

# Solid State Chemistry

Power point presentation prepared by:

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## References:

1. [https://www.tf.uni-kiel.de/matwis/amat/def\\_en/kap\\_2/basics/b2\\_1\\_6.html](https://www.tf.uni-kiel.de/matwis/amat/def_en/kap_2/basics/b2_1_6.html)
2. <https://www.toppr.com/ask/question/derive-braggs-equation/>
3. <https://www.slideshare.net/GOVINDARAJP6/solid-state-chemistryppt>

# SOLID STATE CHEMISTRY

The branch of physical chemistry which deals about structure and properties of solid.

Types of solid :

❖ Crystalline solid



❖ Amorphous solid



# SOLID STATE CHEMISTRY

CRYSTALLINE SOLID	AMORPHOUS SOLID
<ul style="list-style-type: none"><li>❖ Ordered arrangement</li><li>❖ Anisotropic</li><li>❖ Sharp melting point</li><li>❖ Electrical and thermal conductivity</li></ul>	<ul style="list-style-type: none"><li>❖ No ordered arrangement</li><li>❖ Isotropic</li><li>❖ No sharp melting point</li><li>❖ Not conduct electricity and heat</li></ul>

# Crystallography

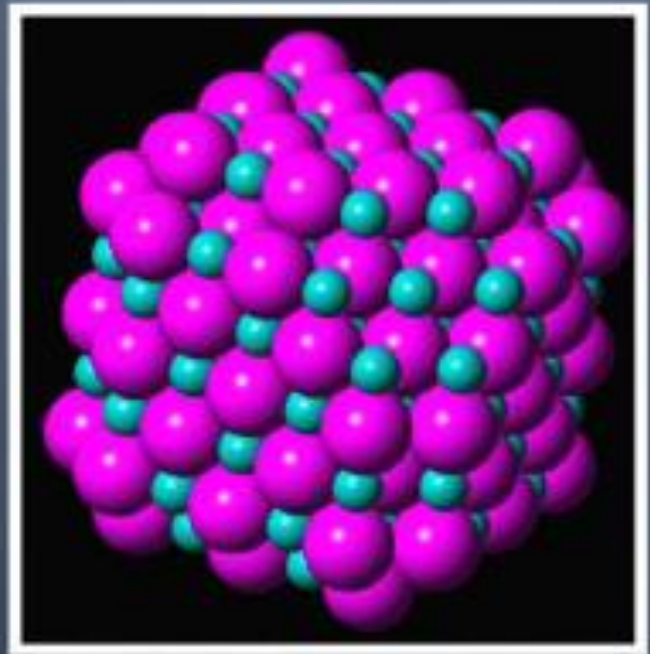
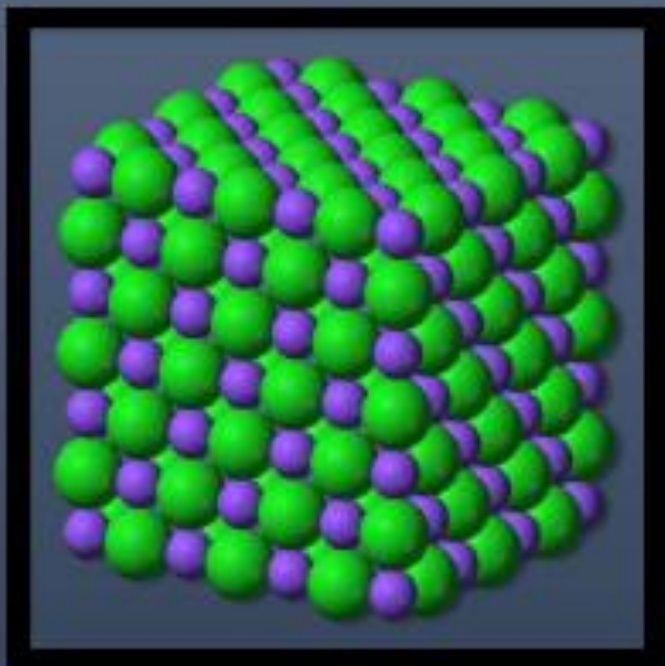
It is the experimental science of determining the arrangement of atoms in crystalline solids

## Laws of crystallography:

Crystallography is based on the fundamental laws

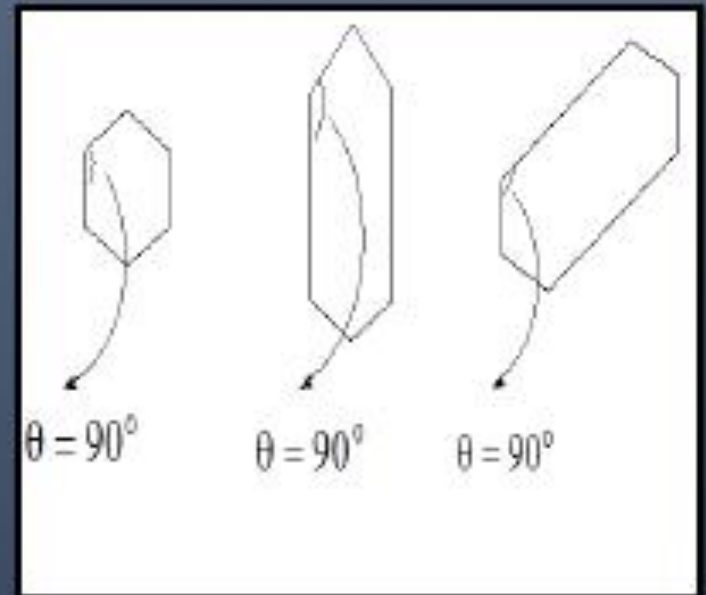
- Law of constancy of interfacial angles
- Laws of rational indices
- Law of constancy of symmetry

# Crystal Morphology



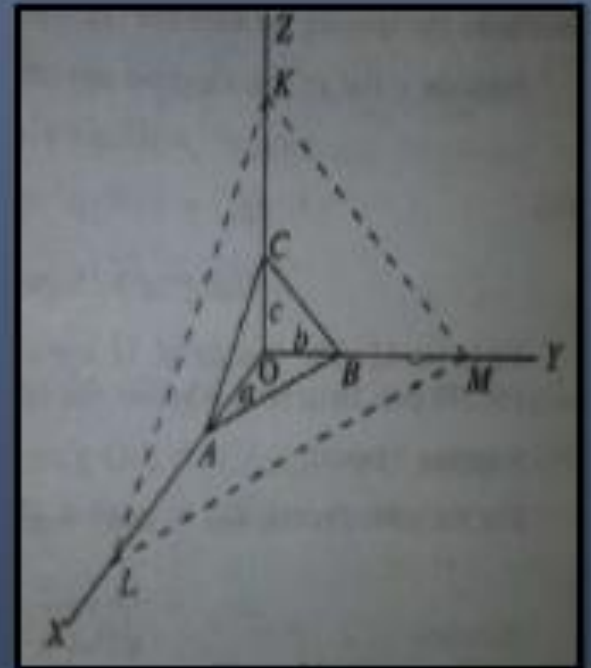
## Law of Constancy of Interfacial Angles

This law states that angle between adjacent corresponding faces is interfacial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal.



## Law of Rational indices

This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell)  $a$ ,  $b$ ,  $c$  or some simple whole number multiples of them ,e.g..  $na, n'b, n''c$  etc. are simple whole numbers .





## Law of constancy of symmetry

- This law states that all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and Centre of symmetry.
- The total number of Planes ,Axes and Centre of symmetries possessed by a crystal is called elements of symmetry.

