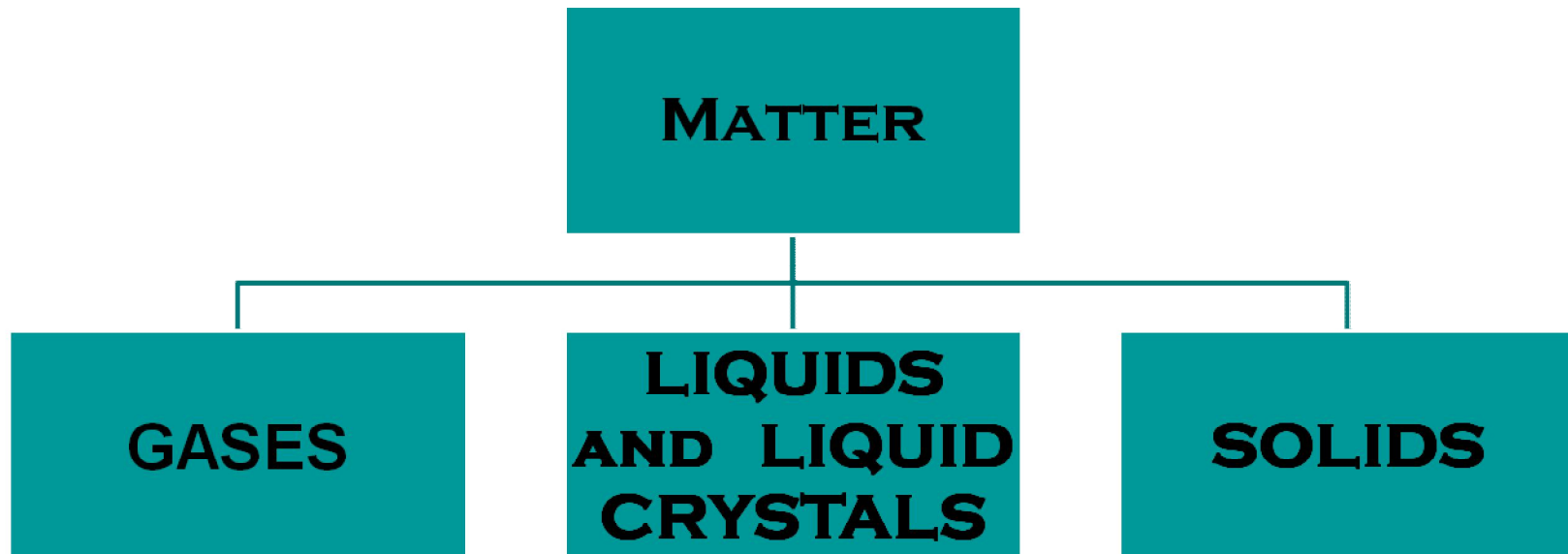


Solid State Chemistry

- ❖ Introduction, unit cell, Bravais lattice, analysis of cubic crystals.
- ❖ Crystallography: three laws of crystallography- Weiss indices, Miller indices with numerical, X ray diffraction- Bragg's law and numerical.
- ❖ Crystal defects and imperfections, their effect on properties of crystals. Preparation of semiconductors. Fullerene and its application.
- ❖ Phase Rule: introduction, phase rule, one component system.
- ❖ Chemistry In Nanoscience: carbon nanotubes, fullerenes, quantum dots, graphine, synthesis of nanoparticles, uses, application

matter



What is a solid?

- ❖ Solids consist of atoms or molecules *executing thermal motion* about an equilibrium position *fixed at a point* in space.
- ❖ Solids can take the form of crystalline, polycrystalline, or amorphous materials.
- ❖ Solids (at a given temperature, pressure, and volume) *have stronger bonds* between molecules and atoms than liquids.
- ❖ Solids *require more energy* to *break the bonds*.

Definite shape and volume
Slow diffusion
High rigidity.

SOLID MATERIALS

Crystalline

Amorphous
(Non-crystalline)

Single Crystal

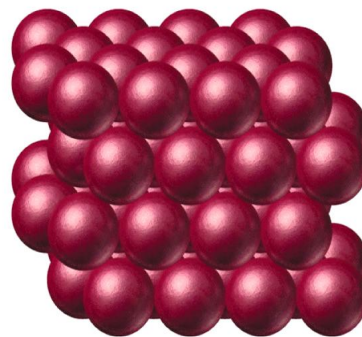
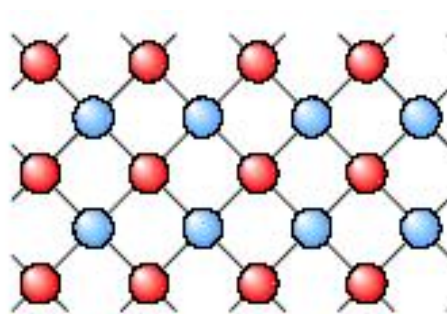
Polycrystalline

Types of Solids

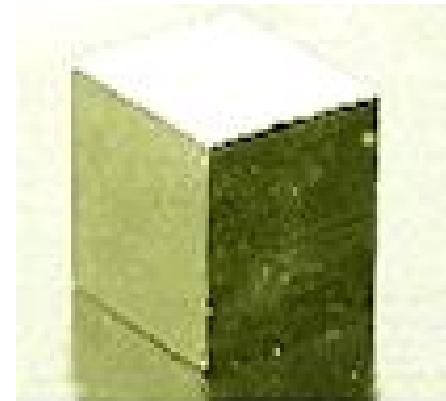
- Single crystal, polycrystalline, and amorphous, are the three general types of solids.
- Each type is characterized by the size of ordered region within the material.
- An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity.

Crystalline Solid

- ❖ Crystalline Solid is the solid form of a substance in which the *atoms or molecules* are arranged in a definite, repeating pattern in three dimension.
- ❖ Single crystals, ideally **have a high degree of order**, or regular geometric periodicity, throughout the *entire volume of the material*.

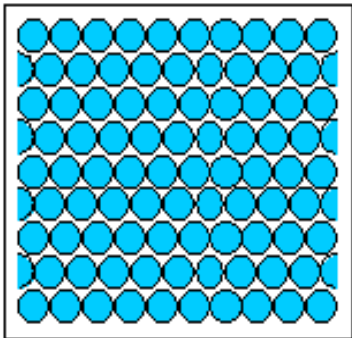


(a) Crystalline solid

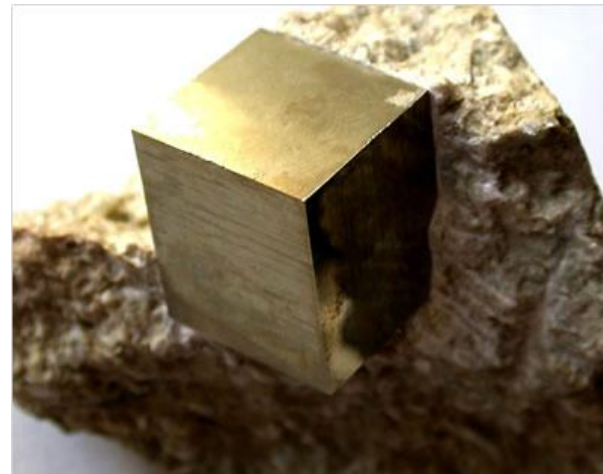
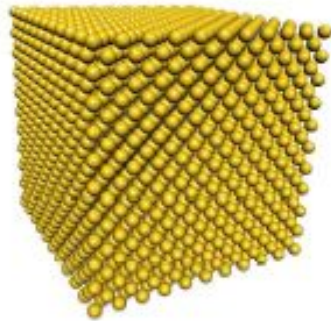


Crystalline Solid

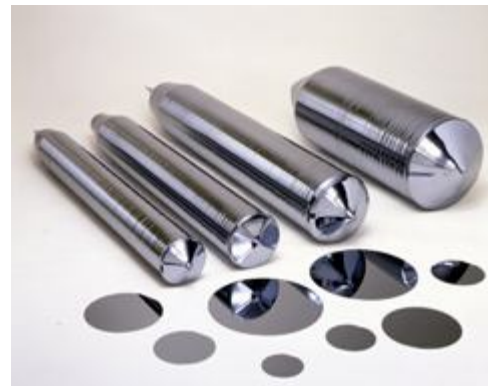
- Single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry



Single Crystal



Single Pyrite
Crystal



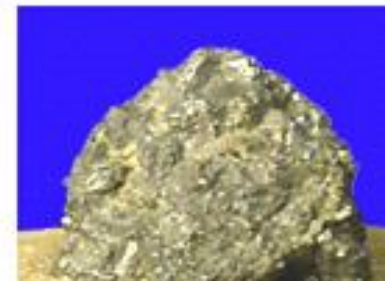
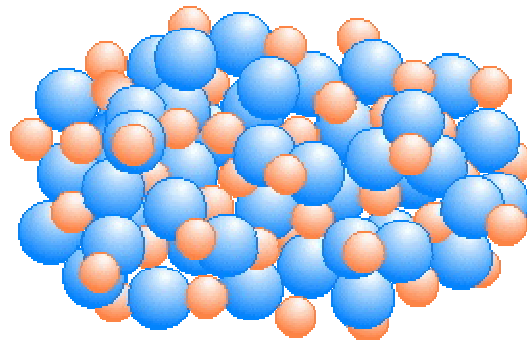
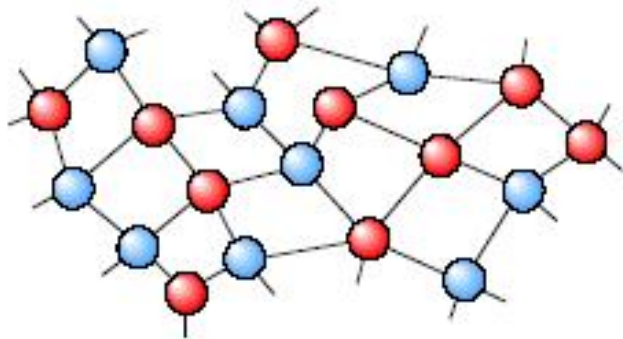
Single Silicon
Crystal

Polycrystalline Solid

- Polycrystal is a material made up of an aggregate of *many small single crystals* (also called crystallites or grains).
- Polycrystalline material **have a high degree of order over many atomic or molecular** dimensions.
- These *ordered regions*, or single crystal regions, **vary in size and orientation** wrt **one another**.
- These regions are called as *grains (domain)* and are separated from one another by *grain boundaries*. The **atomic order** can vary from **one domain to the next**.
- The grains are usually *100 nm - 100 microns in diameter*. Polycrystals with grains that are <10 nm in diameter are called **nanocrystalline**.

Amorphous Solid

- Amorphous (Non-crystalline) Solid is composed of randomly orientated atoms, ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used in solar cells and thin film transistors.



Crystalline solids	Amorphous solids
They have long range order	They have short range order
They have definite melting point	Do not have definite melting point
They break into two pieces with plane surfaces	They break into two pieces with irregular surface
They are anisotropic because these substances show different property in different direction	They are isotropic because these substances show same property in all directions
There is a sudden change in volume when it melts	There is no sudden change in volume on melting
These possess symmetry	Do not possess any symmetry

Crystallography

A crystal is a solid substance having definite geometrical shape with flat faces and sharp edges.

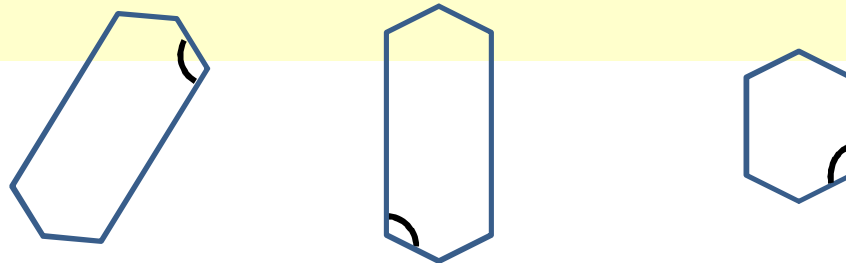
The branch of science which deals with the geometry , properties and structures of crystals and crystalline substances is called as crystallography.

Law of constancy of interfacial angles

A crystalline substance can crystallize under different conditions to give crystals having faces with different shapes and size.

However the angle of intersection of any two corresponding faces would always be found to be the same.

Law states that " the shape and size of the crystals of a certain compound or element may vary with the conditions under which crystallization occurs, but the angles between the two corresponding faces are always constant".



