Corners:  $8 \times \frac{1}{8} = 1$ ,
- ✓ faces:  $6 \times \frac{1}{2} = 3$ ,
- ✓ interior: 4.

### No. of atoms per unit cell

$$\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) + 4 = 8$$

- ✓ So, total number of atoms present in a diamond cubic unit cell is  $1 + 3 + 4 = 8$ ,  
Since each carbon atom is surrounded by four more carbon atoms, the co-ordination number is 4



Si, Ge also crystallize in the diamond structure.

In diamond crystal structure,

- ✓ Each C-atom forms directional covalent bonds with 4 other C-atoms that occupy 4-corners of the cube in tetrahedral structure
- ✓ Diamond structure is formed with **tetrahedral units** with bond length of 1.53 Å and bond angle 109.5°
- ✓ Diamond cubic structure is combination of two interpenetrating fcc sub lattices displaced along the body diagonal of cubic cell by  $1/4^{\text{th}}$  length of the diagonal.

(0, 0, 0)

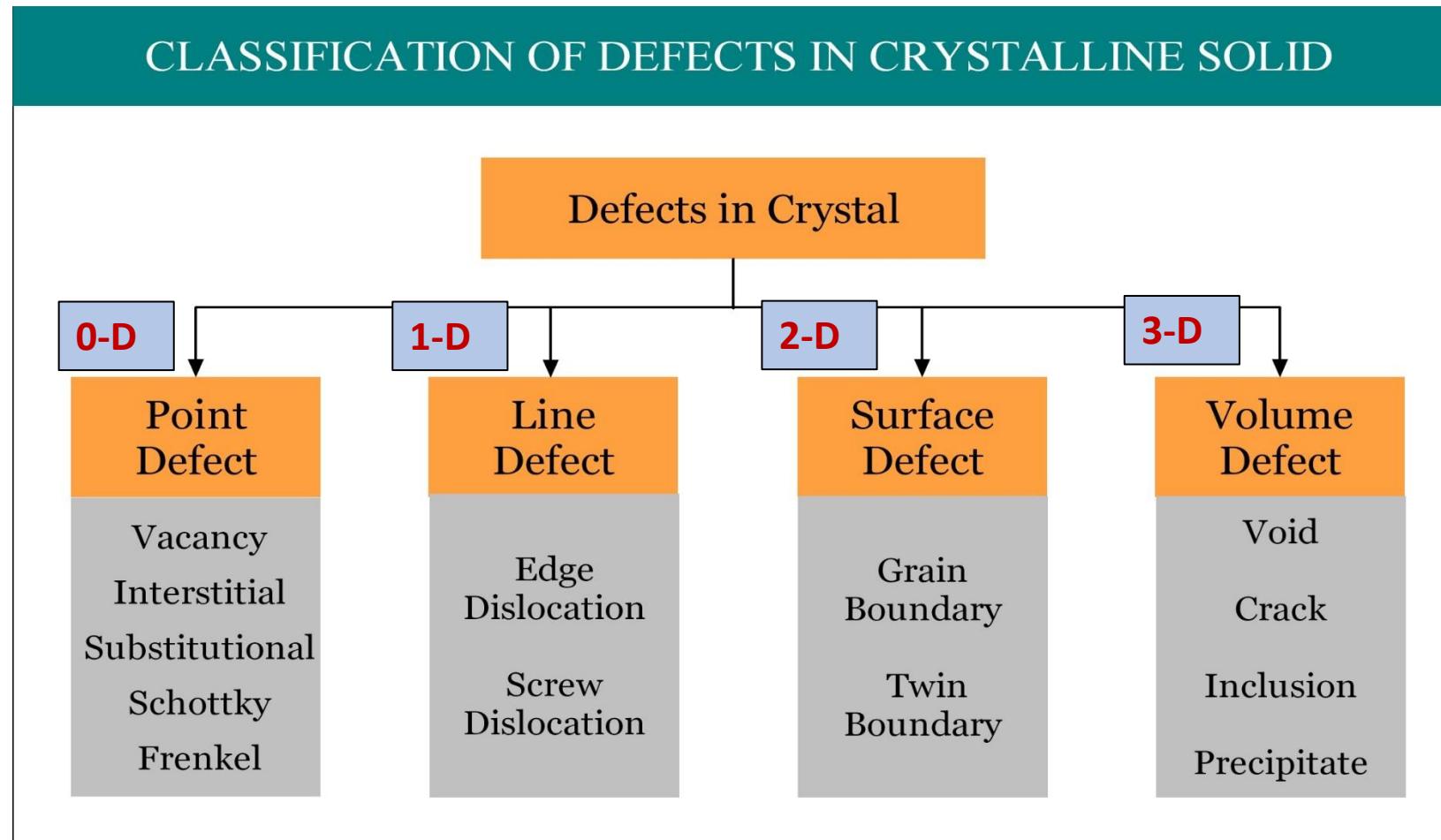
( $\frac{1}{4}$ ,  $\frac{1}{4}$ ,  $\frac{1}{4}$ )