Total number of elements of symmetry in cubic crystal=23

i.e., Plane of symmetry number is 9

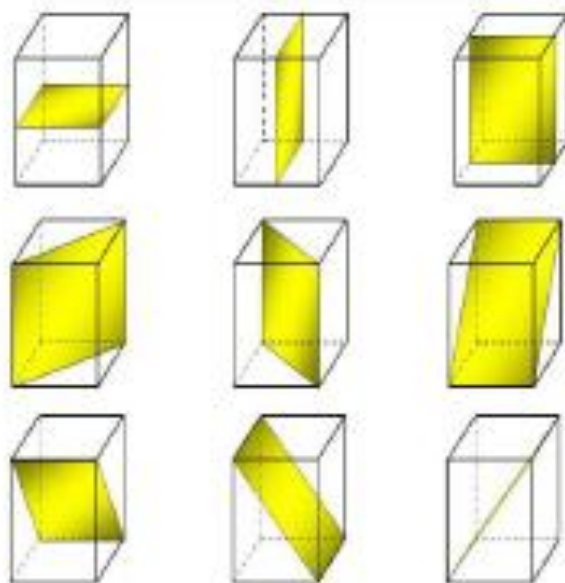
Axes of symmetry number is 13

Centre of symmetry number is 1



# Elements of symmetry in cubic crystals

The 9 Plane Symmetries of the Cube

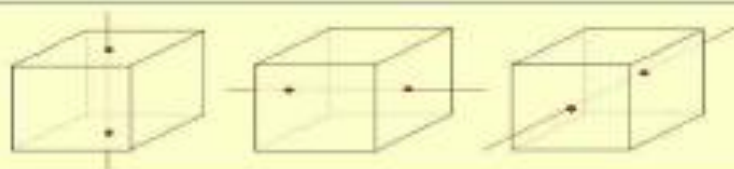


Rectangular plane of symmetry = 3

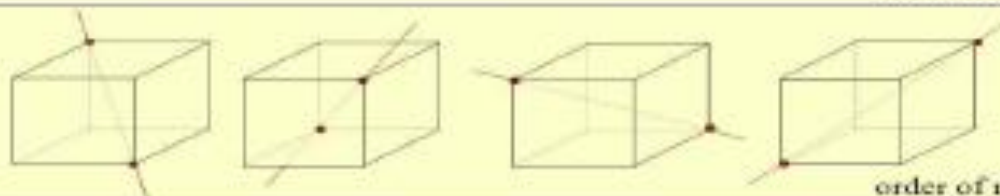
Diagonal plane of symmetry = 6

# Elements of symmetry in cubic crystals

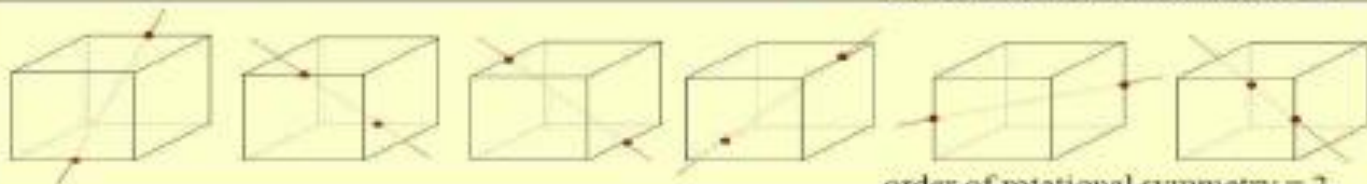
## The 13 Axes of Rotation of a Cube



order of rotational symmetry = 4

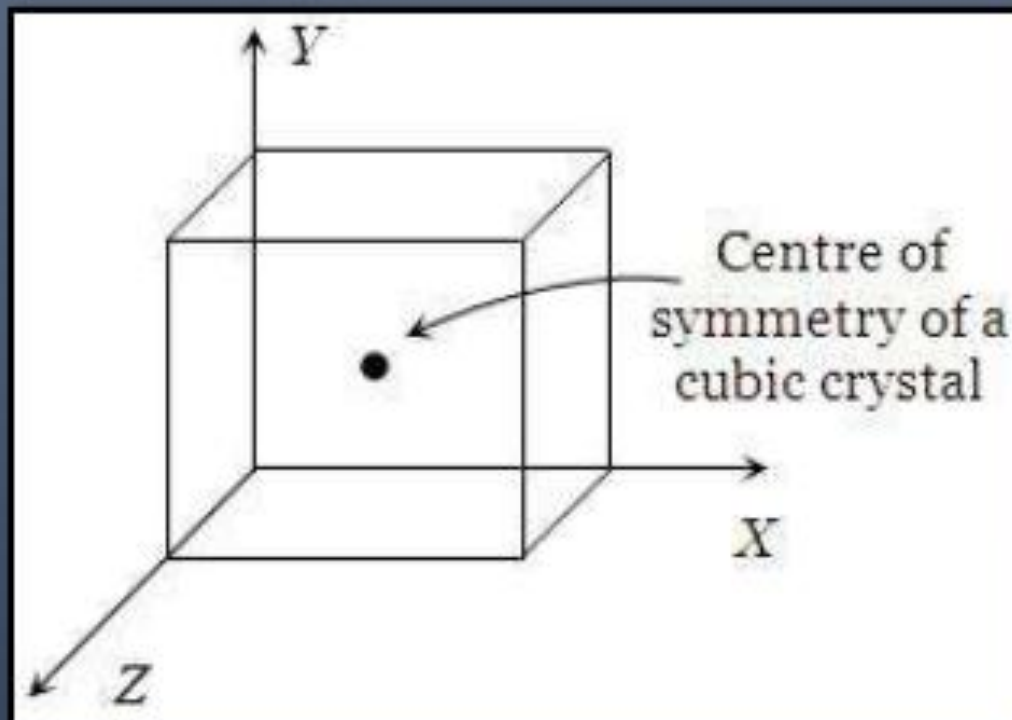


order of rotational symmetry = 3



order of rotational symmetry = 2

## Elements of symmetry in cubic crystals



Order of centre of symmetry = 1

# Symmetry operation in crystal

A symmetry operation is an operation performed on a crystal of such that the crystal transformed into a state indistinguishable from the starting state.

## Three types of symmetry operation :

- ❖ Plane of symmetry
- ❖ Axis of symmetry
- ❖ Centre of symmetry

## Plane of symmetry in crystal

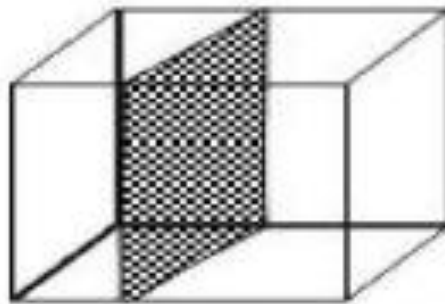
It is an imaginary plane on a crystal system with respect to this plane the crystal is divided into two halves, one half is the mirror image of the other half.

### Two types of plane symmetry:

- ❖ Rectangular plane of symmetry
- ❖ Diagonal plane of symmetry

## Rectangular plane of symmetry

It is an imaginary plane passing through the mid points of two opposite faces of a crystal with respect to this plane the crystal is divided into two halves ,one half is the mirror mage of other.

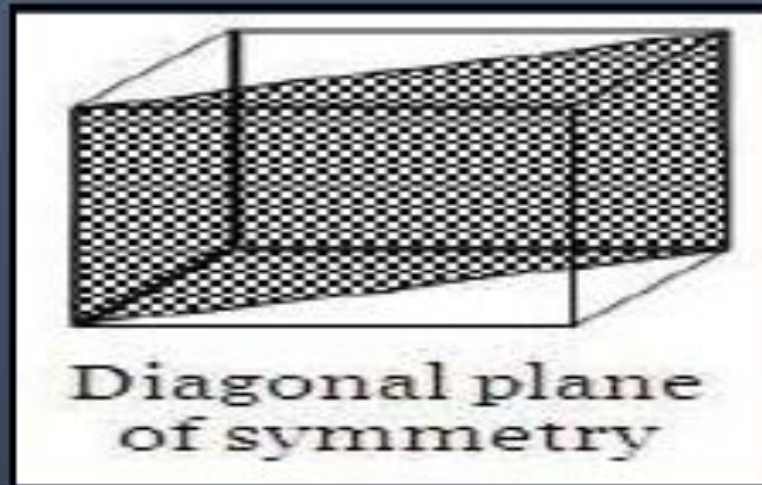


Rectangular plane of  
symmetry



## Diagonal plane of symmetry

It is an imaginary plane passing through the diagonal of two opposite faces of a crystal with respect to this plane the crystal is divided into two halves ,one half is the mirror mage of other





## Rotational axis of symmetry in crystal

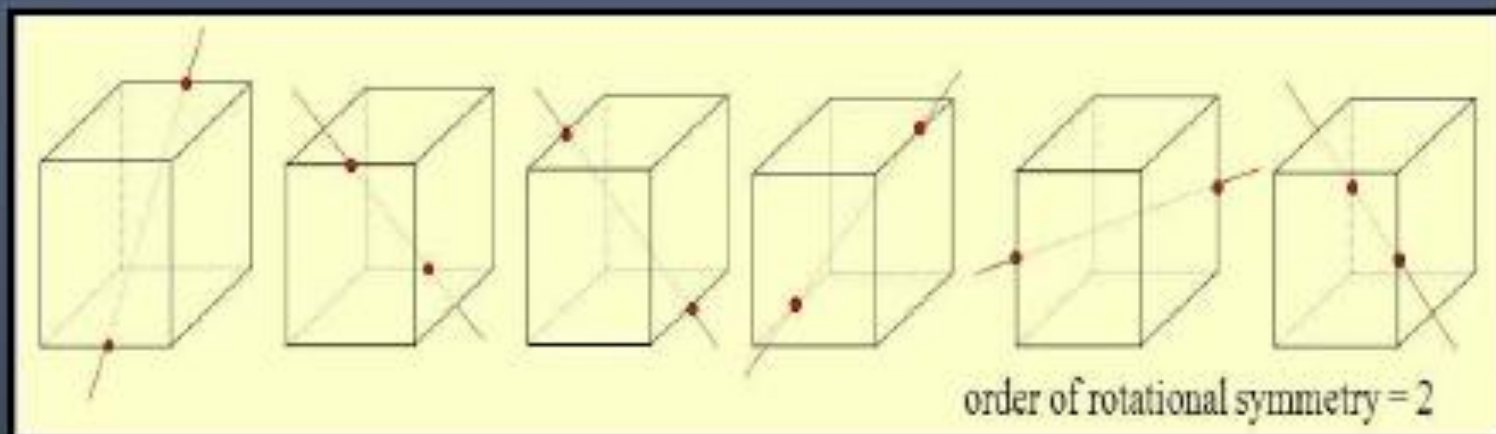
It is imaginary line passing through the crystal system with respect to this axis the crystal is rotated by an angle gives same appearance of the crystal system.