Law of rational indices

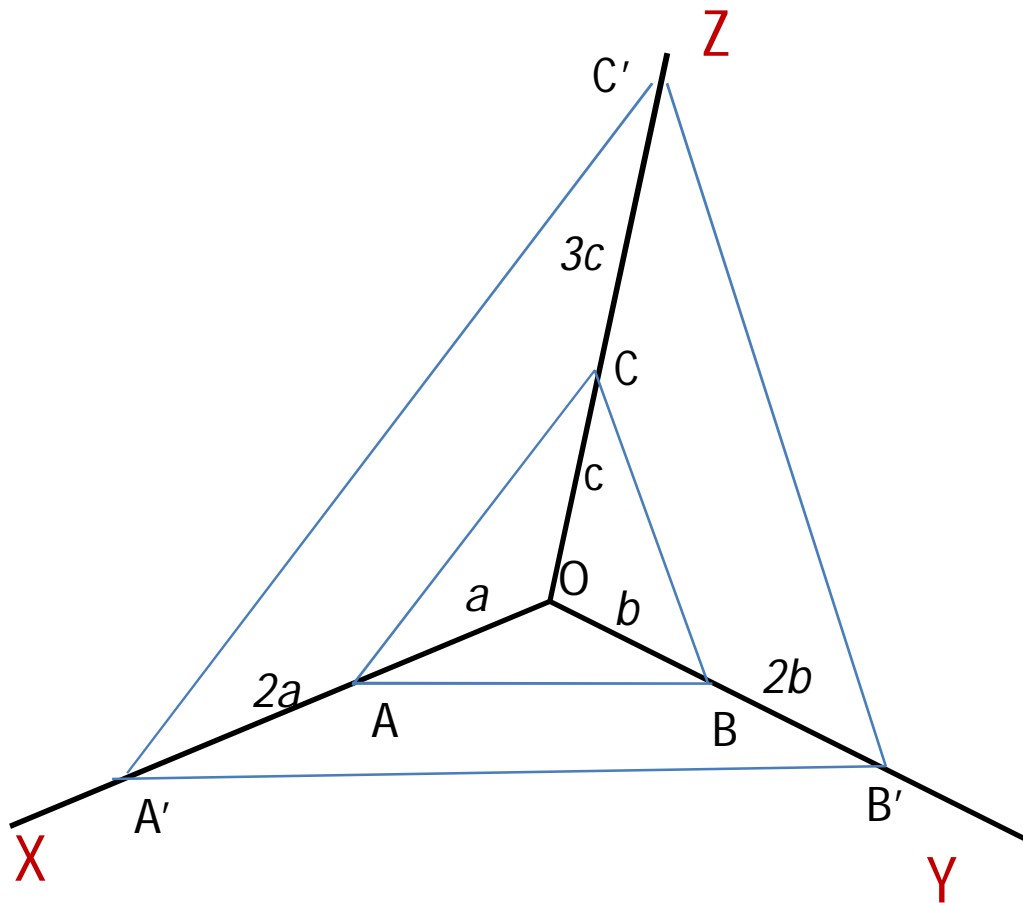
- ❖ Geometry of the crystal can be described by choosing 3 mutually perpendicular axes.
- ❖ The axes are such that all the faces of the crystals will either be cutting the axis at definite distance from the origin or the faces will be parallel to the axis.
- ❖ When the faces are parallel to the axis the intercept is assumed to be at infinity.

Law states that “It is possible to choose along the three coordinate axes, unit distance (a , b , and c) which may or may not be of the same length such that the ratio of the three intercepts of any plane in the crystal is given by $(ha:Kb:lc)$ where h , k and l are integral number”

“All the faces cut a given axis at distance from the origin which bear a simple ratio to one another”

Crystal planes are defined by the intercepts they make on the crystal axes of the unit cell. The inverse of these fractions are the Miller Indices of the planes.

Miller Indices



Weiss Indices

$$2a:2b:3c$$

Take Reciprocal

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

Multiply of least common multiple

$$1/2 \times 6, 1/2 \times 6, 1/3 \times 6$$

Miller Indices (hkl)

$$(332)$$

Miller indices of a plane is a set of three numbers h , k and l that defines a set of parallel planes in a crystal

How to determine the miller indices of a plane?

1. Choose the origin
2. Find the intercept that first such plane makes with the crystallographic axes.
3. Obtain the reciprocals
4. Clear the fractions

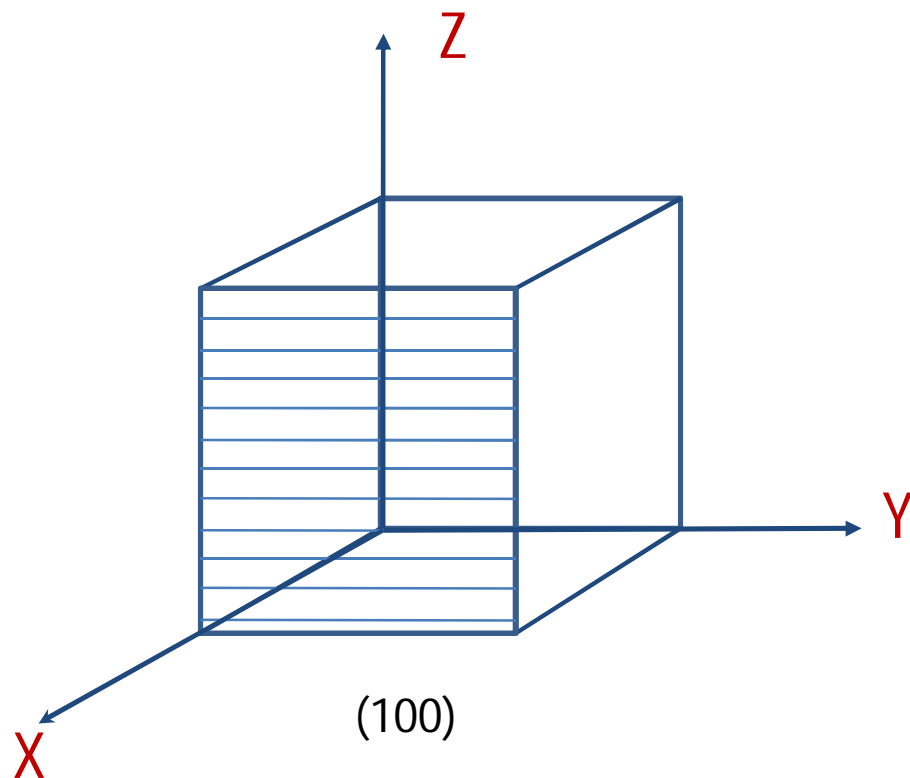
The set of numbers thus obtained in relation with the axes a , b and c are h , k , and l respectively.

Miller Indices

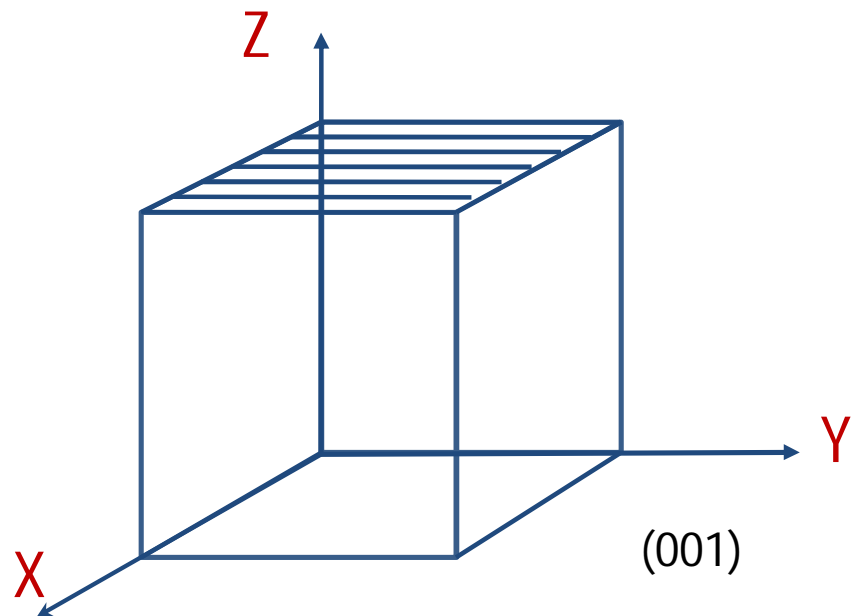
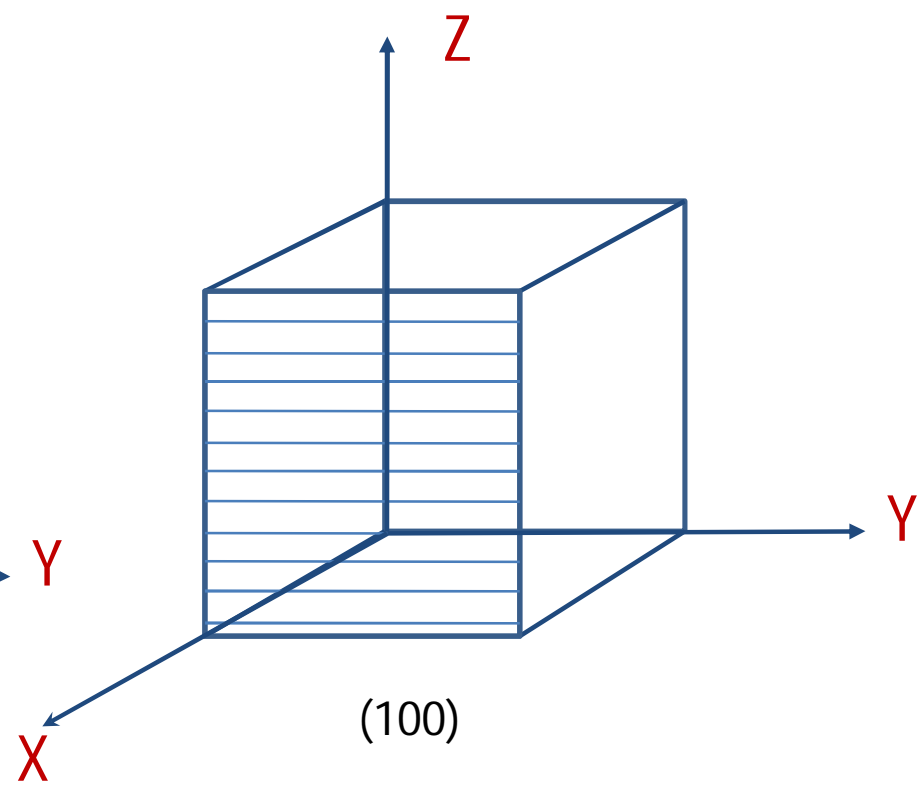
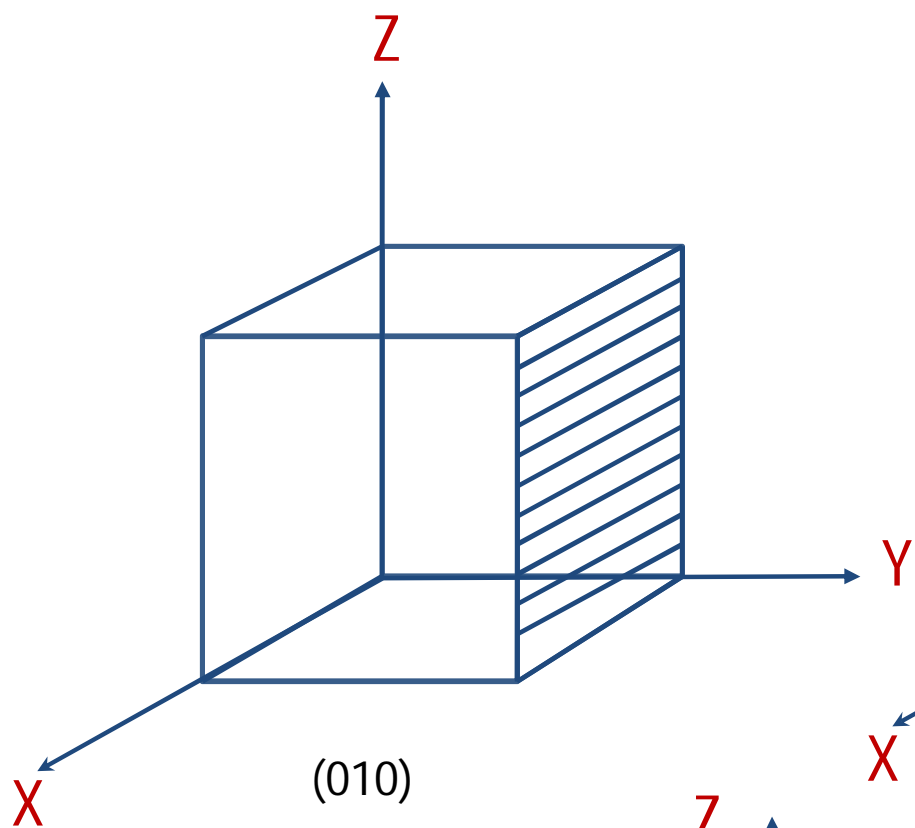
$$h = \frac{a}{\text{Intercepts of the plane along the X-axis}}$$