\* Refer class notes for calculation of radius and Packing fraction

# Crystal Defects

- In real solids, on account of thermodynamic considerations and crystal growth, some atoms are not found at places where they should be. The atoms may occupy sites where they do not belong. These are known as defects in crystals.
- A defect or an imperfection is any deviation from the perfect periodic arrangement of atoms observed in real crystals.

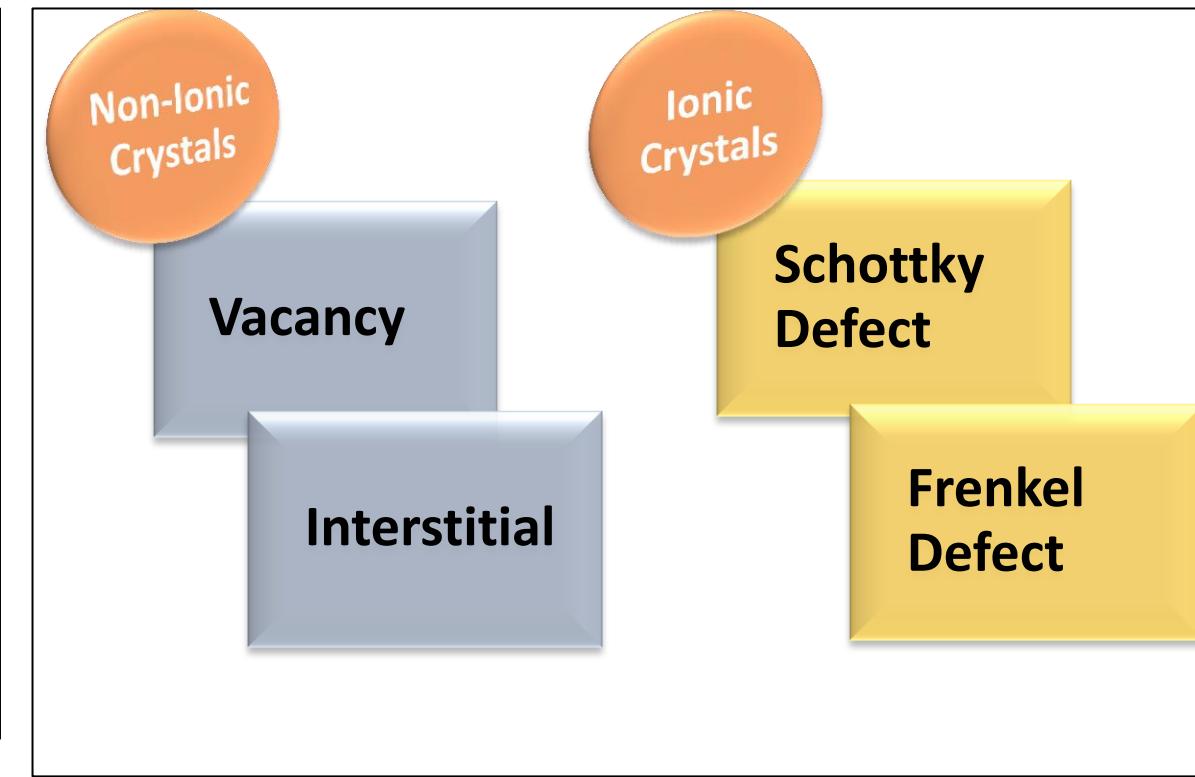
# Classification of Defects in crystalline Solids