### Types of Rotational axis of symmetry:

- ❖ Two - fold Rotational axis of symmetry
- ❖ Three - fold Rotational axis of symmetry
- ❖ Four - fold Rotational axis of symmetry
- ❖ Six - fold Rotational axis of symmetry

## Two –fold rotational axis of symmetry

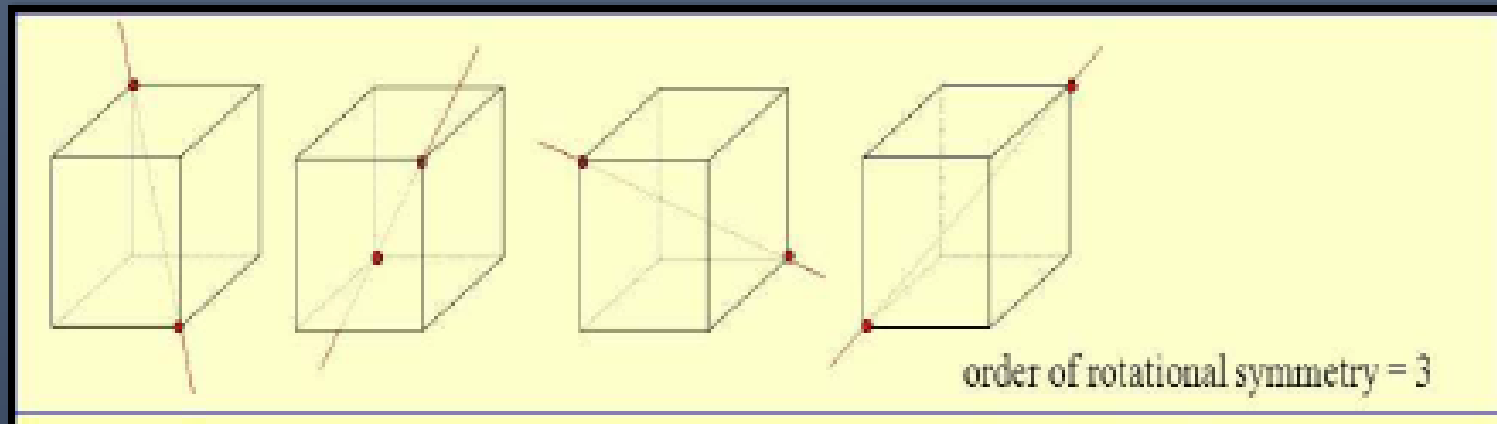
It is the rotation of a crystal with respect to an imaginary line passing through the crystal by an angle  $180^\circ$  gives similar appearance of the crystal system



The total number of two –fold axis of symmetry in cubic crystal = 6

## Three-fold rotational axis of symmetry

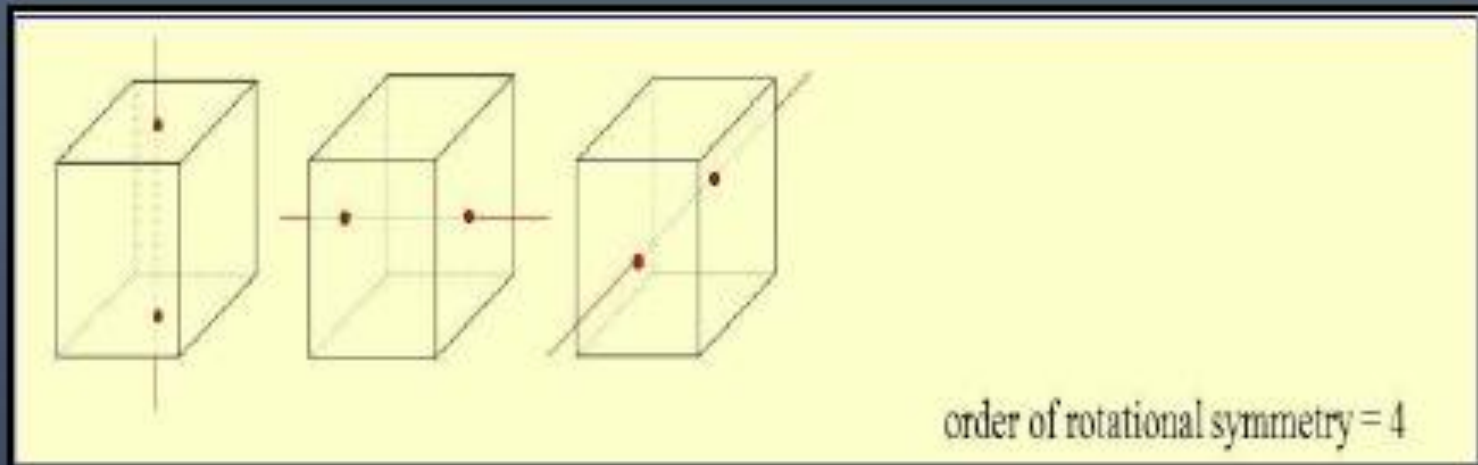
It is the rotation of a crystal with respect to an imaginary line passing through the crystal by an angle  $120^\circ$  gives similar appearance of the crystal system



The total number of three-fold axis of symmetry in cubic crystal = 4

## Four –fold rotational axis of symmetry

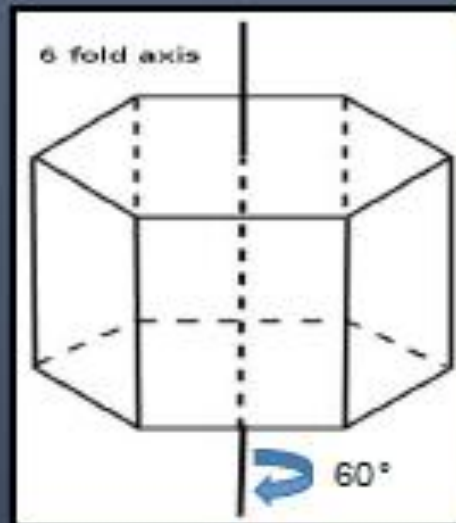
It is the rotation of a crystal with respect to an imaginary line passing through the crystal by an angle  $90^\circ$  gives similar appearance of the crystal system



The total number of three –fold axis of symmetry in cubic crystal =3

## Six –fold rotational axis of symmetry

It is the rotation of a crystal with respect to an imaginary line passing through the crystal by an angle  $60^\circ$  gives similar appearance of the crystal system.

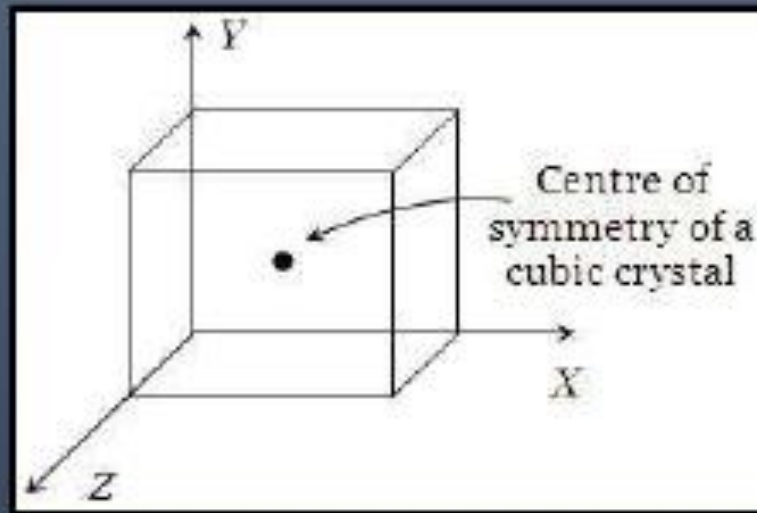


The total number of six –fold axis of symmetry in hexagonal crystal = 7

Order of rotational symmetry = 6

## Centre of symmetry in crystal

It is a point in the crystal with respect to this point a line drawn in opposite direction that intersects the surface of the crystal at equal distance in both directions.



All crystal system has only one Centre of symmetry



## Miller indices

It is a set of integers  $\{h,k,l\}$  which are used to describe a given plane in a crystal.

The procedure for determining the miller indices are as follows:

- ❖ Prepare a three column table with the unit cell axes at the top of the columns
- ❖ Enter in each column the intercept [expressed as a multiple of  $a,b,c$  ] of the plane with these axes
- ❖ Invert all numbers
- ❖ Clear fractions to obtain  $h,k,l$



# Calculation of miller indices

Calculation of the miller indices of crystal plane which cut through the crystal axes at  $(2a,3b,c)$  is shown below:

Unit intercept	a	b	c
Intercept multiple for a plane	2	3	1
Reciprocal of all number	$1/2$	$1/3$	1
Convert the fraction into whole number	3	2	6

So , the miller indices are  $(3,2,6)$  for a plane  $(2a,3b,c)$

## Calculation of Interplanar distance of crystal system

Miller indices are used to calculate interplanar distance of a crystal system. That means the relationship between miller indices and interplanar distance is given as :

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \rightarrow [1]$$

Where h,k,l are the miller indices of the planes and a,b,c are the unit intercepts of the plane.

For a cubic system :  $a = b = c$  ,so that equation [1] becomes

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

## Calculation of Interplanar distance of crystal system

For tetrahedral system :  $a = b \neq c$  , so that equation [1] becomes

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \longrightarrow [3]$$

For an orthorhombic system :  $a \neq b \neq c$  , so that equation [1] becomes

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \longrightarrow [4]$$

## Calculation of Interplanar distance of crystal system

### Example :

The Parameters of an orthorhombic unit are  $a = 50\text{pm}$  ,  $b = 100\text{ pm}$  and  $c = 150\text{pm}$  . Determine the spacing between the (123) planes.

For an orthorhombic unit cell, the interplanar distance is given as:

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

on substituting the values of  $a$  ,  $b$  ,  $c$  ,  $h$  ,  $k$  and  $l$  in the above equation gives

## Calculation of Interplanar distance of crystal system

$$\frac{1}{(d_{hkl})^2} = \frac{1}{(d_{123})^2} = \left(\frac{1}{50\text{pm}}\right)^2 + \left(\frac{2}{100\text{pm}}\right)^2 + \left(\frac{3}{150\text{pm}}\right)^2$$

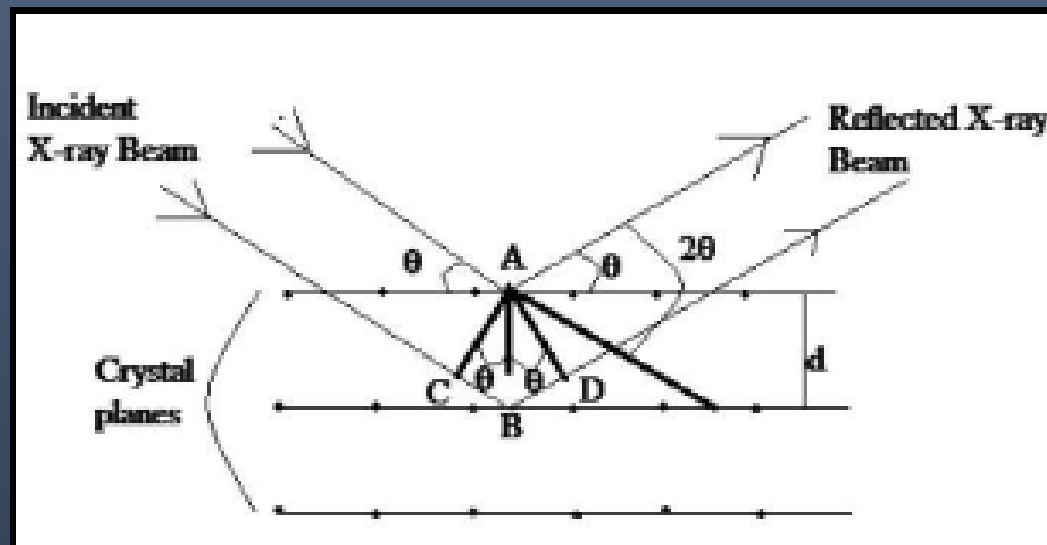
$$\frac{1}{(d_{123})^2} = \frac{3}{(50\text{pm})^2}$$

$$\frac{1}{(d_{123})} = \sqrt{\frac{3}{(50\text{pm})^2}} = \frac{\sqrt{3}}{50\text{pm}}$$

$$\frac{1}{d_{123}} = \frac{50\text{pm}}{\sqrt{3}} = 29\text{pm}$$

# X-ray diffraction

Scattering of x-rays by crystal atoms or ions producing a diffraction pattern that yields information about the structure of the crystal.



