

Unit-I

Engineering Physics-I

 **INTRODUCTION TO CRYSTAL PHYSICS**

 **CRYSTALLINE AND NONCRYSTALLINE SOLIDS**

 **SPACE LATTICE**

 **CRYSTAL STRUCTURE**

 **LATTICE PARAMETERS**

 **CRYSTAL SYSTEMS**

 **BRAVAIS LATTICES**

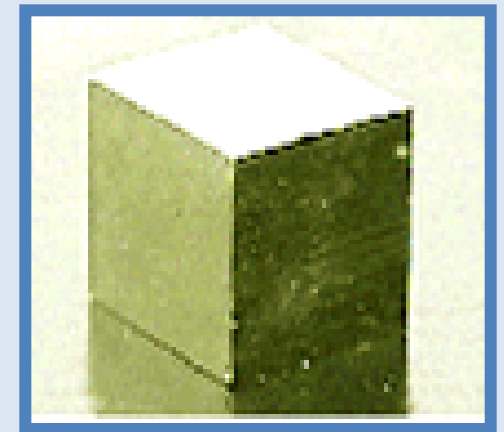
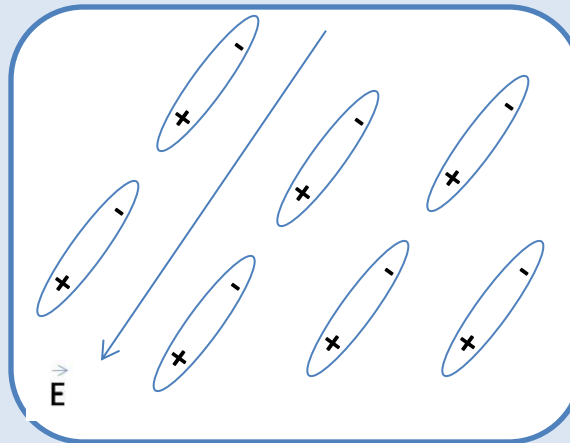
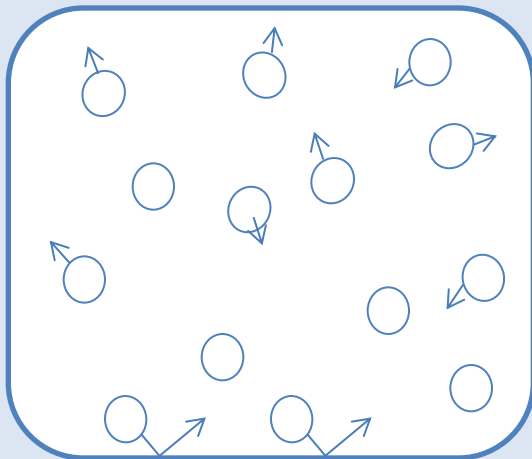
INTRODUCTION TO CRYSTAL PHYSICS

MATTER

GASES

**LIQUIDS
AND LIQUID
CRYSTALS**

SOLIDS



INTRODUCTION TO CRYSTAL PHYSICS

- Matter exists in three states viz. solids, liquids and gases.
- All these states are composed of atoms and molecules.
- When we focus the solids, they are classified into many types based on several properties like electrical, mechanical, magnetic, optical, thermal etc.,.
- The main reason for these different properties of solids is their crystal structure.

INTRODUCTION TO CRYSTAL PHYSICS

‘What is Crystal Physics?’

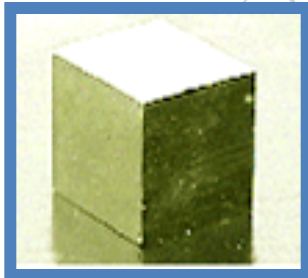
Crystal Physics’ or ‘*Crystallography*’ is a branch of physics that deals with the study of all possible types of crystals and the physical properties of crystalline solids by the determination of their actual structure by using X-rays, neutron beams and electron beams.

CLASSIFICATION OF SOLIDS

SOLID MATERIALS

CRYSTALLINE

Single Crystal



POLYCRYSTALLINE



**AMORPHOUS
(NON-CRYSTALLINE)**



CLASSIFICATION OF SOLIDS

Solids can broadly be classified into two types based on the **arrangement of units of matter.**

The units of matter may be **atoms, molecules or ions.**

They are,

- ✚ Crystalline solids and
- ✚ Non-crystalline (or) Amorphous solids

CRYSTALLINE SOLIDS

- # A substance is said to be crystalline when the arrangement of units of matter is **regular** and **periodic**.
- # A crystalline material has directional properties and therefore called as **anisotropic** substance.
- # A crystal has a **sharp melting point**.
- # It possesses a **regular shape** and if it is broken, all broken pieces have the same regular shape.