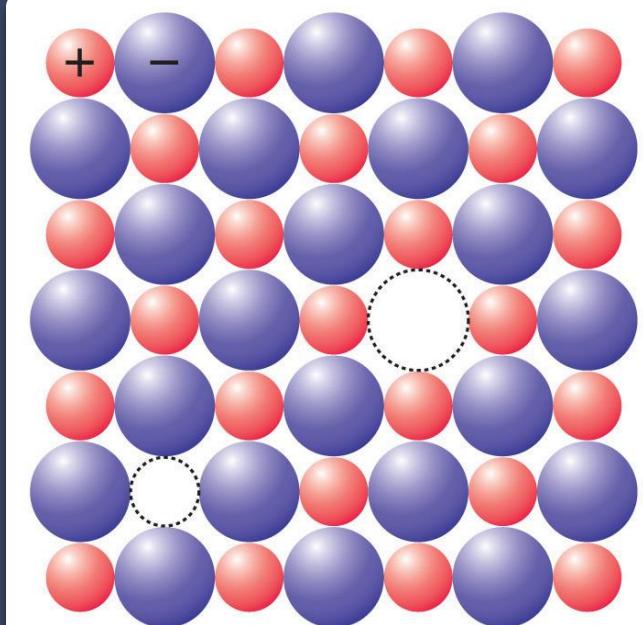


# Point Defects (0-Dimension)

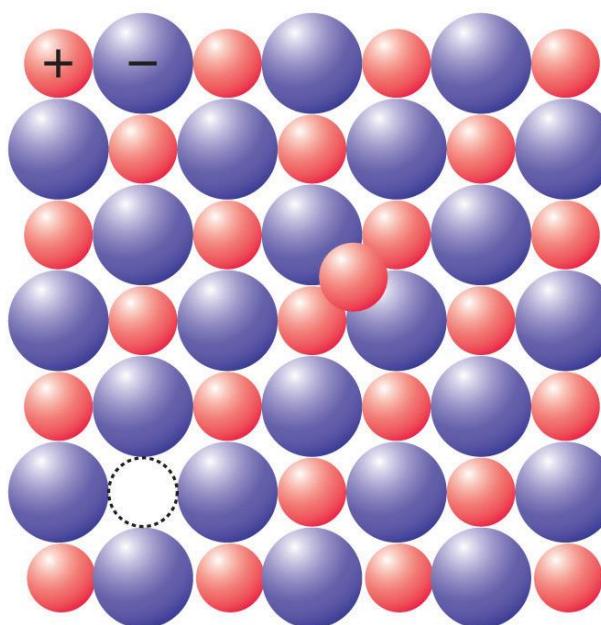
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- 1. Vacancies (Schottky defects)**
- 2. Interstitial (Frenkel defects)**
- 3. Impurities**
  - a. Interstitial impurity**
  - b. Substitutional impurity**
- 4. Electronic defects**