# Bragg equation

The reflections of x-rays can take place only at certain angles which are related by the wavelength of the x-rays and the interplanar distance in the crystal in an equation called Bragg equation.

$$2d \sin \theta = n\lambda$$

Where,

$n$  = order of reflection

$d$  = interplanar distance

$\theta$  = angle of scattering

$\lambda$  = wavelength of x-rays



# Derivation of Bragg's Equation:

The phases of the beams coincide when the incident angle equals reflecting angle. The rays of the incident beam are in phase and parallel upto point z, which is the point at which top beam strikes the top layer. The second beam passes to next layer and is scattered by B. The second beam travels extra distance  $AB + BC$ . This extra distance is an integral multiple of the wavelength.

$$n\lambda = AB + BC.$$

But  $AB = BC$

$$\text{hence, } n\lambda = 2AB \dots \dots \dots (1)$$

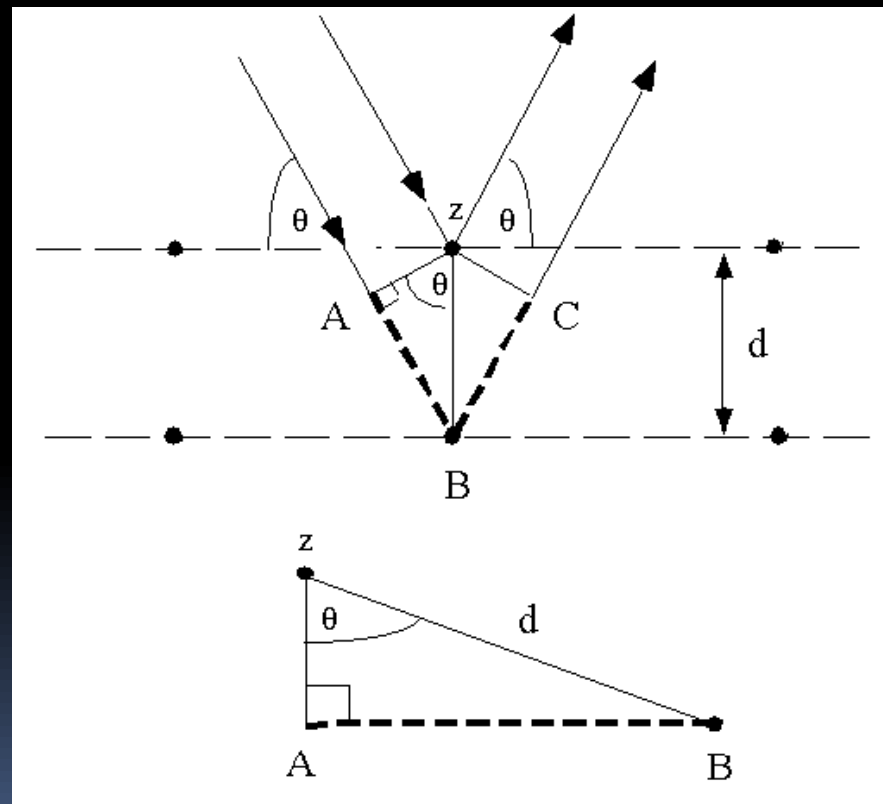
$d$  is the hypotenuse of the right triangle  $Abz$ .  $Ab$  is opposite to angle  $\theta$

$$AB = d \sin \theta \dots \dots \dots (2)$$

Substitute equation (2) in equation (1)

$$n\lambda = 2d \sin \theta$$

This is equation for Bragg's law

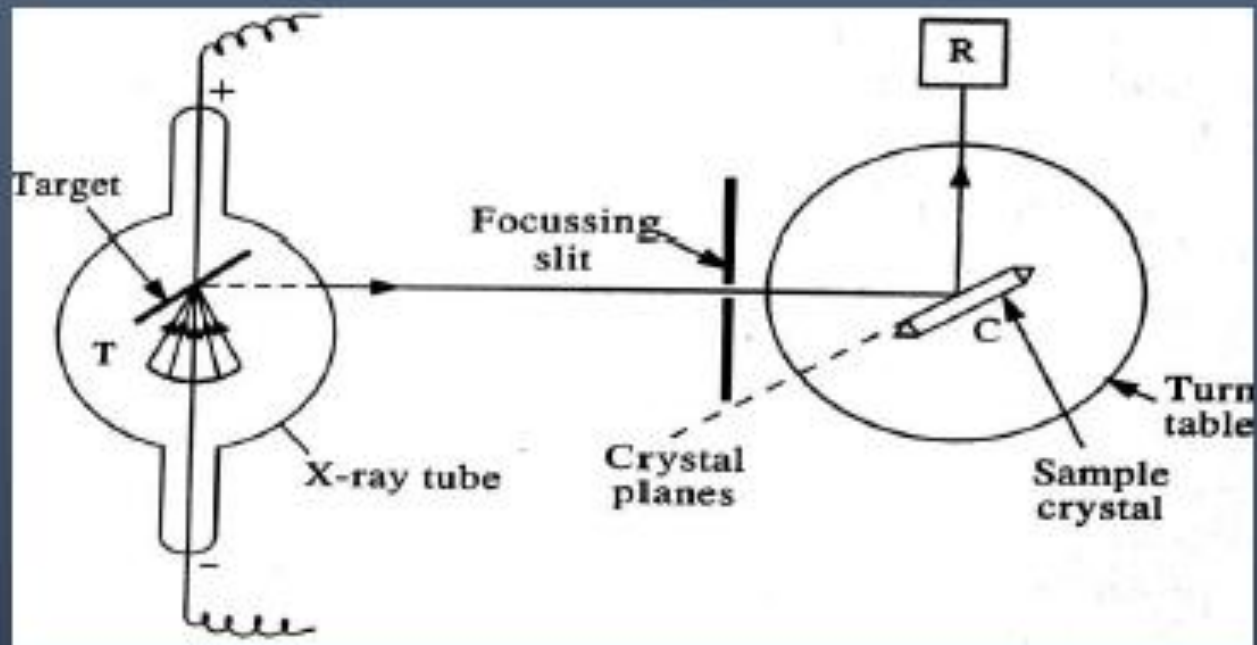


## Experimental determination of interplanar distance for a crystal

- On the basis of X-ray diffraction , interplanar distance for a crystal is determined by an instrument called x-ray spectrometer or x-ray diffractometre
- Methods used in the determination of interplanar distance are :
  1. Rotating crystal method
  2. Powder method(Debye Scherrer method)

## Rotating crystal method

- X-ray spectrometer for the rotating crystal method is shown in figure.
- x-ray generated in the tube T allow to strike a single crystal mounted on a turned table



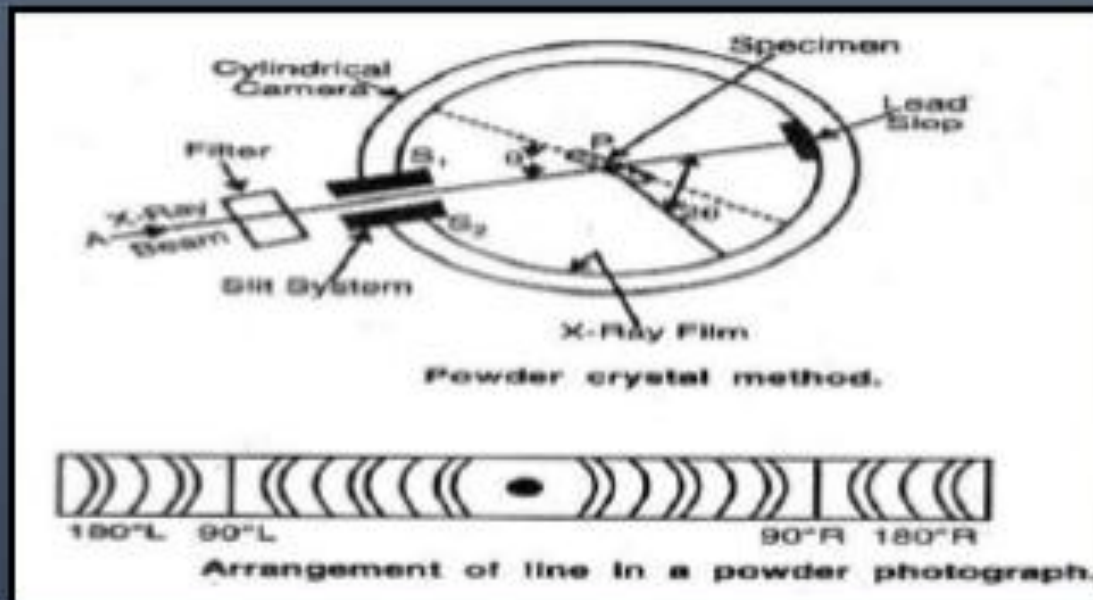
## Rotating crystal method

- The crystal is rotated so as to increase the glancing angle at which the x-rays are incident at the exposed face of the crystal
- The intensity of the reflected rays are measured on the recording device R
- The angles for which reflections are maximum give the value of  $\theta$
- The lowest angle at which the maximum reflection occurs corresponds to  $n = 1$  . This is called first order reflection
- The next higher angle at which the maximum reflection occur is corresponds to second order reflection ( $n = 2$ ) , and so on
- Substituting wavelength of x-ray ( $\lambda$ ) ,  $\theta$  and  $n$  values in Bragg equation , the interplanar distance for a crystal can be calculated