CRYSTALLINE SOLIDS

✚ A crystalline material can either be a **single** (mono) crystal or a **polycrystal**.

✚ A single crystal consists of only **one crystal**, whereas the polycrystalline material consists of **many crystals** separated by well-defined boundaries.

Examples

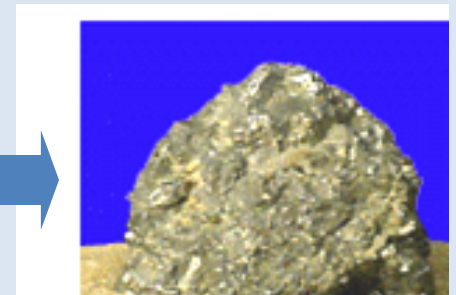
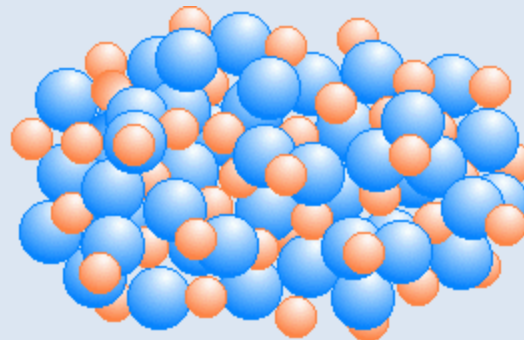
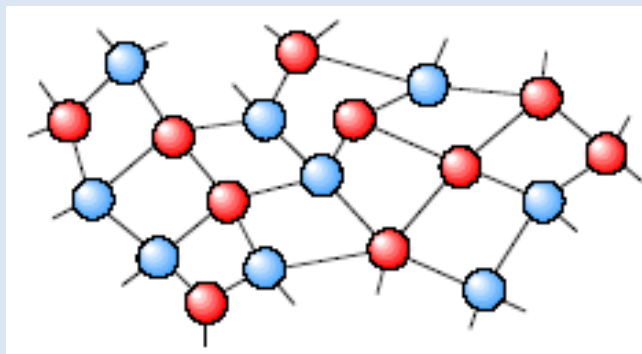
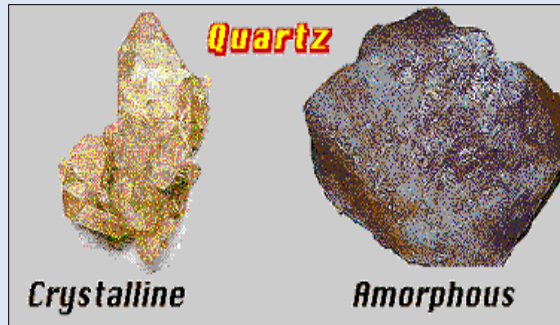
Metallic crystals – Cu, Ag, Al, Mg etc,

Non-metallic crystals – Carbon, Silicon, Germanium

NON CRYSTALLINE SOLIDS

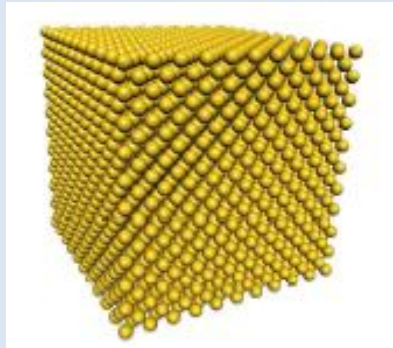
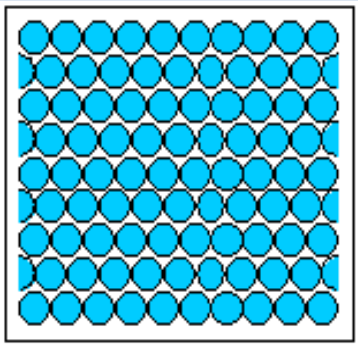
- ✚ In amorphous solids, the constituent particles are arranged in an orderly manner. They are **randomly distributed**.
- ✚ They do not have directional properties and so they are called as '**isotropic**' substances.
- ✚ They have **wide range of melting point** and do not possess a regular shape.
Examples: Glass, Plastics, Rubber etc.,