(a) Schottky defect



(b) Frenkel defect

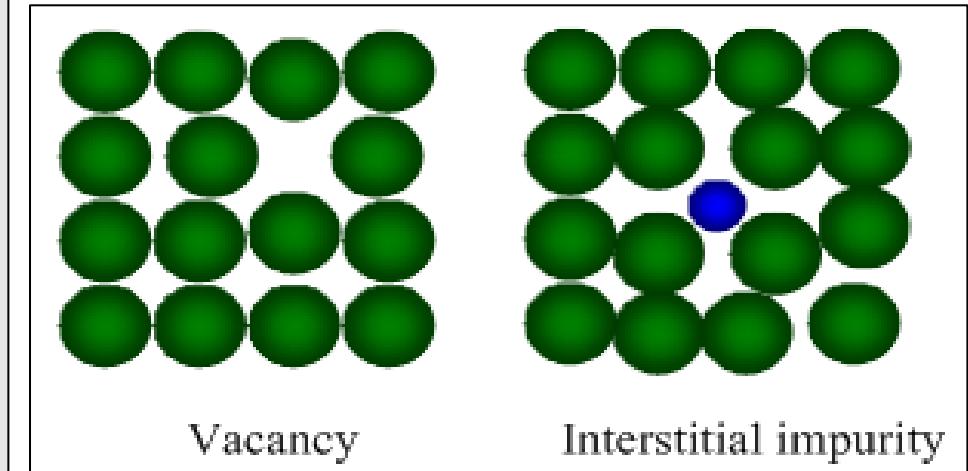
Schottky  
and Frenkel  
defects

# Defects in Non-ionic Crystals

## 1. Vacancies

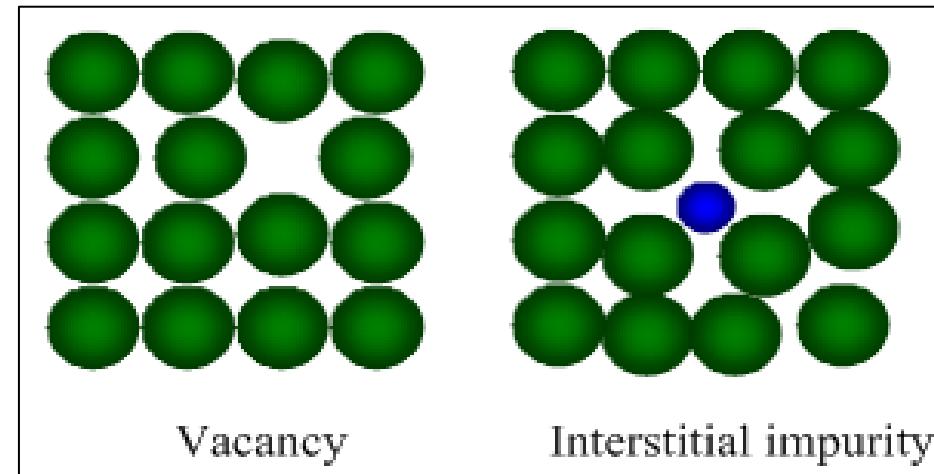
- A vacancy is the **absence of an atom** from a site normally occupied in the lattice.
- These are produced during solidification as a result of local disturbances or thermal vibrations of atoms at high temperatures.
- Vacancies form in close packed metallic structures.
- Concentration of vacancies in a crystal depends on the temperature.

$$n = N \exp\left(\frac{-E_v}{kT}\right)$$



## 2. Interstitials

- An interstitial is an **extra atom on a non-lattice site.** It may be a foreign atom or a regular atom.
- It arises when an atom occupies a position in the lattice that is not normally occupied in the perfect crystal.
- This type of defects increase the density of crystals.
- It produces lattice strain, as it pushes the surrounding atoms further apart.