$$d = \frac{n\lambda}{2\sin\theta}$$

## Debye - Scherrer method (powder method)

- The experimental arrangement of powder crystal method is shown in figure



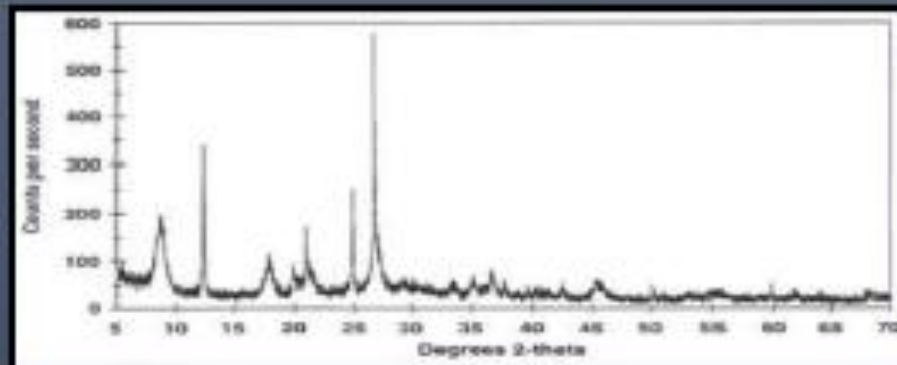


## Debye - Scherrer method (powder method)

- A is a source of X-rays which can be made monochromatic by a filter
- Allow the X-ray beam to fall on the powdered specimen P through the slits  $S_1$  and  $S_2$ . The function of these slits is to get a narrow beam of X-rays
- Fine powder P, struck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This enables sharp lines to be obtained on the photographic film which is surrounding the powder crystal in the form of a circular arc
- The X-rays after falling on the powder passes out of the camera through a cut in the film so as to minimize the fogging produced by the scattering of the direct beam
- As the sample and detector are rotated, the intensity of the reflected X-rays is recorded
- When the geometry of the incident X-rays impinging the sample satisfies the Bragg equation, constructive interference occurs and a peak in intensity occurs

## Debye - Scherrer method (powder method)

- A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor



- The peaks represent positions where the X-ray beam has been diffracted by the crystal lattice. The set of interplanar distances can be calculated from the 2-theta values by using Bragg equation ( $d = n\lambda / 2\sin\theta$ ) where,  $\theta$  is the half of the 2-theta value obtained from the X-ray diffraction spectrum



# The Laue method

The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.

The diffracted beams form arrays of spots, that lie on curves on the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of  $d$  and  $q$  involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one zone. Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis.

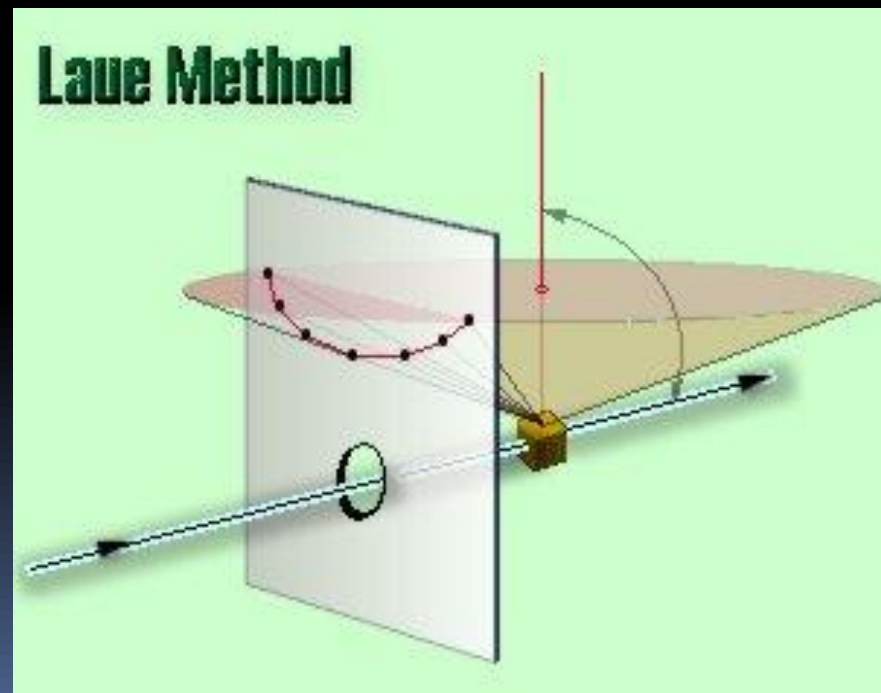
There are two practical variants of the Laue method,

- The back-reflection and
- The transmission Laue method.

## Back-reflection Laue

In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

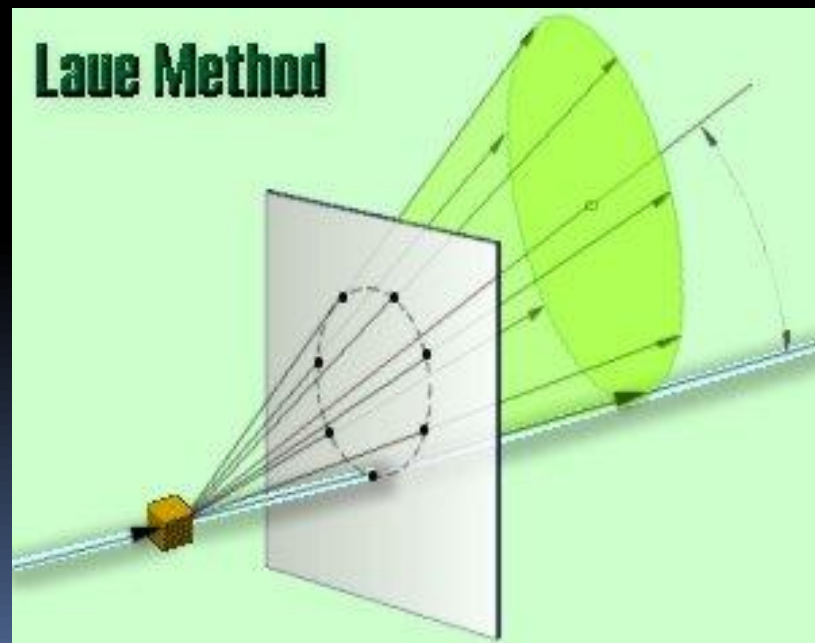
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



## Transmission Laue

In the transmission Laue method, the film is placed behind the crystal to record beams which are transmitted through the crystal.

One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Crystal orientation is determined from the position of the spots. Each spot can be indexed, i.e. attributed to a particular plane, using special charts. The Greninger chart is used for back-reflection patterns and the Leonhardt chart for transmission patterns.

The Laue technique can also be used to assess crystal perfection from the size and shape of the spots. If the crystal has been bent or twisted in anyway, the spots become distorted and smeared out.

## Types of crystal

Solid crystals classified into four types :

- ❖ Molecular crystals
- ❖ Covalent crystals
- ❖ Ionic crystals
- ❖ Metallic crystals

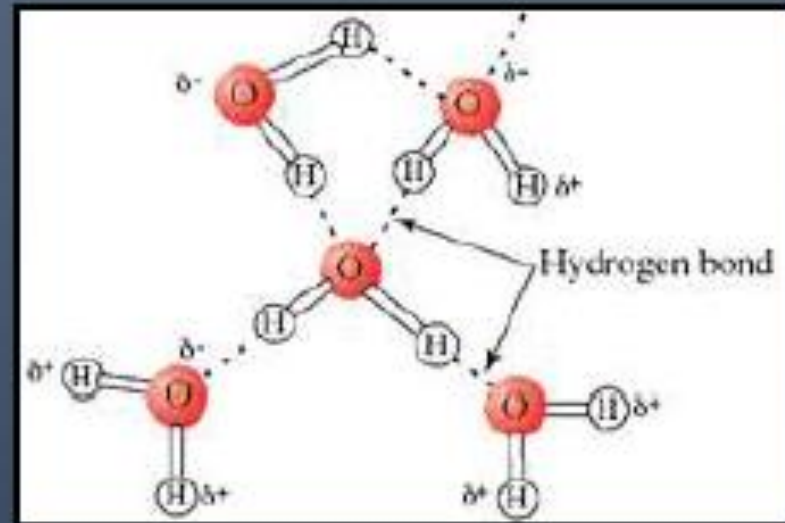
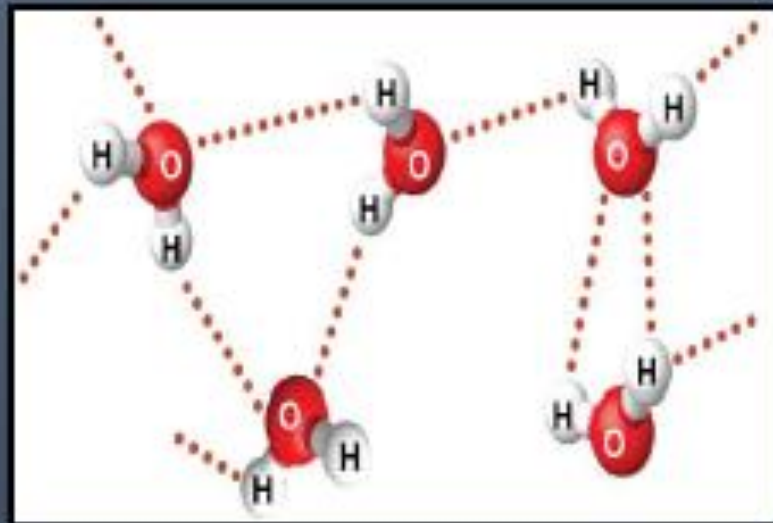
## Molecular crystals

- ❖ Lattice points are occupied by neutral molecules.
- ❖ The molecules are held together by Vander Waal's forces and dipole –dipole interaction.
- ❖ Very soft solids.
- ❖ Low melting point and boiling point.
- ❖ Poor conductors of electricity.
- ❖ Volatile nature.