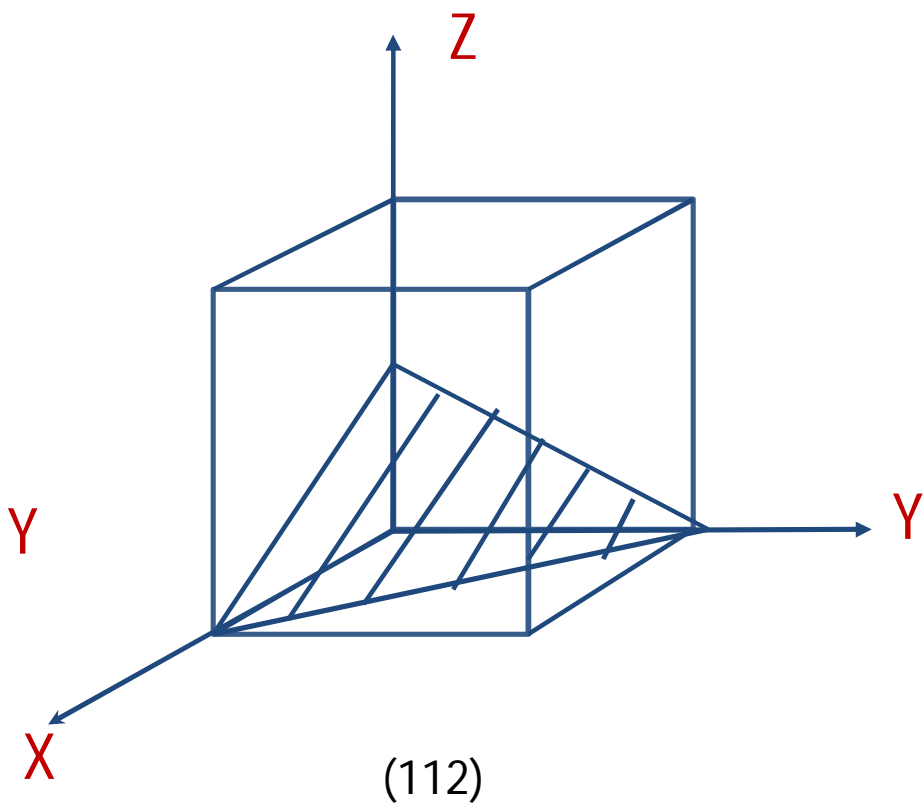
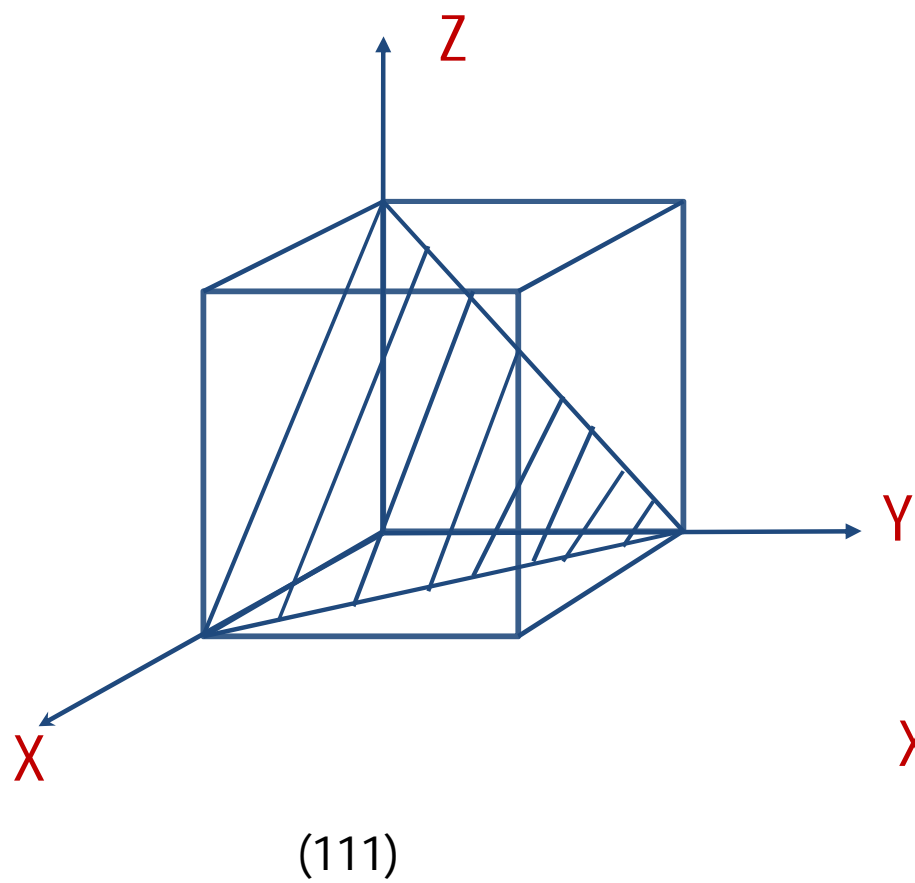
$$k = \frac{b}{\text{Intercepts of the plane along the Y-axis}}$$

$$l = \frac{c}{\text{Intercepts of the plane along the Z-axis}}$$



Axis	X	Y	Z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller Indices (100)			



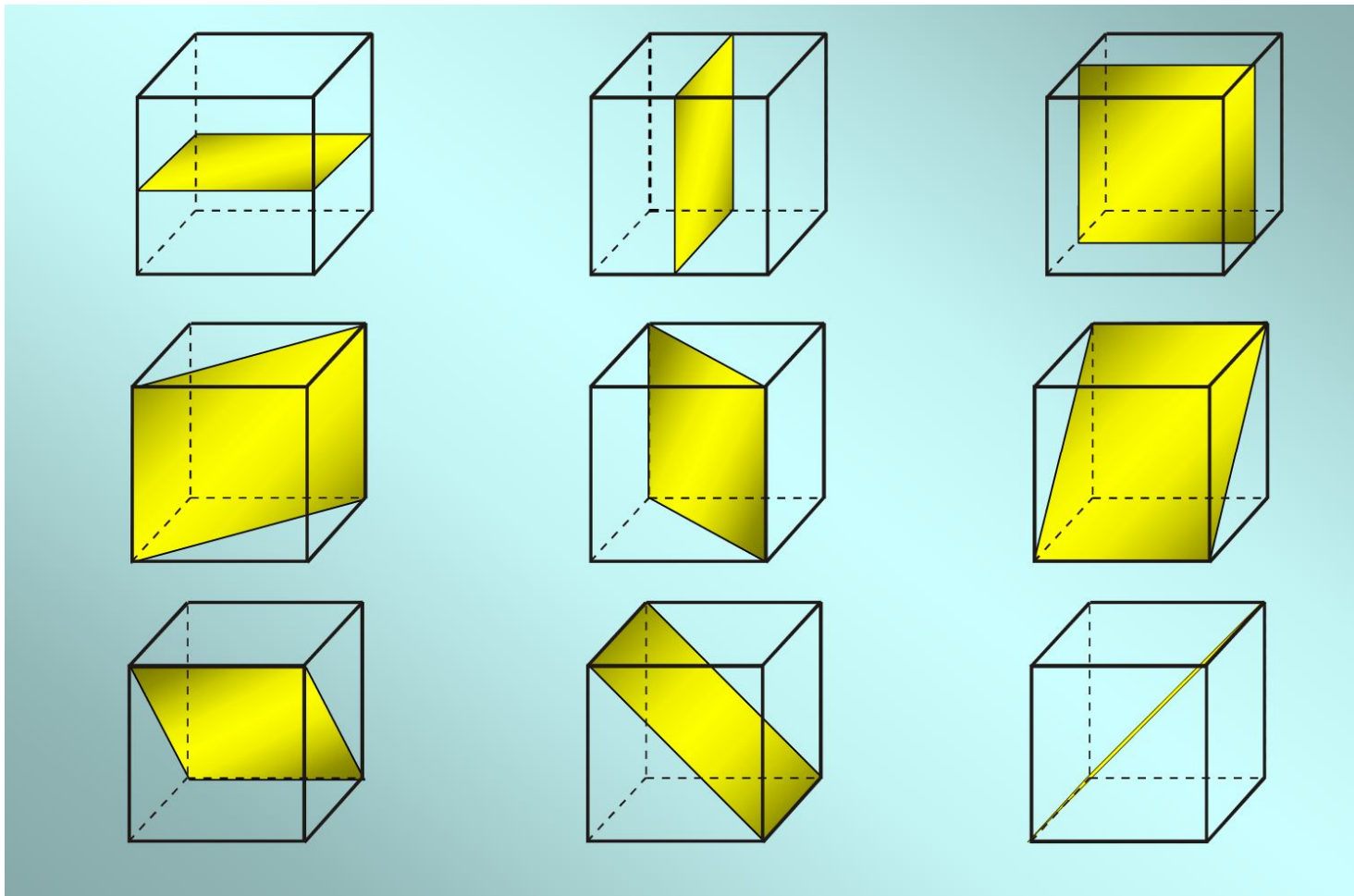


Law of Symmetry

Law states that : "All crystals of the same substance possesses same number of symmetry."

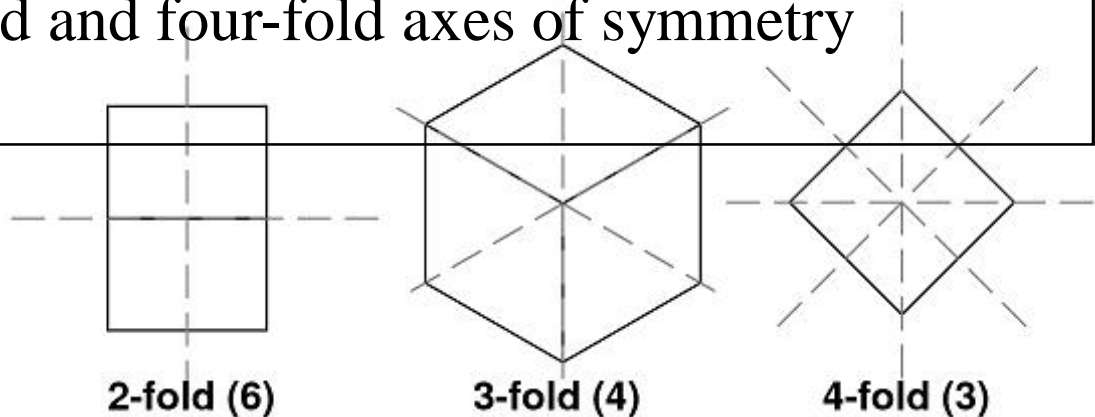
Plane of symmetry: An imaginary plane by which if a crystal is divided into two parts , one part becomes the mirror image of the other.

Planes of Symmetry for a cube = 9



Axis of symmetry: An imaginary line through the crystal about which if the crystal is rotated through 360° , it appears same more than once.

- ❖ This is an axis passing through the crystal such that if the crystal is rotated around it through some angle, the crystal remains invariant.
- ❖ The axis is called '**n-fold, axis**' if the angle of rotation is $\frac{360}{n}$.
- ❖ If equivalent configuration occurs after rotation of 180° , 120° and 90° , the axes of rotation are known as two-fold, three-fold and four-fold axes of symmetry respectively.