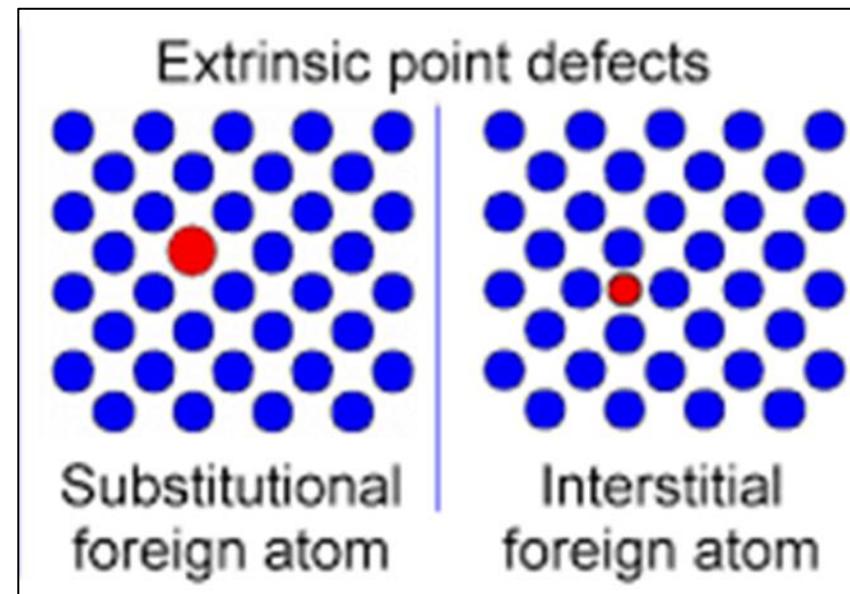


### 3. Impurities

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**a. Interstitial impurity:** It is a small sized atom occupying the void space in the parent crystal, without displacing the any of the host atoms from its site.

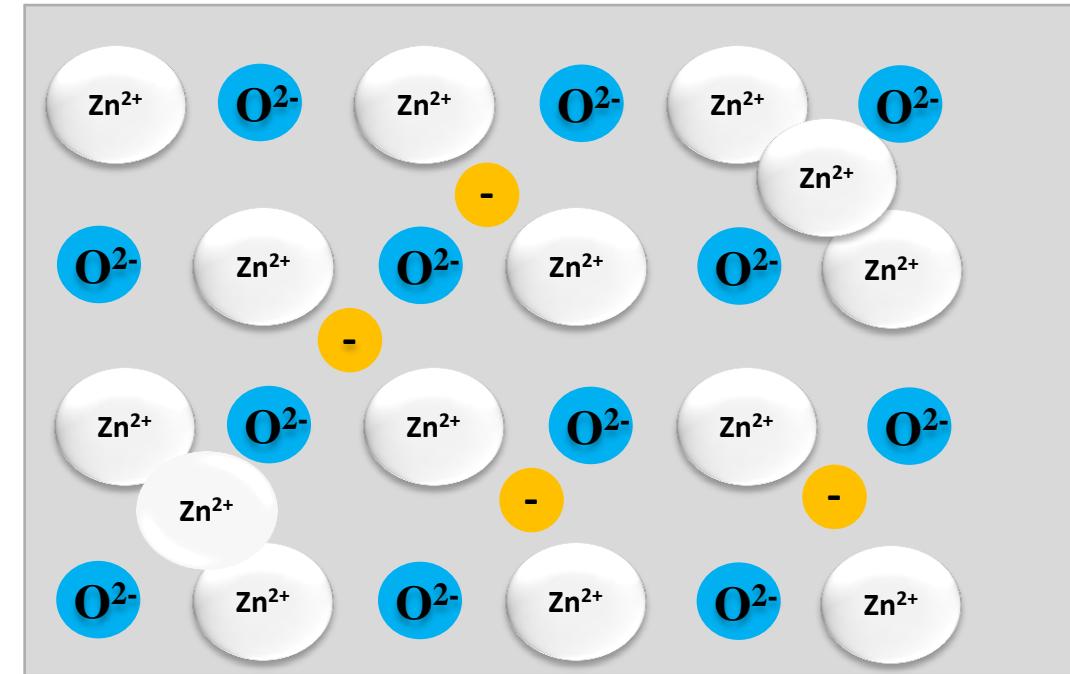
**b. Substitutional impurity:** It arises when a host atom in the lattice is replaced by a foreign atom. The substitutional atom remains in the regular lattice site.



## 4. Electronic defects

- ✓ Errors in charge distribution in solid materials are called electronic defects.
- These defects are produced when the composition of an ionic crystal does not correspond to the exact stoichiometric formula.
- The non stoichiometric composition is caused by an excess of metal ions.