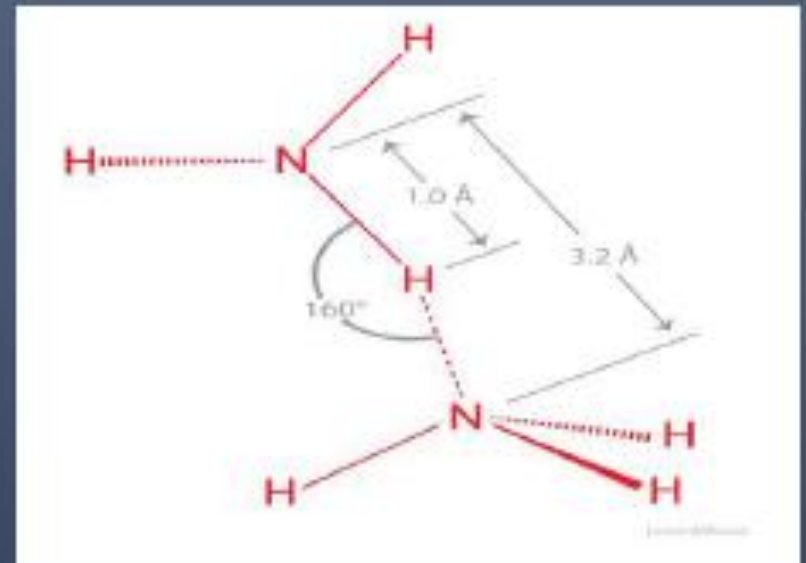
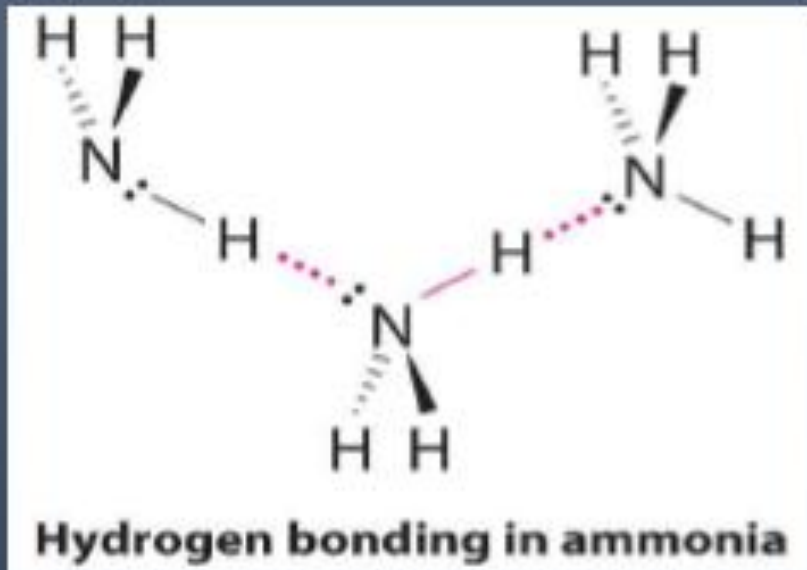
Example : water and ammonia.



## Structure of Molecular crystal - Water



## Structure of Molecular crystal - Ammonia



## Ionic crystals

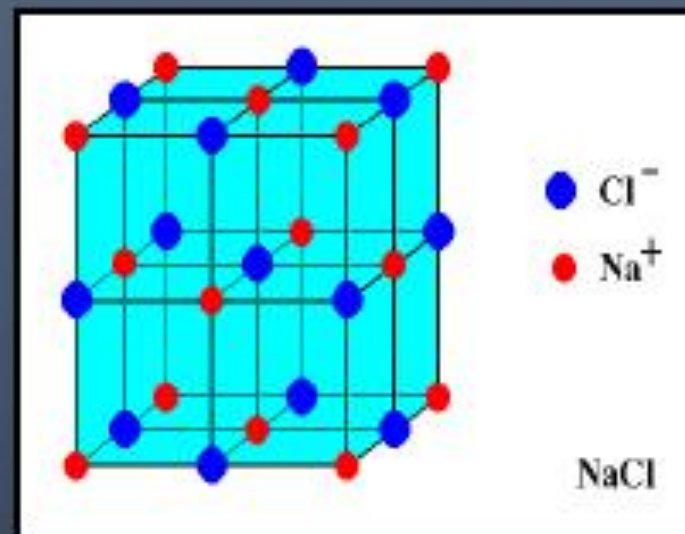
- ❖ Lattice points are occupied by positive and negative ions.
- ❖ Hard and brittle solids.
- ❖ High melting and boiling points due to very strong electrostatic forces of attraction.
- ❖ Poor conductors of electricity in solids state but good in molten state.
- ❖ Heat of vaporization is high.
- ❖ Soluble in water.

Example: NaCl , KCl and CsCl.

# Structure of Ionic crystal- NaCl

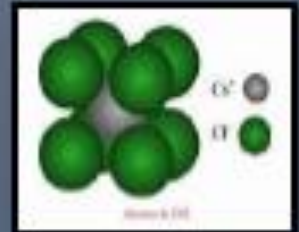


- Face Centred cubic crystal type
- Co-ordination number 6:6
- Calculation of number of NaCl unit in an unit cell is as follow :
  - $\text{Cl}^-$  at corners  $(8 \times 1/8) = 1$
  - $\text{Cl}^-$  at face centres  $(6 \times 1/2) = 3$
  - $\text{Na}^+$  at edge centres  $(12 \times 1/4) = 3$
  - $\text{Na}^+$  at body centres = 1
  - Unit cell contents are  $4(\text{Na}^+ \text{Cl}^-)$
  - thus number of NaCl units per unit cell is 4

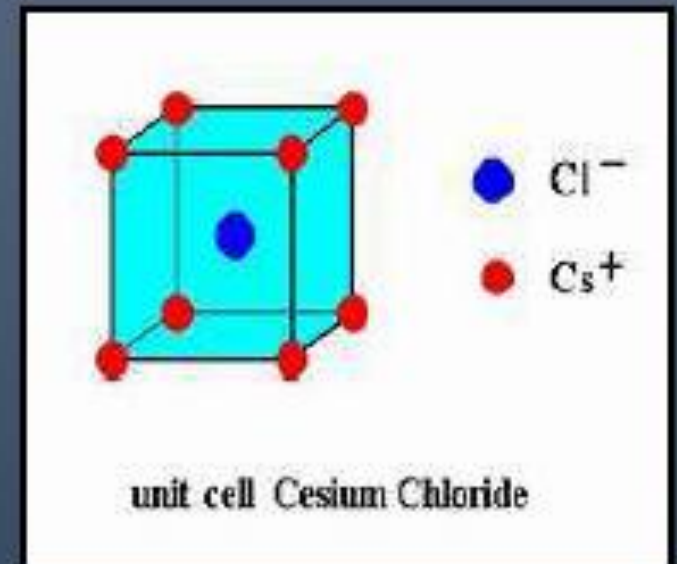


Note: Many salts and oxides have this structure, e.g. KCl, AgBr, KBr, PbS, MgO, FeO, etc.

## Structure of Ionic crystal- CsCl

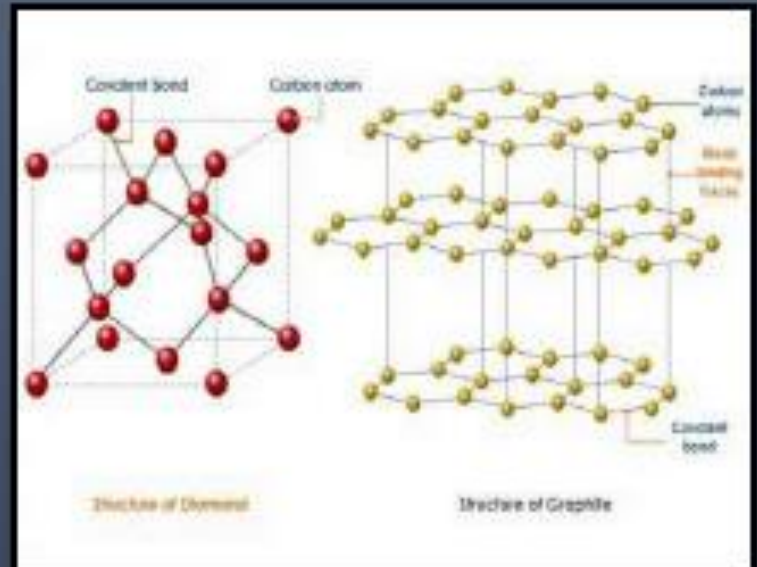


- Body Centred cubic crystal type
- Co-ordination number 8:8
- Calculation of number of CsCl unit in an unit cell is as follow :
  - Cl<sup>-</sup> at corners (8 X 1/8) =1
  - Cs<sup>+</sup> at body centres =1
  - Thus number CsCl units per unit cell is 1