Centre of Symmetry: A point in the crystal such that any line drawn through it will intersect the surface of the crystal at equal distance in both directions

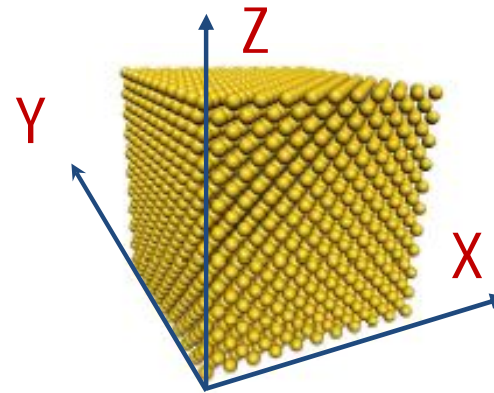
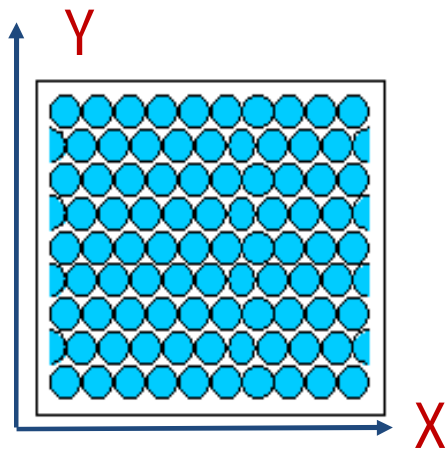
(a) Centre of symmetry	1
(b) Planes of symmetry	9
(Straight planes -3, Diagonal planes -6)	
(c) Diad axes	6
(d) Triad axes	4
(e) Tetrad axes	3

Total number of symmetry elements =	23

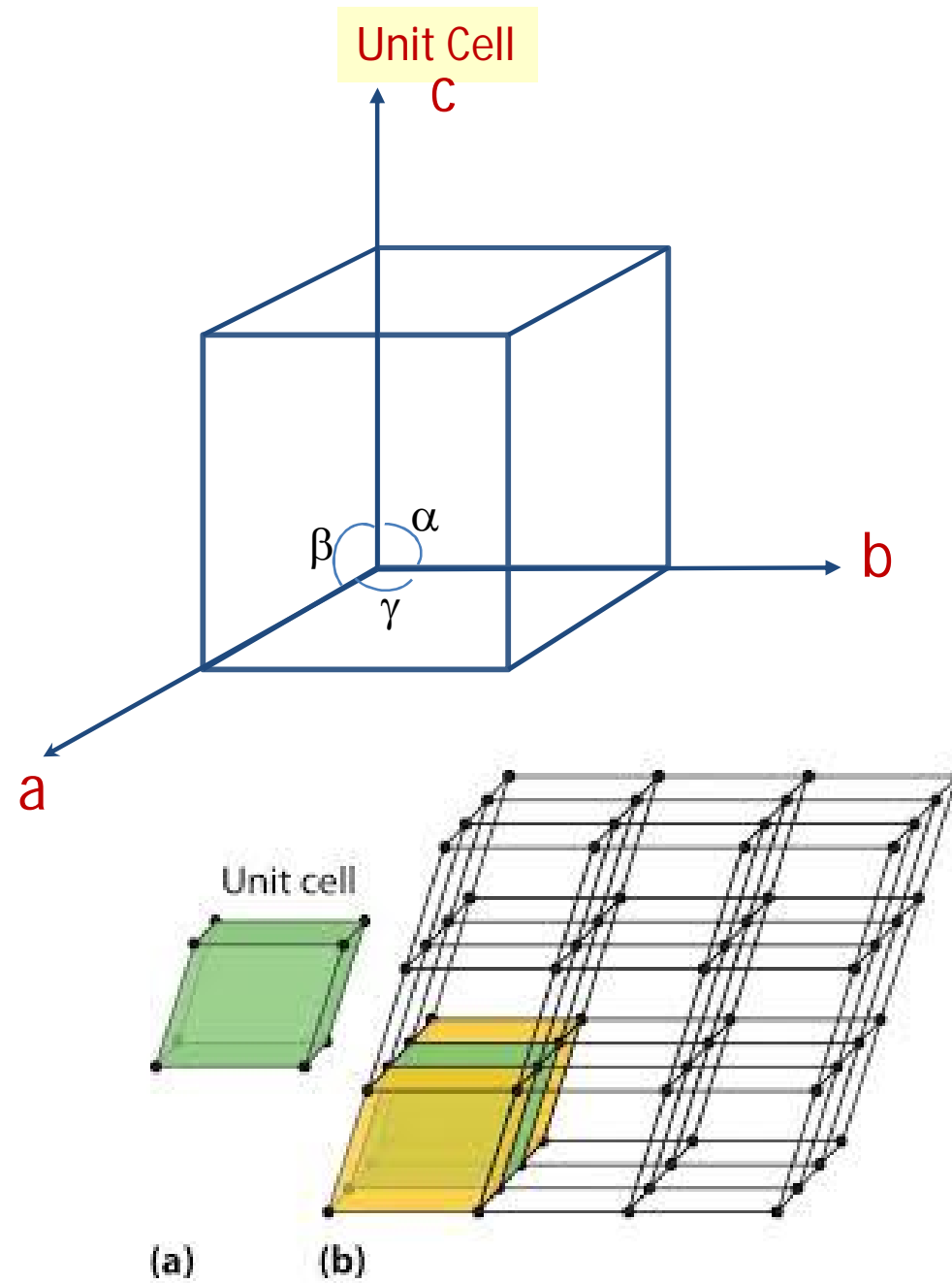
Thus the total number of symmetry elements of a cubic structure is 23.

Crystal Lattice or space lattice

- ❖ A crystal can be imagined as a periodic arrangement of atoms or molecules.
- ❖ If we carry out a translation operation by a fixed distance in a X direction , it will create a linear array of atoms.
- ❖ If we do the same translation in Y direction , it will generate periodically repeating atoms on a XY plane and it is known as two dimensional plane lattice.
- ❖ Similarly when third translation is added , we get a three dimensional arrangement of atoms called as space lattice.



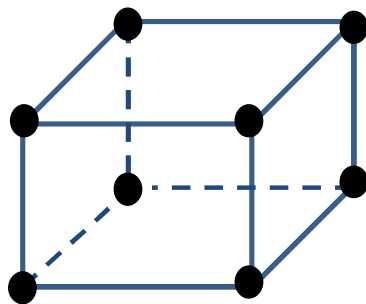
- ❖ Crystal lattice is an highly ordered three dimensional structure formed by constituents such as atoms, molecules or ions.
- ❖ If the constituents are represented as points then the lattice can be regarded as infinite set of points repeating in space in a regular manner.
- ❖ The unit cell is the smallest repeating/building unit in space of crystal.
- ❖ Repeat ion of unit cell in three dimensions form a space lattice of a crystalline substance.



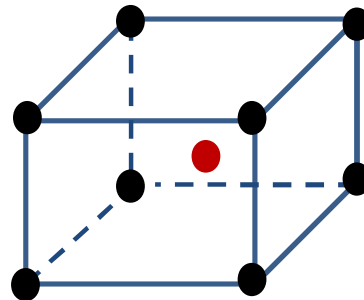
Bravais Lattice

- ❖ All the crystal structures can be represented by using only 14 types of space lattice or 14 types of unit cells.
- ❖ Thus there are 14 types of space lattices known as Bravais lattices.

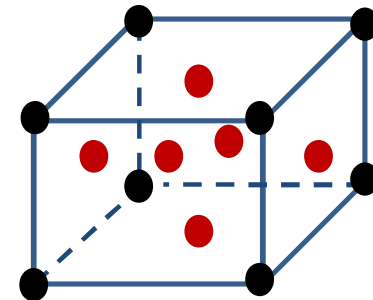
Cubic



$$a = b = c$$

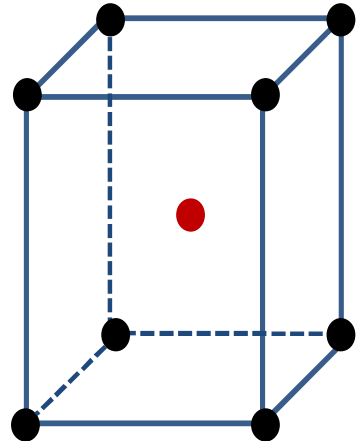
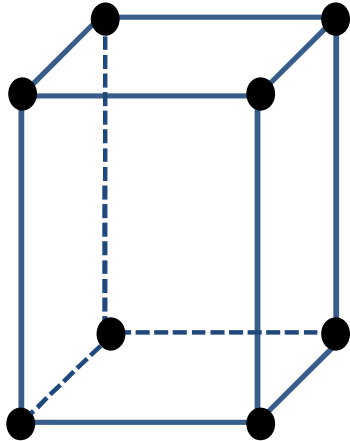


$$\alpha = \beta = \gamma = 90^\circ$$



NaCl, KCl, diamond, ZnS, Cu

Tetragonal

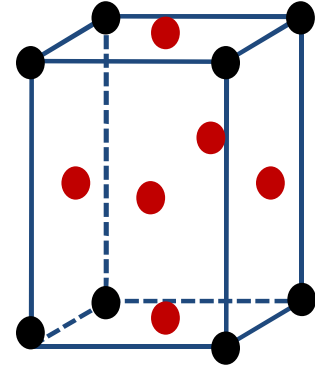
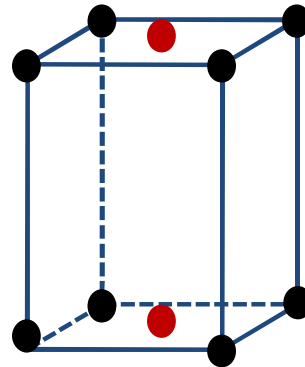
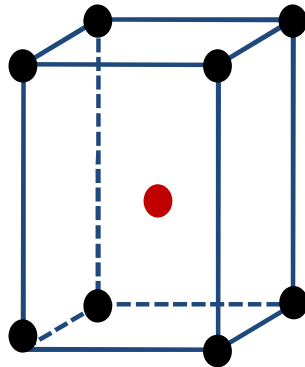
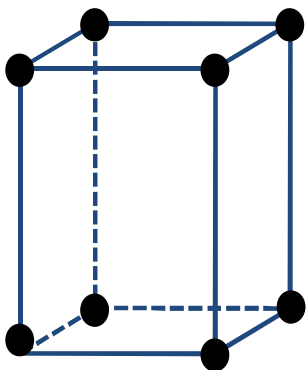