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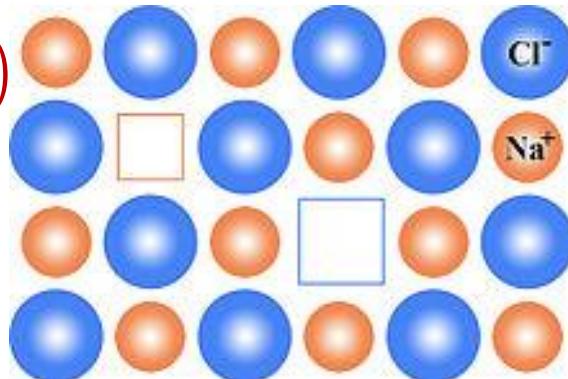


# Defects in Ionic Crystals

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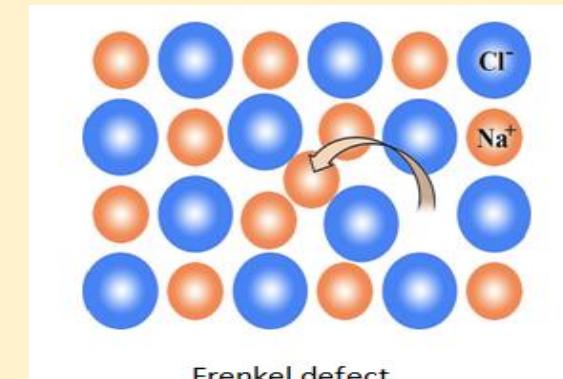
## Schottky Defect

- ✓ Equal number of cations and anions are missing from the lattice sites.
- ✓ Found in compounds where cations and anions are of same size.
- ✓ Density of solid decreases.
- ❖ Combination of-
  - Cation vacancy and anion vacancy.



## Frenkel Defect

- ✓ A cation leaves normal site and occupies an interstitial site.
- ✓ found in compounds where anions are of much larger size than cation.
- ✓ Density of solid remains same.
- ❖ Combination of
  - Cation vacancy and cation interstitial defect



# Equilibrium Concentration of Schottky defects in Ionic Crystals

In ionic crystals point defects occur in pairs. A Schottky defect occurs when cation-anion pair goes missing from the respective lattice positions.

Consider that a crystal contains equal no. of cations and anions.

Let       $N$  = total no. of ions

$n$  = no. of Schottky defects

No. of different ways in which cation defects can be produced =  ${}^N C_n$

No. of different ways in which anion defects can be produced =  ${}^N C_n$

Probability of distribution in which  $n$  Schottky defects can be produced is given by

$$W = \left[ \frac{N!}{(N-n)! n!} \right]^2 \quad \text{_____} (1)$$

Change in entropy as a result of creation of vacancies, is given by Boltzmann equation as

$$\Delta S = k \log_e W \quad \text{_____} (2)$$

$$\Delta S = k \log_e \left[ \frac{N!}{(N-n)! n!} \right]^2$$

$$\Delta S = 2k \log_e \left[ \frac{N!}{(N-n)! n!} \right]$$

$$\Delta S = 2k [ \log_e N! - \log_e (N-n)! - \log_e n!] \quad \text{_____} (3)$$

**Using Stirling's Approx.**

$\log_e x! \approx x \log_e x - x$  for  $x \gg 1$  into above equation, we get

$$\Delta S = 2k [(N \log_e N - N) - (N-n) \log_e (N-n) + (N-n) - n \log_e n + n]$$

$$\Delta S = 2k [(N \log_e N) - (N-n) \log_e (N-n) - n \log_e n] \quad \text{_____} (4)$$

In formation of defects, a change in free energy occurs, which is given by

$$\Delta G = \Delta H - T \Delta S$$

As the process takes place at constant volume

$$\Delta H = \Delta E$$

where  $\Delta E$  is the change in internal energy of the crystal.