# Covalent crystals

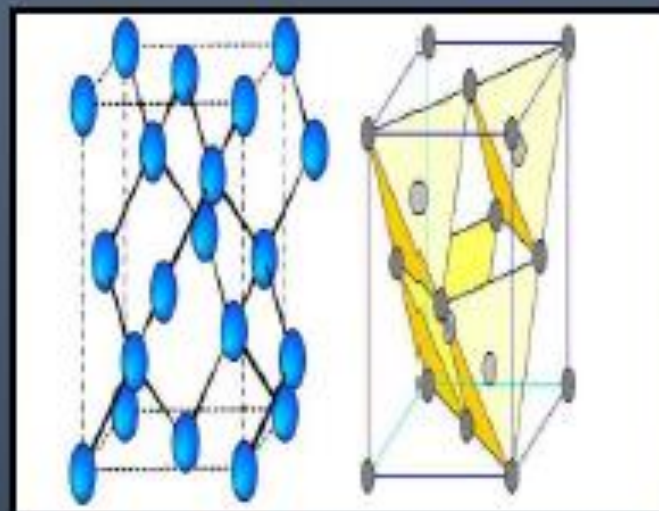
- Lattice points are occupied by neutral atoms
- Atoms are held together by covalent bonds
- Hard solids
- High melting point
- Poor conductors of electricity
- Examples: diamond and graphite





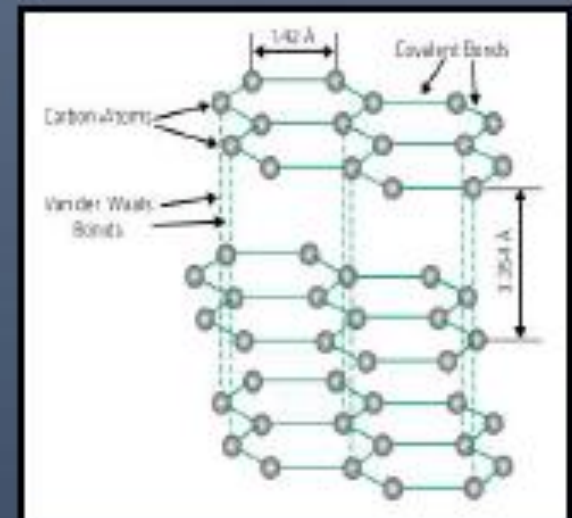
## Covalent crystal - Diamond

- Each carbon atom is covalently bonded to four other carbon atoms by involving  $sp^3$  hybridization
- Rigid three dimensional regular tetrahedron network
- Very hard ,high density and melting point
- Shiny , transparent and unreactive
- Bad conductor of electricity



## Covalent crystal - Graphite

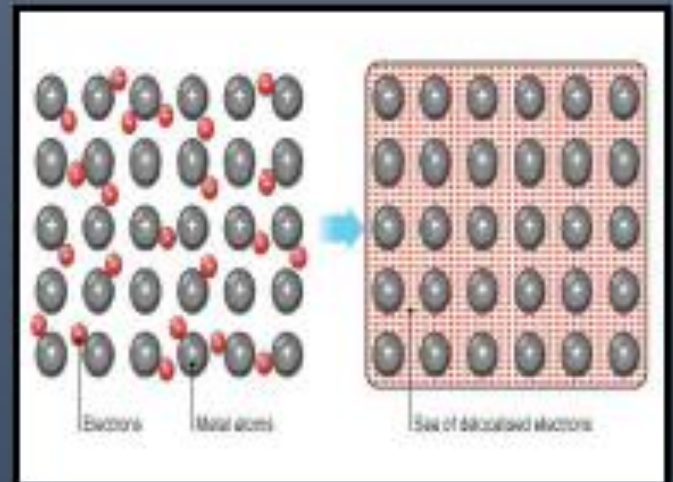
- Each carbon atom covalently bonded to three other carbon atom by involving  $sp^2$  hybridization
- All atoms in a single plane are linked to give flat hexagons
- The hexagons are held together in sheet like structures, parallel to one another i.e. layer lattices structure
- Each layer are held together by Van der Waals forces
- Good conductor of electricity because of availability of non bonded free electrons
- Soft and used as lubricants



# Metallic crystal

- Lattice points are occupied by positive metal ions surrounded by a sea of mobile electrons
- Soft to very hard
- Metals have high tensile strength
- Good conductors of electricity
- Malleable and ductile
- Bonding electrons in metals remain delocalized over the entire crystal
- High density

Examples: All metals



## Defects in crystal-point defects

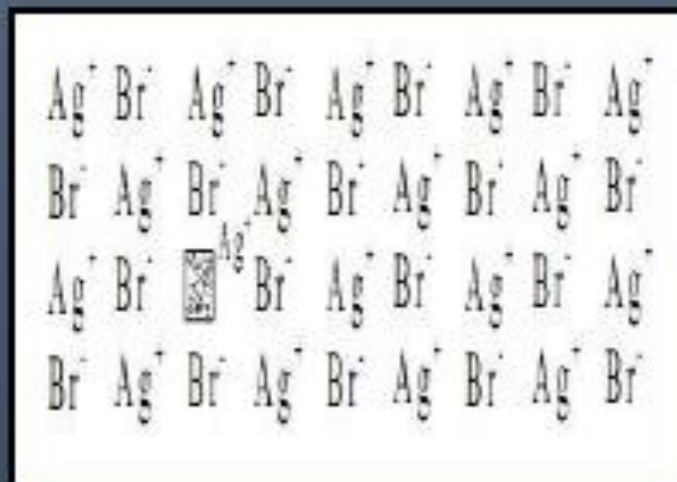
- The imperfection in crystal structure due to the missing or dislocation of atoms or ions is called point defects
- This can be arise due to thermal vibration and imperfect packing during the crystallization

### Types of point defects:

- ❖ Frenkel defect
- ❖ Schottky defect

# Frenkel defect

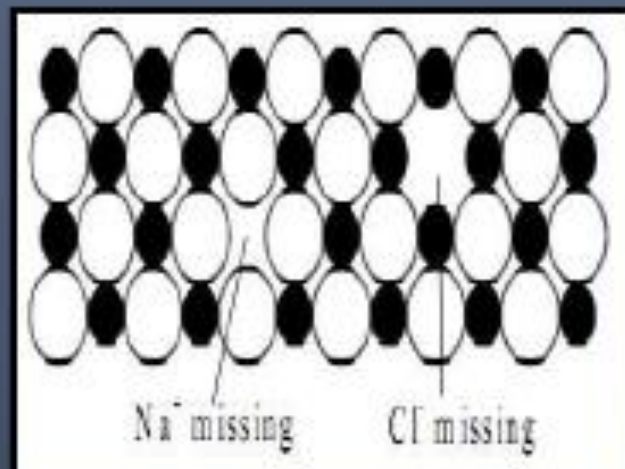
- A Frenkel defect is also known as frenkel pair or frenkel disorder ,it is a type of point defect in a crystal lattice
- The defect forms when an atom or smaller ion leaves its place in the lattice, creating a vacancy ,and becomes an interstitial by lodging in a nearby location.
- Example: AgBr





## Schottky defect

- Schottky defects arise if some of the lattice points in a crystal unoccupied
- The points which are called lattice vacancies
- The existence of two vacancies , one due to a missing of  $\text{Na}^+$  ion and the other due to a missing  $\text{Cl}^-$  ion in a crystal  $\text{NaCl}$
- The crystal remain neutral because the number of missing positive of negative ions is the same
- Example:  $\text{NaCl}$



## Electrical property of crystal

On the basis of electrical property , crystalline materials are classified into three types

- Conductor
- Insulator
- Semi conductor

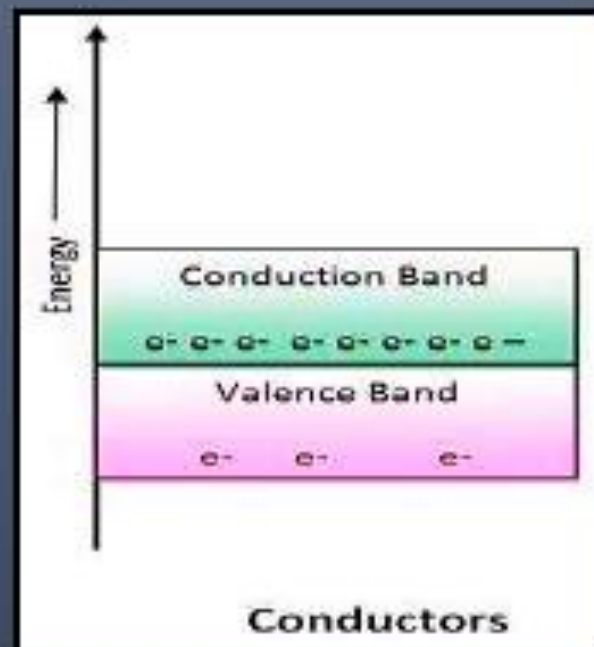
Types of semiconductor:

- p-type semiconductor
- n-type semiconductor



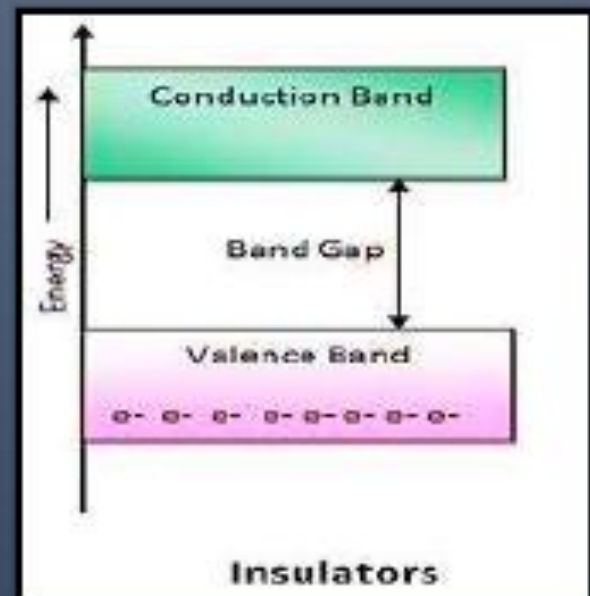
# Conductor

- Crystalline materials that conduct electricity are called conductor
- The energy gap between conduction band and valence band is very low shown in figure
- Availability of more number of free electrons in the conduction band is the responsible for electrical conductivity
- Conductivity of conductor decreases as the temperature increase
- Example : All metals