$$a = b \neq c$$

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

SnO₂, TiO₂, ZrSiO₄

Orthorhombic

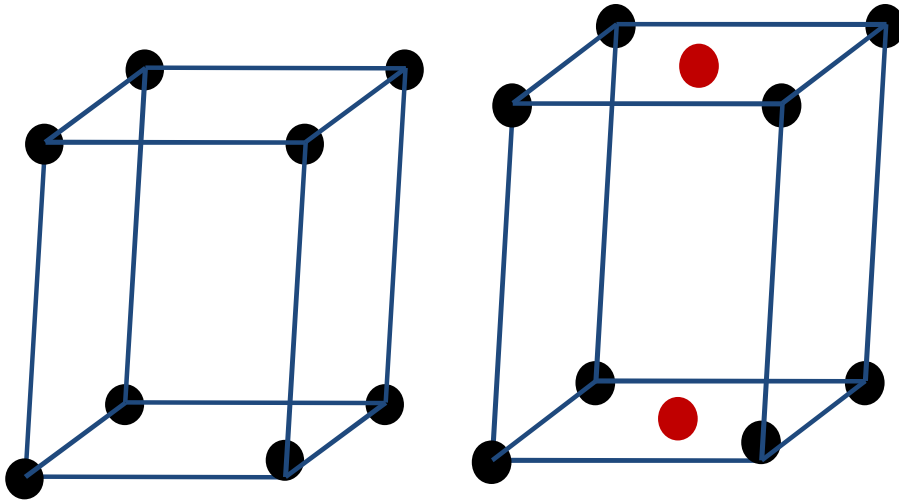


$$a \neq b \neq c$$

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

KNO₃, K₂SO₄, BaSO₄, PbCO₃

Monoclinic

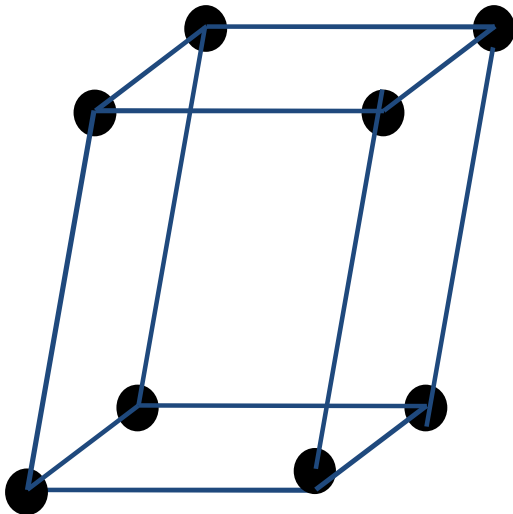


$$a \neq b \neq c$$

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

*CaSO₄·2H₂O, Monoclinic Sulphur,
Na₂SO₄·10 H₂O*

Triclinic

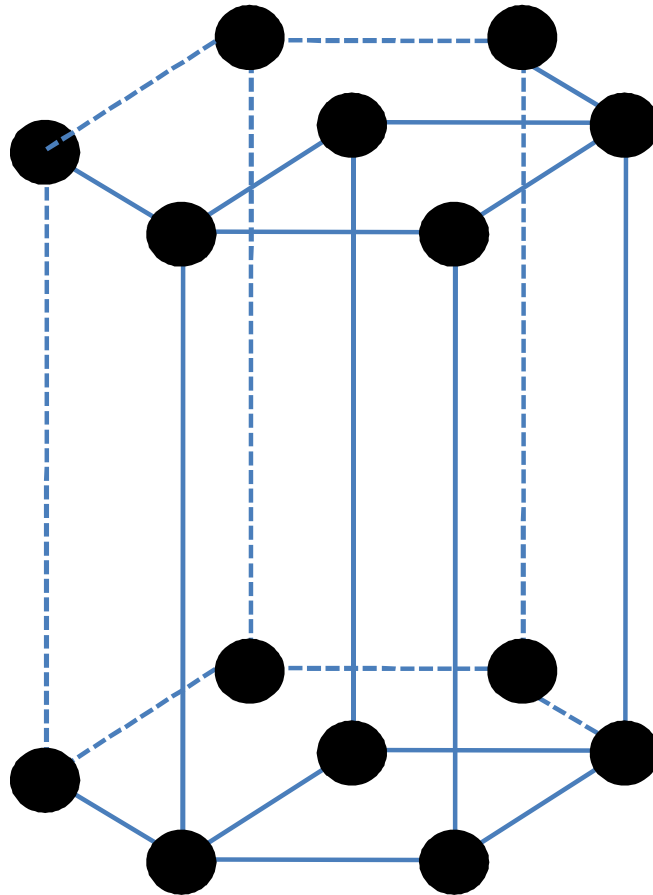


$$a \neq b \neq c$$

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

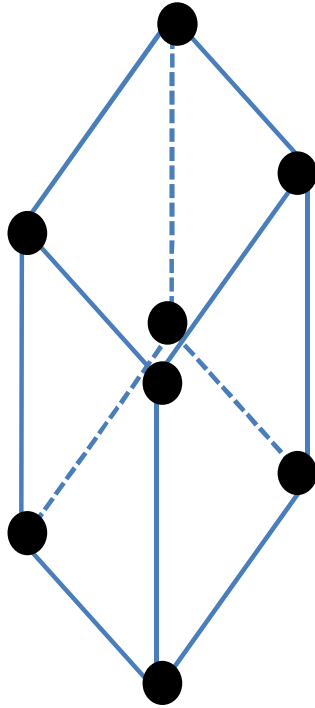
CuSO₄·5H₂O, NaHSO₄, K₂Cr₂O₇

Hexagonal



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

Rhombohedral (Trigonal)



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

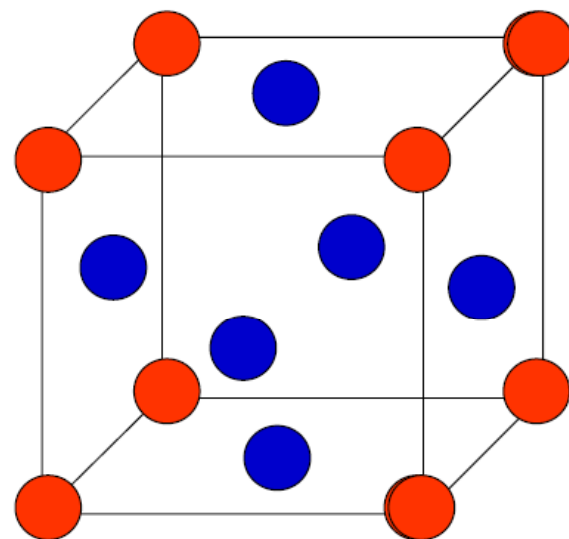
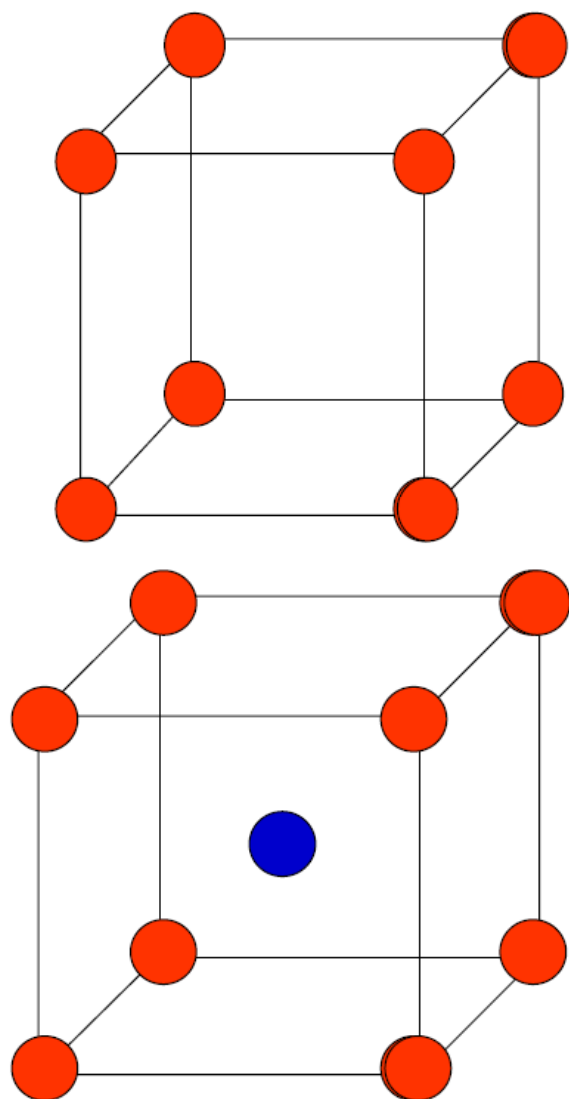
NaNO₃, Al₂O₃, As, Sb, Bi

Analysis of cubic crystals

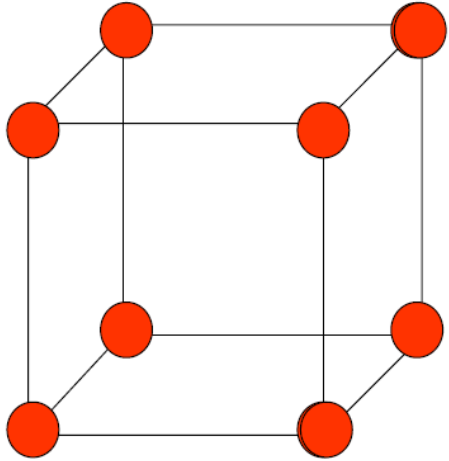
Simple or primitive crystal lattice: There are lattice points only at the 8 corners of the unit cell.

Body Centered crystal lattice: There are lattice points at the 8 corners and the centre of the unit cell.

Face centered crystal lattice: There are lattice points at the 8 corners and in addition there are lattice points at the centre of all faces.



Number of atoms per unit cell

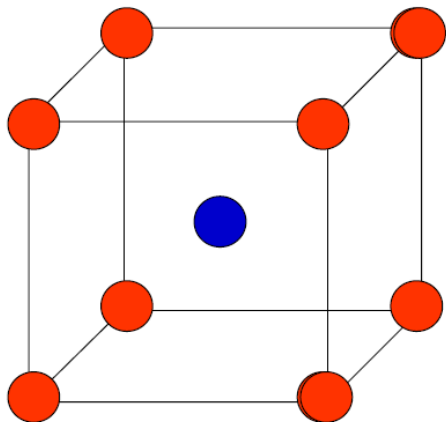


Simple Cubic cell: In this type of structure the atoms are situated at the corners. 1 corner is shared by 8 unit cells.

So one corner contributes $1/8^{\text{th}}$ atom to a unit cell.

So the 8 corners will be contributing

$$1/8 \times 8 = \mathbf{1 \text{ atom / unit cell.}}$$



Body centered Cubic cell: In this type of structure the atoms are situated at the corners and 1 atom is at the centre.

So one corner contributes $1/8^{\text{th}}$ atom to a unit cell.

So the 8 corners will be contributing

$$1/8 \times 8 = 1 \text{ atom / unit cell.}$$

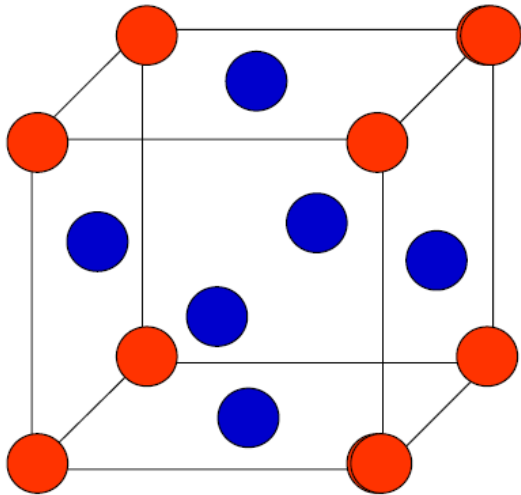
In addition there is 1 atom located at the centre .

Therefore total no. of atoms per unit cell

$$= 1 \text{ (atom at centre)} + 1/8 \times 8 \text{ (from 8 corners)}$$

$$= \mathbf{2 \text{ atoms per unit cell of BCC}}$$

Number of atoms per unit cell



Face centered Cubic cell: In this type of structure the atoms are situated at the corners and 1 atom is at the each face. In total there are 6 faces in a cube. Each face is shared between 2 unit cells. So one face contributes $\frac{1}{2}$ atom. So 6 faces will contribute 3 atoms.

Therefore total no. of atoms per unit cell
= 1 (from corners) + 3 (from 6 faces)
= 4 atoms per unit cell of FCC

Type of cell	Simple Cubic	Body Centered Cubic (BCC)	Face Centered Cubic (FCC)
Number of atoms per unit call	1	2	4

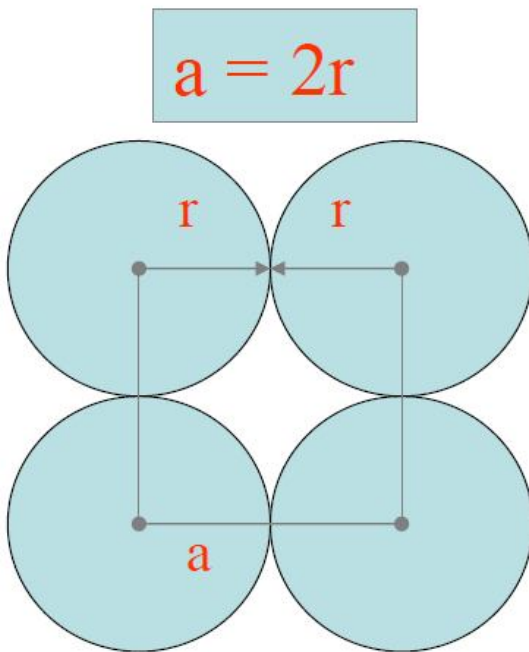
Coordination Number

- The number of touching neighbors
- SC is 6
- BCC is 8
- FCC is 12

Atomic Radius of a cubic lattice

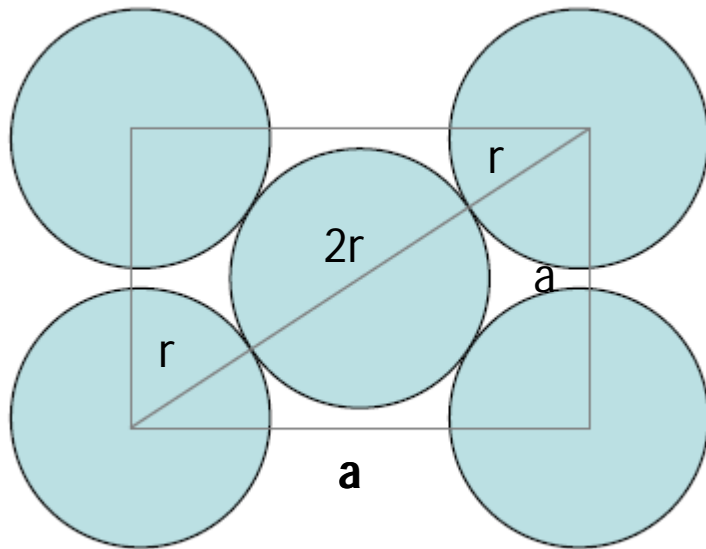
Half the distance between two immediate neighbors in a unit cell is called as atomic radius r .