Hence,

$$\Delta G = \Delta E - T \Delta S \quad \text{_____} \quad (5)$$

If  $E_s$  = is the average energy required to create a Schottky defect, then

$\Delta E$  is the energy change due of creation of  $n$  defects.

$$\Delta E = n E_s$$

$$\Delta G = n E_s - 2kT [N \log_e N - (N-n) \log_e (N-n) - n \log_e n]$$

$$\frac{\partial \Delta G}{\partial n} = \frac{\partial}{\partial n} \{ n E_s - 2kT [N \log_e N - (N-n) \log_e (N-n) - n \log_e n] \}$$

$$= E_s - 2kT \frac{\partial}{\partial n} [N \log_e N - (N-n) \log_e (N-n) - n \log_e n]$$

$$\begin{aligned}
 &= E_s - 2kT \left[ -\left(\frac{N-n}{N-n}\right)(-1) - \log_e(N-n)(-1) - \frac{n}{n} - \log_e n \right] \\
 &= E_s - 2kT \{1 + \log_e(N-n) - 1 - \log_e n\}
 \end{aligned}$$

$$\frac{\partial \Delta G}{\partial n} = E_s - 2kT \log_e \left( \frac{N-n}{n} \right)$$

**As per equilibrium condition,  $\frac{\partial \Delta G}{\partial n} = 0$**

So,

$$\begin{aligned}
 E_s - 2kT \log_e \left( \frac{N-n}{n} \right) &= 0 \\
 E_s &= 2kT \log_e \left( \frac{N-n}{n} \right) \\
 \left( \frac{N-n}{n} \right) &= \exp \left( \frac{E_s}{2kT} \right)
 \end{aligned}$$

**No. of defects << Total no. of ion pairs**

i.e.  $n \ll N$

Therefore, we can approximate that  $(N-n) \approx N$

$$\left(\frac{N}{n}\right) = \exp\left(\frac{E_s}{2kT}\right)$$

$$\left(\frac{n}{N}\right) = \exp\left(\frac{-E_s}{2kT}\right)$$

$$n = N \exp\left(\frac{-E_s}{2kT}\right)$$

- The above equation shows that the concentration of defects in an ionic crystal depends on the temperature.
- It increases exponentially as the temperature of the crystal is increased.
- The average energy required to produce Schottky defects is characteristics of the solid and depends on the nature of the solid.

## Equilibrium Concentration of Frenkel defects in Ionic Crystals

Consider that a crystal contains equal no. of cations and anions.

Let  $N$  = total no. of ions

$n$  = no. of Frenkel defects i.e.  $n$  cation or anion vacancies and  $n$  interstitial ions in the crystal

No. of different ways in which vacancy defects can be produced =  ${}^N C_n$

If  $N_i$  is the number of interstitial positions, then the

No. of different ways in which interstitial defects can be produced =  ${}^{N_i} C_n$

Probability of distribution in which  $n$  Frenkel defects can be produced is given by

$$W = \left[ \frac{N!}{(N-n)! n!} \right] \cdot \left[ \frac{N_i!}{(N_i-n)! n!} \right] \quad \text{--- (1)}$$

*Then proceed in the similar way as we did in previous derivation of Schottky defects!!!!*

$$\Delta S = k \log_e W$$

$$\Delta S = k \log_e \left[ \frac{N!}{(N-n)! n!} \cdot \frac{N_i!}{(N_i-n)! n!} \right]$$

$$= [\log_e N! - \log_e (N-n)! - \log_e n! + \log_e N_i! - \log_e (N_i-n)! - \log_e n!]$$

*Using Stirling's Approx.*

$\log_e x! \approx x \log_e x - x$  for  $x \gg 1$  into above equation, we get

$$\Delta S = k [(N \log_e N - N) - (N-n) \log_e (N-n) + (N-n) - n \log_e n + n + (N_i \log_e N_i - N_i) - (N_i-n) \log_e (N_i-n) + (N_i-n) - n \log_e n + n]$$

$$\Delta S = k [N \log_e N + N_i \log_e N_i - (N-n) \log_e (N-n) - (N_i-n) \log_e (N_i-n) - 2n \log_e n]$$