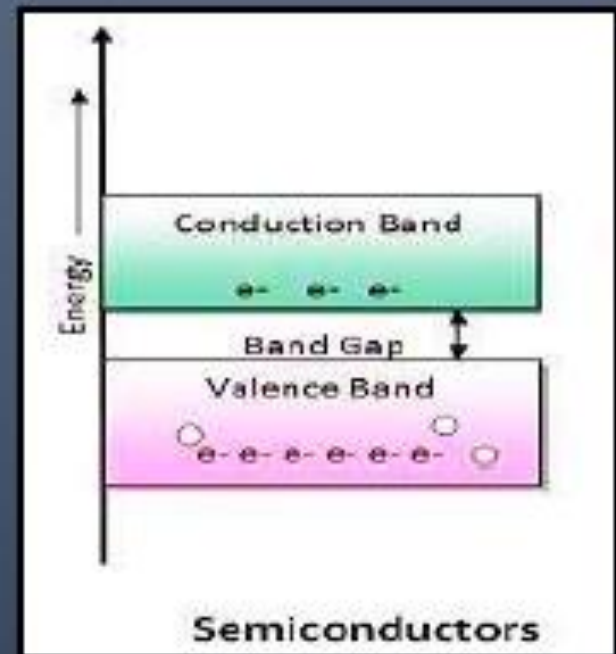
# Insulator

- Crystalline materials that does not conduct electricity are called insulator
- The energy gap between conduction band and valence band is very high shown in figure
- Non availability of free electrons in the conduction band is the responsible for its insulating property
- Example : diamond and quartz



# Semi conductor

- Crystalline materials that has a conductivity between conductor and insulator are called semiconductor
- The energy gap between conduction band and valence band is moderate shown in figure
- Availability of few number of free electrons in the conduction band is the responsible for electrical conductivity
- Conductivity of semi conductor increases as the temperature increase



# Types of Semi conductor

Semi conductor can be classified as :

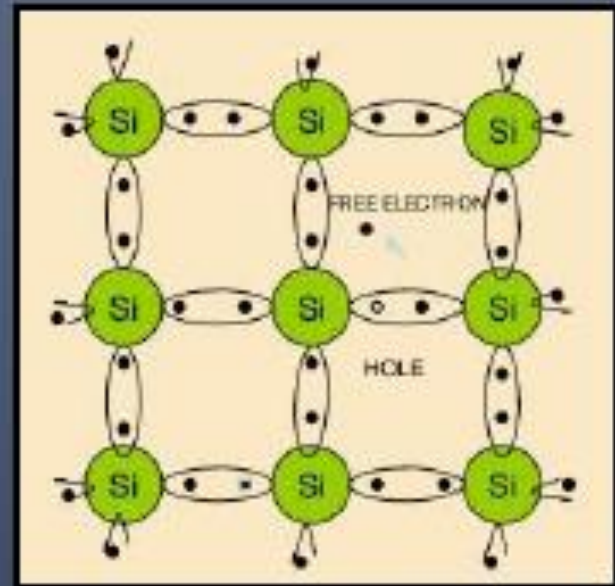
- Intrinsic semiconductor
- Extrinsic semiconductor

Extrinsic semiconductor are further classified as:

- n-type semiconductor
- p-type semiconductor

# Intrinsic semiconductor

- Semiconductor in pure form is known as intrinsic semiconductor
- Conductivity is only slight
- Conductivity increases with rise in temperature
- At room temperature number of electrons equal to number of holes
- Example : pure germanium and pure silicon





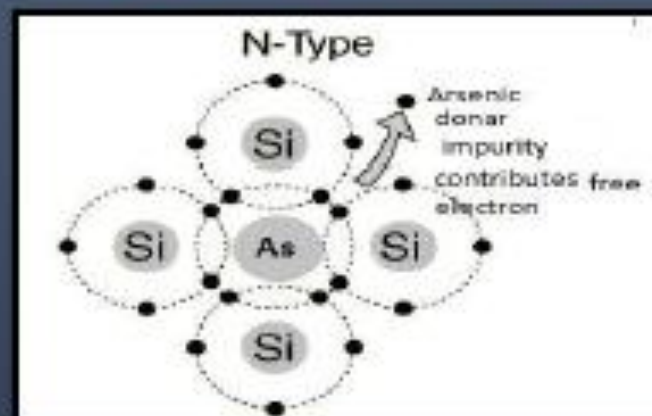
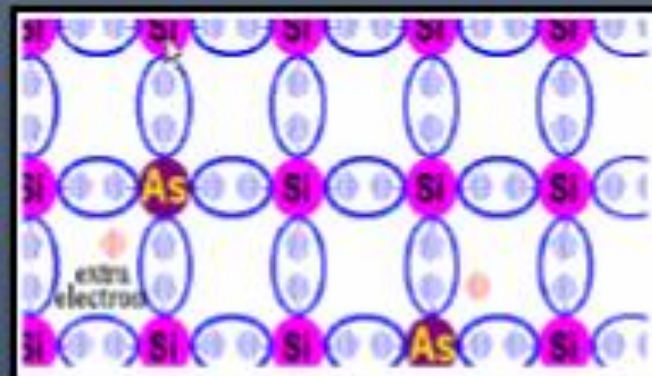
## Extrinsic Semiconductor

- An extrinsic semiconductor is an improved intrinsic semiconductor with a small amount of impurities by a process known as Doping .
- Doping process improves and control the conductivity of semiconductor
- Doping process produces two groups of semiconductor:
  - n-type semiconductor
  - p-type semiconductor



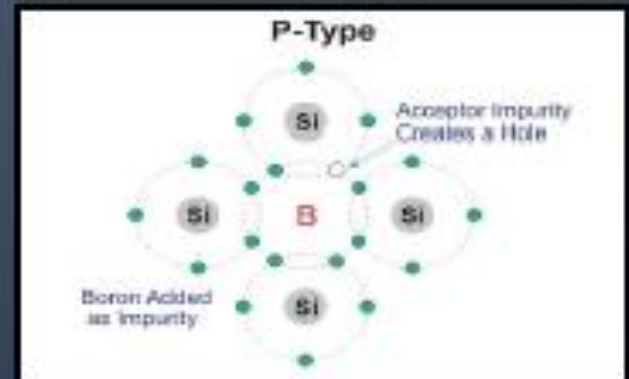
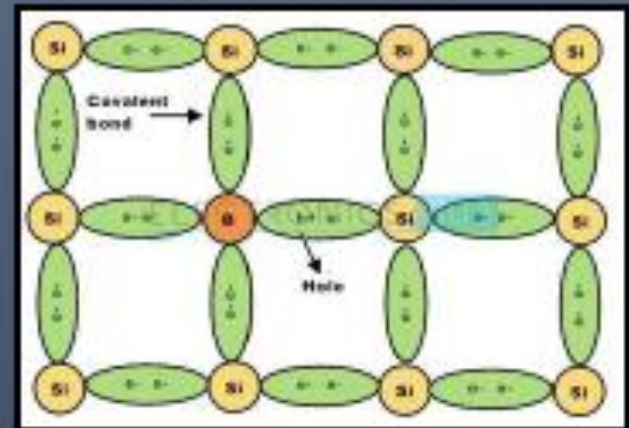
## n-type semiconductor

- The pure crystalline silicon(Si) form a crystal lattice by having each atom share all of its 4 valence electrons with neighboring atoms
- The crystalline array is “doped” with arsenic which has five valence electrons, the behavior of the lattice will change
- Four bonds will be still be made but there will be a leftover electron that can wander through the crystal. This is called n-type semiconductor



# p-type semiconductor

- The pure crystalline silicon(Si) form a crystal lattice by having each atom share all of its 4 valence electrons with neighboring atoms
- The crystalline array is “doped” with boron which has three valence electrons, the behavior of the lattice will change
- Boron offers 3 of the four electrons that a silicon atom needs, each silicon center is left with a hole. This is called p-type



## Determination of Avogadro number

- The number of atoms or molecules in a mole of any substance called **Avogadro number**. This number was found to be  $6.022 \times 10^{23}$  ( $N_A$ )

- Density of Unit Cell :  $d = \frac{Z}{a^3} \times \frac{M}{N_A}$

Where,

$d$  = Density (g/cm<sup>3</sup>)

$Z$  = number of atoms per unit cell

$a$  = Edge length in cm

$M$  = Molar mass in g/mol

- So the Avogadro number:

$$N_A = \frac{Z}{a^3} \times \frac{M}{d}$$

- On substituting  $Z$ ,  $M$ ,  $a$  and  $d$  in the above equation the Avogadro number ( $N_A$ ) can be calculated

## Determination of Avogadro number

### \* Example :

The density of a solid compound KCl is  $1.9893 \text{ g/cm}^3$  and the length of a side unit cell is  $6.29082 \text{ \AA}$  as determined by X-ray diffraction. Calculate the Avogadro's number. Molar mass of KCl is  $74.55 \text{ g/mol}$

### \* Given parameters :

Since KCl belongs to fcc type the no. of ions per unit cell ( $Z$ ) for fcc is 4

$$d = 1.9893 \text{ g/cm}^3 \qquad a = 6.29082 \text{ \AA} = 6.29082 \times 10^{-8}$$

$$M = 74.55 \text{ g/mol} \qquad Z = 4$$

### \* On substituting the above parameters in the following equation:

$$\begin{aligned} N_A &= \frac{Z}{a^3} \times \frac{M}{d} \\ &= \frac{4 \times 74.55}{(6.29082 \times 10^{-8})^3 \times 1.9893} = \frac{298.2 \times 1024}{495.26} = 6.02 \times 10^{23} \\ N_A &= 6.023 \times 10^{23} \end{aligned}$$



Thank you!