Simple Cubic Cell



$$r = a/2$$

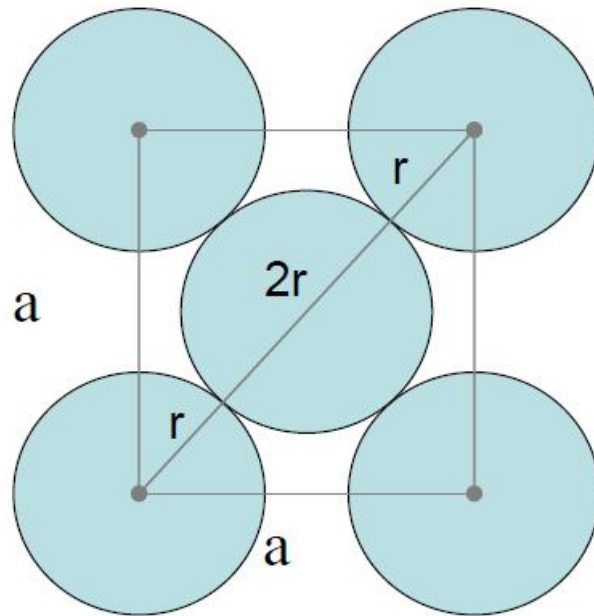
Body Centered Cubic Cell



$$(4r)^2 = (a^2 + a^2) + a^2 \\ = 3a^2$$

$$\text{Body diagonal} = \sqrt{3}a = 4r \quad \Rightarrow \quad r = \frac{\sqrt{3}a}{4}$$

Face Centered Cubic Cell



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

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

$$8r^2 = a^2$$

$$r^2 = a^2/8$$

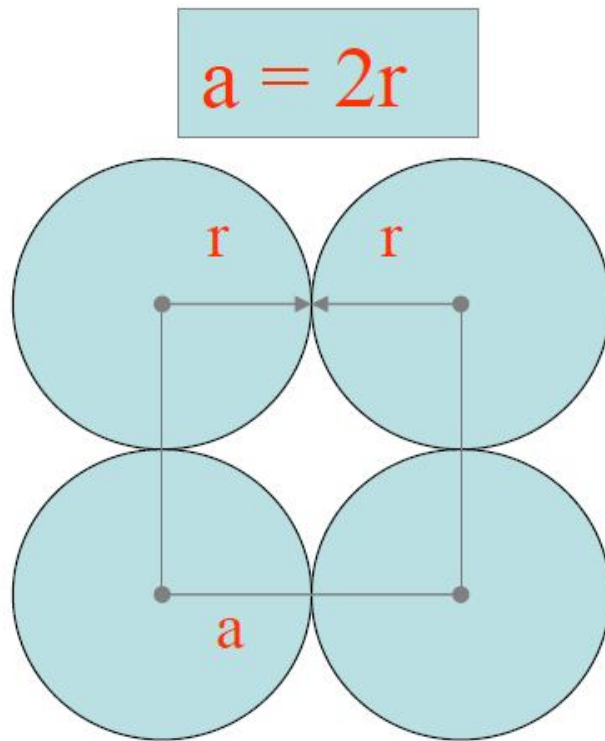
$$r = a / \sqrt{8}$$

Packing Factor

- The fraction of the cell that is filled up with atom (The rest is empty)
- Packing Factor = $\frac{\text{Atom volume}}{\text{Cell volume}}$
- Find the maximum packing factor

Simple Cubic

Each corner contains 1/8 of a sphere



$$V_{sph} = 8\left(\frac{1}{8}\right)\frac{4}{3}\pi r^3$$

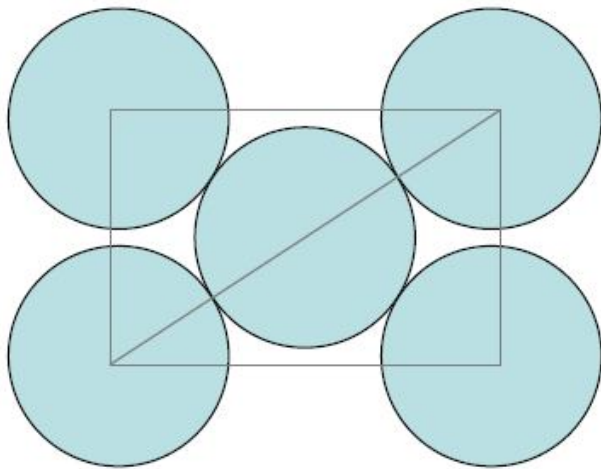
$$= \frac{4}{3}\left(\frac{a}{2}\right)^3 = \frac{4}{3}\pi \frac{a^3}{8} = \frac{\pi}{6}a^3$$

$$\text{Packing fraction} = f = \frac{V_{sph}}{V_{cube}} = \frac{\frac{\pi a^3}{6}}{a^3} = \frac{\pi}{6} = 0.52$$

Body Centered Cubic (BCC)

$$\text{Body diagonal} = \sqrt{3}a = 4r \quad \Rightarrow \quad r = \frac{\sqrt{3}a}{4}$$

$$\text{Total number of spheres} = 8 \left(\frac{1}{8} \right) + 1 = 2$$



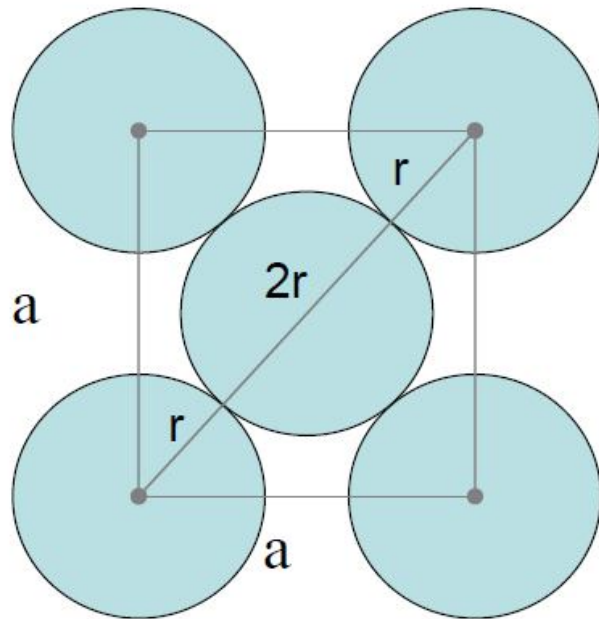
$$V_{sph} = (1) \frac{4\pi}{3} r^3 + (1) \frac{4\pi}{3} r^3 = (2) \frac{4\pi}{3} r^3$$

$$V_{sph} = 2 \left(\frac{4\pi}{3} \right) \left(\frac{\sqrt{3}a}{4} \right)^3 = \frac{\sqrt{3}\pi a^3}{8}$$

$$\text{Packing fraction} = f = \frac{V_{sph}}{V_{cube}} = \frac{\frac{\sqrt{3}\pi a^3}{8}}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

Face Centered Cubic (FCC)

$$\text{Face diagonal} = \sqrt{2} a = 4r \quad \Rightarrow \quad r = \frac{\sqrt{2} a}{4}$$



$$\text{Total number of spheres} = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4$$

$$V_{sph} = (1) \frac{4\pi}{3} r^3 + (3) \frac{4\pi}{3} r^3 = (4) \frac{4\pi}{3} r^3$$

$$V_{sph} = 4 \left(\frac{4\pi}{3} \right) \left(\frac{\sqrt{2}a}{4} \right)^3 = \frac{\sqrt{2}\pi a^3}{6}$$

$$\text{Packing fraction} = f = \frac{V_{sph}}{V_{cube}} = \frac{\frac{\sqrt{2}\pi a^3}{6}}{a^3} = \frac{\sqrt{2}\pi}{6} = 0.74$$

Calculation of density of Cubic Crystal

Let Z be the number of formula units (atoms or molecules)

M be the mass of substance

' a ' be the unit cell length.

$$\text{Volume of the unit cell} = a^3$$

$$\begin{aligned}\text{Mass of unit cell} &= [\text{no. of formula units in the unit cell}] \times \\ &\quad [\text{mass of each formula unit}] \\ &= Z \cdot m \\ &= Z \times (M/N_A)\end{aligned}$$

$$\begin{aligned}\therefore \text{Density } (\rho) &= \text{Mass of unit cell} / \text{Volume of Unit Cell} \\ &= Z \cdot M/N_A / a^3\end{aligned}$$

$$\text{Density } (\rho) = Z M / a^3 \cdot N_A$$

Value of Z for

simple cubic lattice = 1

BCC lattice = 2

FCC lattice = 4

A unit cell of NaCl has 4 formula units. The edge length of the unit cell is 0.564 nm. Find the density of Sodium Chloride.

Given $Z = 4$, $a = 0.564 \text{ nm}$.

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$M = 58.4 \text{ g/mol}$

$$\begin{aligned} a^3 &= (0.564 \times 10^{-7})^3 \\ &= 0.1794 \times 10^{-21} \text{ cm}^3 \\ &= 1.7974 \times 10^{-22} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Density } (\rho) &= Z M / a^3 \cdot N_A \\ &= 4 \times 58.5 / 1.7974 \times 10^{-22} \times 6.022 \times 10^{23} \\ &= 234 / 108.05 = \underline{2.16 \text{ g/cm}^3} \end{aligned}$$

The density of face centered cubic metal having atomic mass 60.2 amu is 6.2 g/cm³. Calculate the length of the unit cell edge.

Given $Z = 4$, $a = 0.564$ nm.

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$M = 60.2 \text{ /mol}$

$$\rho = Z M / a^3 \cdot N_A$$

$$\begin{aligned} a^3 &= Z M / \rho \cdot N_A \\ &= 4 \times 60.2 / 6.2 \times 6.022 \times 10^{23} \\ &= 240.8 / 37.32 \times 10^{23} \\ &= 6.45 \times 10^{-23} \end{aligned}$$

$$\begin{aligned} a &= (6.45 \times 10^{-23})^{1/3} \\ &= (64.5 \times 10^{-24})^{1/3} \\ &= 4.01 \times 10^{-8} \text{ cm} \end{aligned}$$

X – RAY DIFFRACTION

- ❖ The interaction of x – rays with matter has helped in understanding of structure of solids.
- ❖ When light falls on an object , which is of the same size of the wavelength of light it is diffracted. This principle is used to investigate the structure of solids.
- ❖ The wavelength of x rays is comparable to the inter planer distance spacing of atoms /ions or molecules forming the solids which is of the order of 100 pm.
- ❖ We can regard a crystal as consisting large number of parallel and equidistant atomic planes.
- ❖ When x rays are incident on crystals they penetrate and are diffracted by atoms forming the crystal.

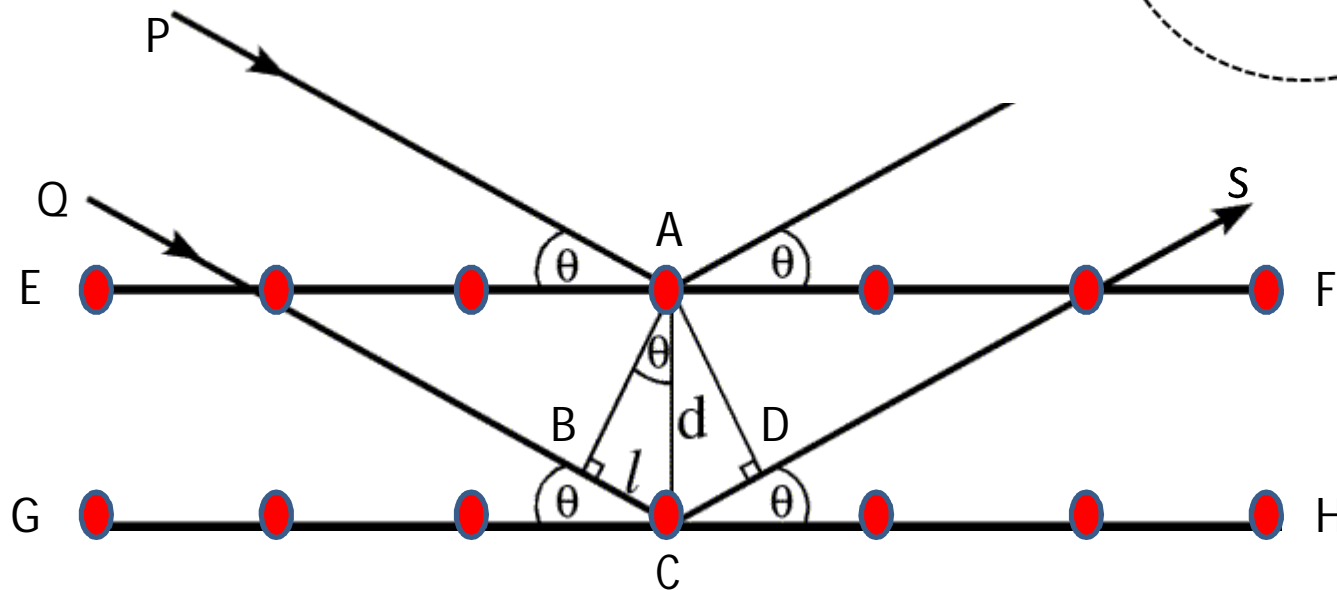
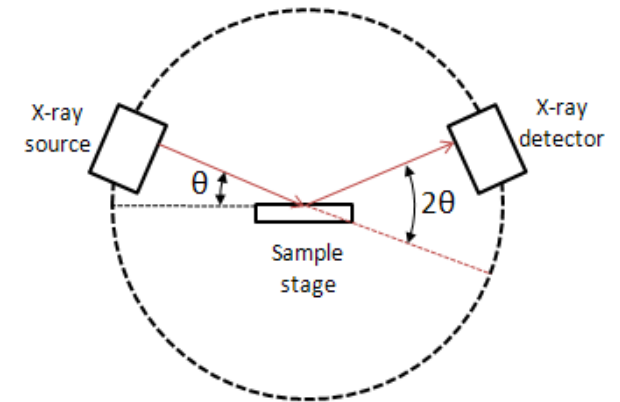
Bragg's Law

It states that " if the path difference between the two rays is an integral multiple of the x – ray wavelength, then the two rays will be in phase and thereby the diffraction pattern will be with enhanced intensity".