In formation of defects, a change in free energy occurs, which is given by

$$\Delta G = \Delta H - T \Delta S$$

As the process takes place at constant volume,  $\Delta H = \Delta E$

**Hence,  $\Delta G = \Delta E - T \Delta S$**

If  $E_f$  is the average energy required to create a Frenkel defect, then  $\Delta E$  is the energy change due of creation of  $n$  defects.

$$\Delta E = n E_f$$

$$\Delta G = n E_f - kT [N \log_e N + N_i \log_e N_i - (N-n) \log_e (N-n) - (N_i-n) \log_e (N_i-n) - 2n \log_e n]$$

$$\frac{\partial \Delta G}{\partial n} = \frac{\partial}{\partial n} \{ n E_f - kT [N \log_e N + N_i \log_e N_i - (N-n) \log_e (N-n) - (N_i-n) \log_e (N_i-n) - 2n \log_e n] \}$$

$$= E_f - kT \frac{\partial}{\partial n} [-(N-n) \log_e (N-n) - (N_i-n) \log_e (N_i-n) - 2n \log_e n]$$

$$= E_f - kT \left\{ - \left[ \left( \frac{N-n}{N-n} \right) (-1) + \log_e (N-n) (-1) + \left( \frac{N_i-n}{N_i-n} \right) (-1) + \log_e (N_i-n) (-1) + \frac{2n}{n} + \log_e n \right] \right\}$$

$$= E_f - kT \{-(-1 - \log_e (N-n) - 1 - \log_e (N_i-n) + 2 + \log_e n)\}$$

$$\frac{\partial \Delta G}{\partial n} = E_f - k T \log_e \left( \frac{N-n}{n} \right) \left( \frac{N_i-n}{n} \right)$$

$$= E_f - k T \log_e \frac{(N-n)(N_i-n)}{n^2}$$

As per equilibrium condition,  $\frac{\partial \Delta G}{\partial n} = 0$

So

$$E_f - k T \log_e \frac{(N-n)(N_i-n)}{n^2} = 0$$

$$E_f = k T \log_e \frac{(N-n)(N_i-n)}{n^2}$$

$$\frac{(N-n)(N_i-n)}{n^2} = \exp \left( \frac{E_f}{kT} \right)$$

No. of defects << Total no. of ion pairs

i.e.  $n \ll N$  and  $n \ll N_i$

Therefore, we can approximate that  $(N-n) \approx N$  and  $(N_i-n) \approx N_i$

$$\left(\frac{N N_i}{n^2}\right) = \exp\left(\frac{E_f}{kT}\right)$$

$$\left(\frac{n^2}{N N_i}\right) = \exp\left(\frac{-E_f}{kT}\right)$$

$$n^2 = N N_i \exp\left(\frac{-E_f}{kT}\right)$$

$$n = \sqrt{N N_i} \exp\left(\frac{-E_f}{2kT}\right)$$

- The above equation shows that the concentration of defects in an ionic crystal depends on the temperature.
- It increases exponentially as the temperature of the crystal is increased.
- The average energy required to produce Frenkel defects is characteristics of the solid and depends on the nature of the solid.

# Effects of defects on Properties of Solids.

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The addition of Carbon atoms in iron increases its tensile strength.

By changing impurities (C, Mn, Cr etc.) or concentration of the impurities, various grades of steel are manufactured.

Addition of copper atoms in gold increases its ductility so that it can be drawn into wires.

Pure Ge and Si are doped with pentavalent and trivalent impurities to increase their electrical conductivity.

Addition of Cu atoms in silver increases its electrical resistivity.

## Reference Books:

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2. S O Pillai, Solid State Physics, 8th edition, New Age International Publishers, 2018
3. Charles Kittel, Introduction to Solid State Physics, 7th Edition, John Wiley & Sons, 2008.