Thus Braggs law can be written as

Path difference = $n \lambda$ where

where $n = 1, 2, 3, \dots$



- ❖ Consider two parallel beams PA and QC to be incident at an angle θ on parallel planes of atoms EF and Gh.
- ❖ Let the distance between the two adjacent planes be 'd'
- ❖ The two rays PA and QC are reflected at an angle θ along AR and CS directions.
- ❖ The path difference between the incident beam **PAR** and **QCS** is given by = extra distance travelled by QCS and compared to PAR.

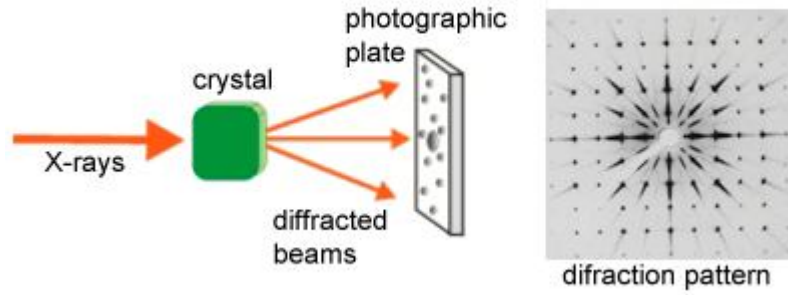
In order to calculate this we draw \perp AB to QC and \perp AD to CS.

$$\begin{aligned}
 \text{Path difference} &= (QC + CS) - (PA + AR) \\
 &= (QB + BC) + (CD + DS) - (PA + AR) \\
 &= BC + CD \\
 &= AC \sin \theta + AC \sin \theta \\
 &= d \sin \theta + d \sin \theta \\
 &= 2d \sin \theta
 \end{aligned}$$

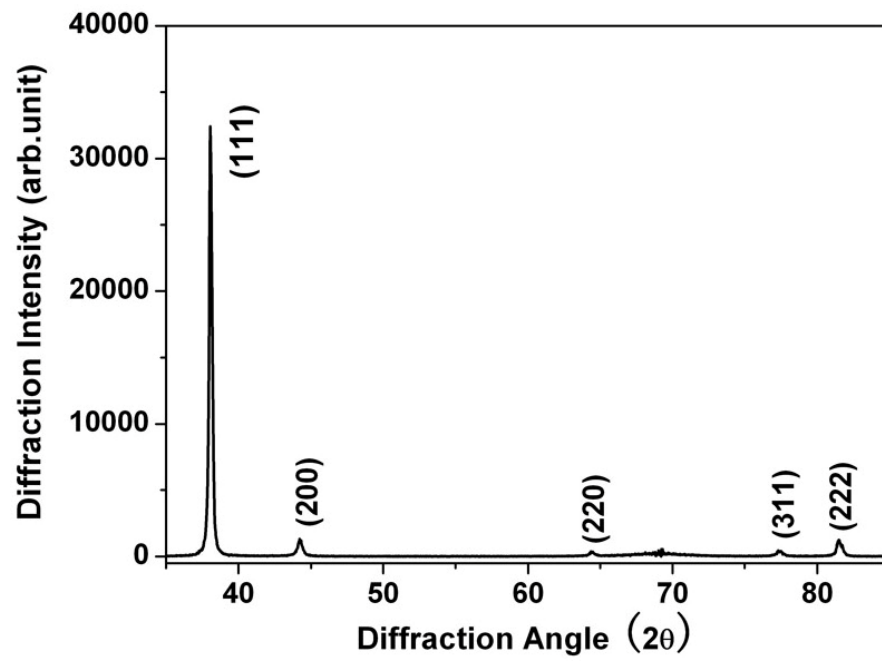
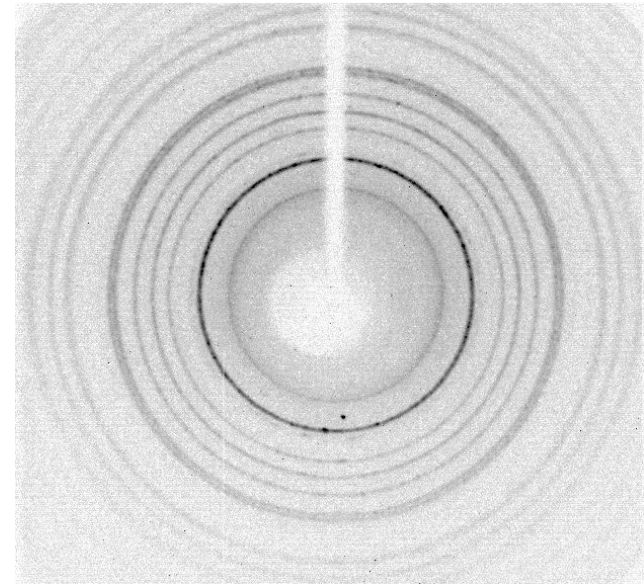
But From Braggs law, Path difference = $n \lambda$

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

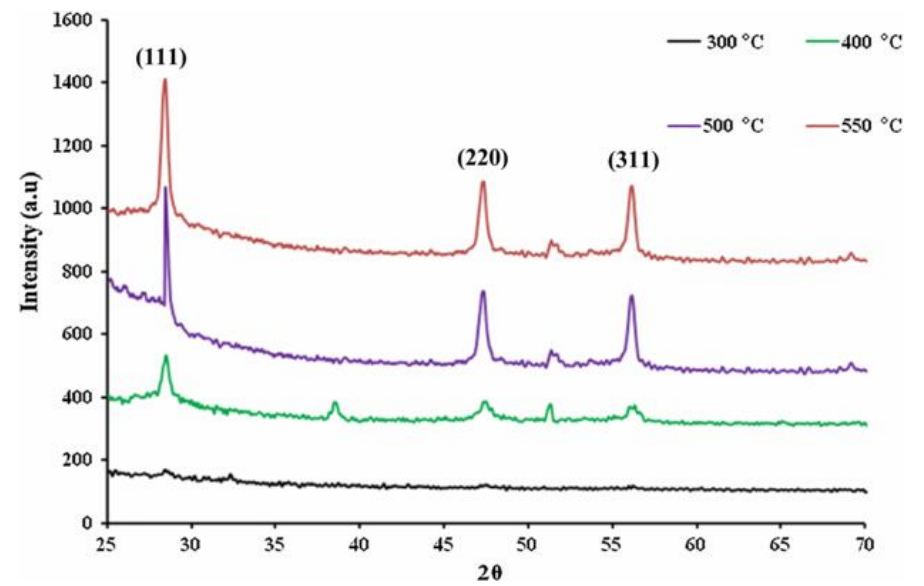




Laue's Method



Single Crystal



Polycrystalline

For a unit cell having dimensions of 300 pm x-ray diffraction pattern was recorded. The wavelength of X-rays used was 150 pm. Find out the glancing angle at which first order diffraction from (110) peak will be observed.

$$n = 1$$

$$\lambda = 150 \text{ pm}$$

$$d = 300 \text{ pm}$$

$$\theta = ?$$

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

$$150 \text{ pm} = 2 \times 300 \text{ pm} \times \sin \theta$$

$$\sin \theta = 150/600$$

$$\sin \theta = 0.25$$

$$\theta = \sin^{-1} (0.25) = 14.4^\circ$$

Crystals Imperfections

Imperfections in crystals: Any deviation from perfectly ordered arrangement of the constituents forming the crystal. This deviation may change the properties of the crystal.

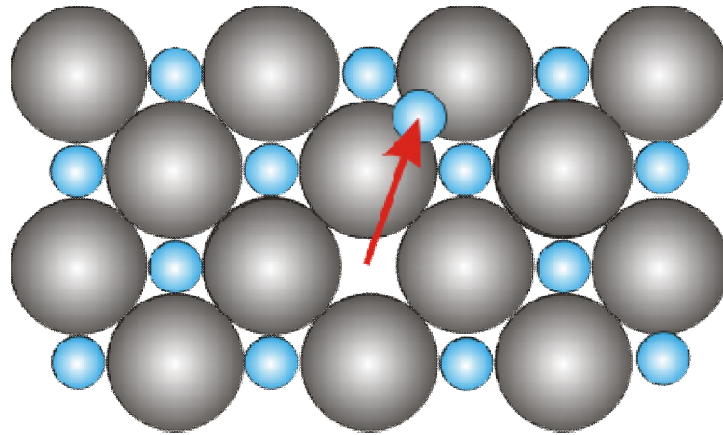
Electronic: Correspond to defects in Ionic crystals. E.g. Si is doped with a trivalent impurity such as B, Al or pentavalent impurity like P, As

Atomic : This corresponds to the defects due to irregularity of atoms or ions in the crystal lattice. This happens when the constituent atoms are

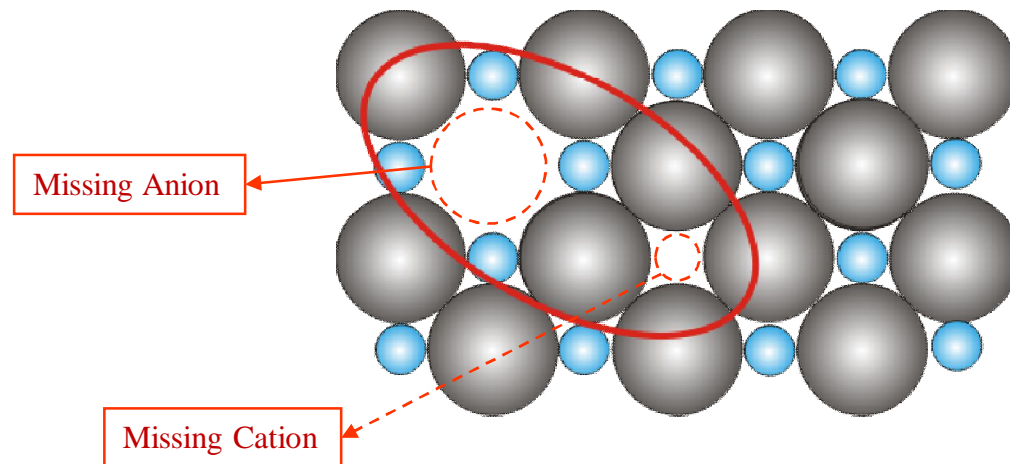
1. Missing from the normal crystal lattice.
2. Dislocated to a position meant for other atoms
3. Shifted to an interstitial void in the crystal lattice.

Stoichiometric Defects

Frenkel defect : when an ion leaves its position in lattice and it enters an interstitial site . As cations are generally smaller in size than anions , this defect is generally caused by cations being displaced from one site to another.



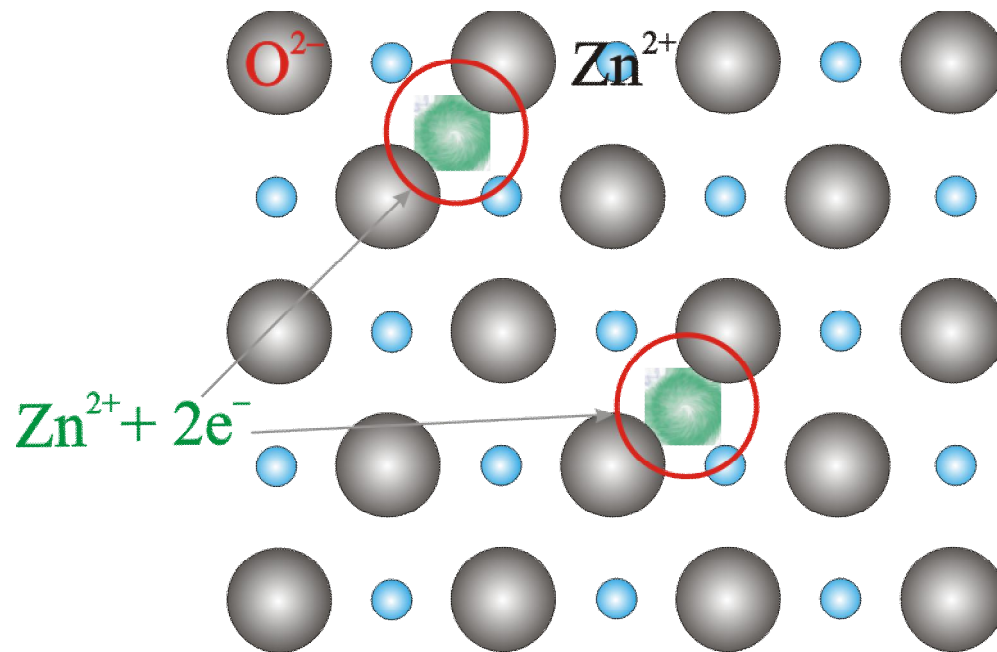
Schottky defect : when a pair of cation and anion is missing from the crystal lattice it is known to be a schottky defect. This reduces the overall density of the crystalline substance.



Schottky Defect	Frenkel Defect
It is due to vacancy at cation site accompanied by vacancy at anion site/	It is due to a cation leaving its position and entering in an interstitial position.
The crystals electrical neutrality is maintained	The crystals electrical neutrality is maintained
It can take place at relatively low energy	It can also take place at relatively low energy
Overall density of crystal is reduced	No change in overall density.
This type of defect occurs in solids having higher coordination number where the cations and anions are having smaller sizes. E.g. NaCl, CsCl	This type of defect is observed in solids where anions are large and cations are small Or the crystal structure is open type with large interstices. CaF ₂ , ZnS

Non stoichiometric defects

- ZnO heated in Zn vapour $\rightarrow \text{Zn}_y\text{O}$ ($y > 1$)
- The excess cations occupy interstitial voids
- The electrons ($2e^-$) released stay associated to the interstitial cation



Preparation of Semiconductors

Involves 3 steps:

- ❖ Purification of pure Ge/Si
- ❖ Doping Techniques
- ❖ Cutting into chips

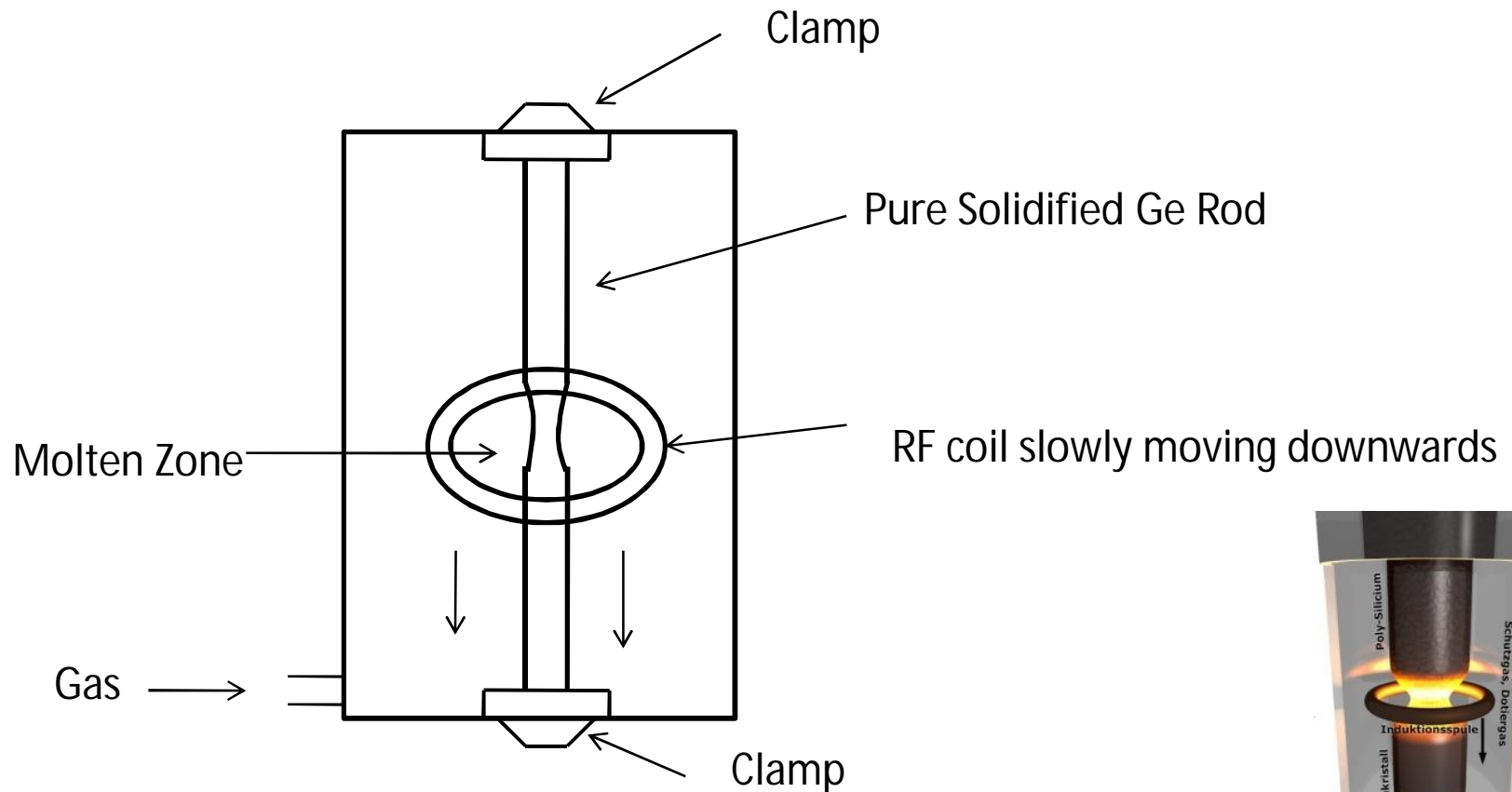
Preparation of pure Si and Ge by **Distillation method**

Metallic Semiconductors such Si, Ge must be of at least 99.9999 or (6N) purity

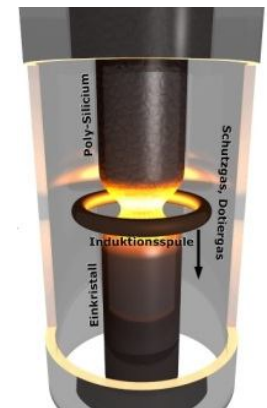
- ❖ Starting raw materials are: trichlorosilane (SiHCl_3) for Silicon and germanium tetrachloride GeCl_4 for Ge.
- ❖ GeCl_4 (b.p. 83.1°C) is taken in a distillation unit and a layer of HCl is kept over it. This allows the removal of As impurity.
- ❖ Further chlorine gas is passed over the charge and it is heated electrically converting the charge to form vapors.
- ❖ The fumes are cooled in a chamber using an ice bath giving pure GeCl_4 free of impurities.
- ❖ It is then reduced using hydrogen gas to obtain pure germanium which is purified further.
- ❖ Similarly procedure is used to get Si from SiHCl_3

Zone refining Technique

- ❖ Technique involving re crystallization.
- ❖ Principle of this method is the fact that the impurities are more soluble in the melt than in the solid material.



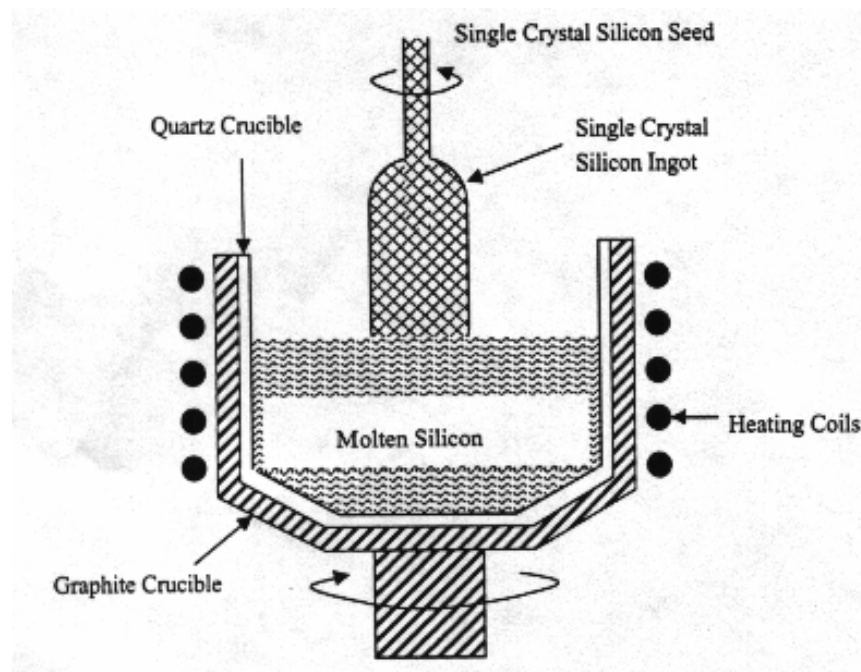
Vertical Zone Refiner



- ❖ A rod of purified Ge is vertically clamped and heated using a RF coil to 1000 °C in a reducing atmosphere.
- ❖ The heating coil is slowly moved from top to bottom.
- ❖ This caused the Ge rod to melt and the impurities are carried away with the molten material.
- ❖ As the RF coil is moved down the molten rod solidifies in the upper portion.
- ❖ When the purification of upper rod is complete the lower part of the separated where the impurities have concentrated.
- ❖ High purity Ge can be obtained by this method.

Czochralski Crystal pulling technique.

- ❖ Ge and Si obtained by distillation and zone refining method are polycrystalline. But most of semiconductor devices required single crystals.
- ❖ This method involves growing the crystal on a single crystal seed.
- ❖ Thus exactly identical arrangements of atoms as that of the seed crystals is grown.



- ❖ The polycrystalline semiconductor (Ge) is taken in a quartz chamber/crucible.
- ❖ The crucible is heated using RF power source.
- ❖ The temperature is kept just above the melting point of Ge.
- ❖ At this stage properly oriented seed crystal which is attached to puller rod is inserted in the melt such that it establishes a surface contact.
- ❖ The seed crystal is rotated carefully and is gradually pulled out.
- ❖ The molten Ge which is in contact with the seed crystal starts solidifying producing orientation identical to that of the seed crystal.
- ❖ The pulling rate is around 1.5 to 5 cm/minute and the rotation speed is maintained around 100 rpm.
- ❖ Finally a single crystal with 5 cm dia and 25 cm length can be obtained.

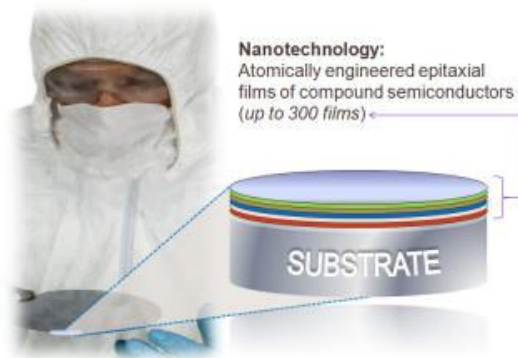
Doping technique.

For obtaining a doped semiconductor calculated quantities of dopant (B or P) is added to the melt before crystal pulling stage. The doping method used are

1. Epitaxy
2. Diffusion technique
3. Ion implantation technique.

Epitaxy technique

- ❖ In this method unified crystal growth or deposition of a thin layer of semiconductor takes place.
- ❖ The material in the epitaxial layer must have lattice spacing and structure identical to that of the substrate. e.g. Si on Ge or Ge on Si.
- ❖ The Si or Ge wafer is placed in a quartz tube reactor which is heated.
- ❖ Then gases containing compounds of Ge or Si mixed with calculated quantities of dopants are introduced in the reactor.
- ❖ The heating is continued till a thin film of dopants is formed over the wafers.
- ❖ This wafer is used for fabrication of semiconducting devices.



Diffusion Technique

- ❖ This method involves synthesis of a semiconductor material by solid or gaseous diffusion of impurity atoms in the crystalline lattice of a semiconductor material without any melting.
- ❖ This process involves heating a dopant say P type.
- ❖ This causes condensing the P –type impurity atoms to condense and diffuse through the wafer resulting in a semiconducting material.
- ❖ This method allows the control over concentration and extent of penetration of impurity atoms.
- ❖ This tech is specially used for preparation of p type or n type semiconductors. It is also used to prepare n-p-n transistor

Cutting into Chips: it is done using techniques such as chemical etching, ultrasonic vibrations, laser beams etc.