EXAMPLES OF CRYSTALLINE AND AMORPHOUS

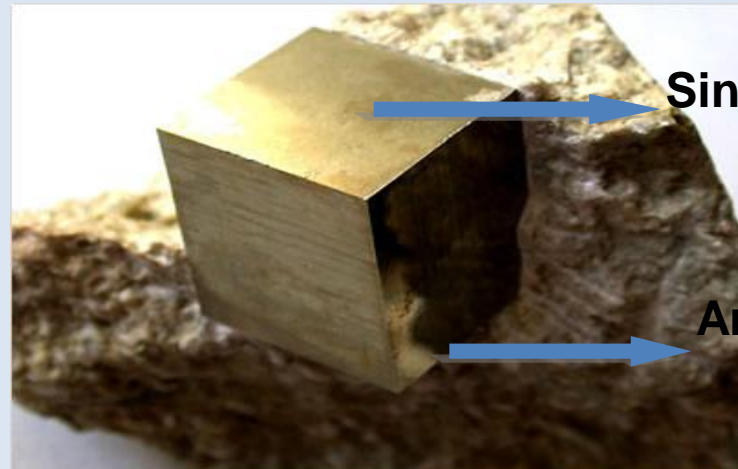


SINGLE CRYSTALS

- **Single crystals** have a periodic atomic structure across its whole volume.
- At long range length scales, each atom is related to every other equivalent atom in the structure by translational or rotational symmetry



Single Crystals

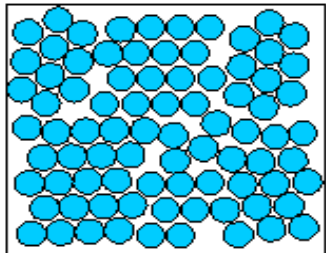


Single Pyrite Crystal

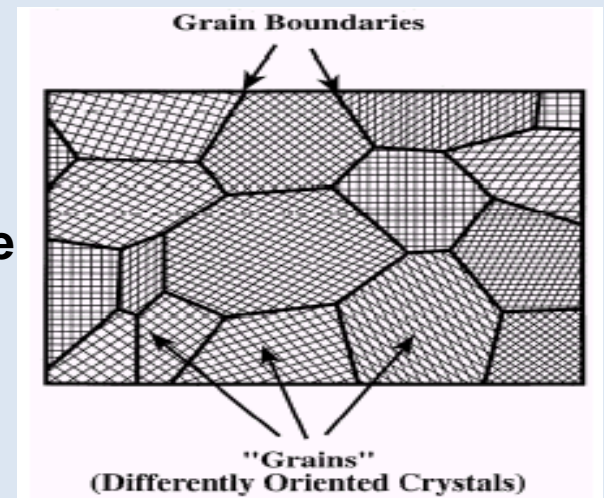
Amorphous Solid

POLYCRYSTALLINE SOLIDS

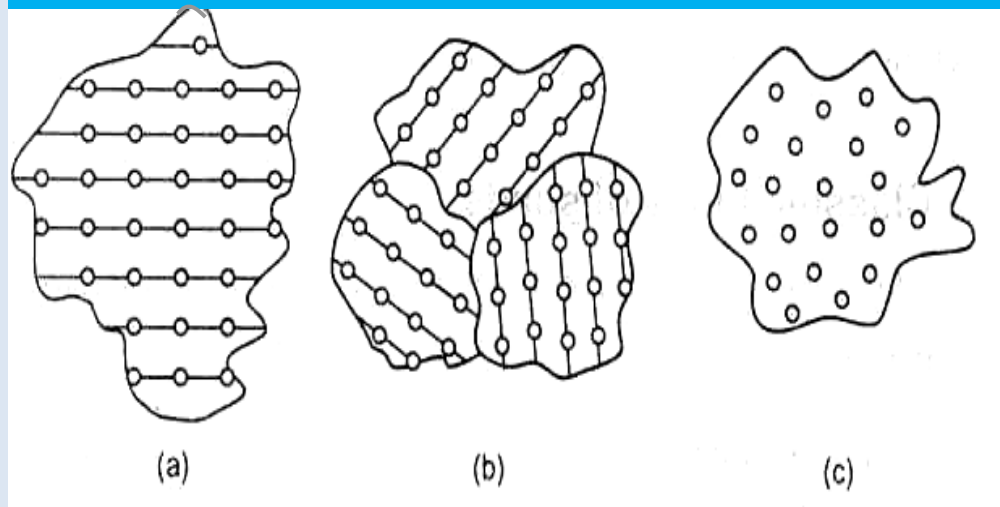
- **Polycrystalline** materials are made up of an aggregate of *many small single crystals* (also called crystallites or grains).
- Polycrystalline materials **have a high degree of order over many atomic or molecular** dimensions.
- **Grains (domains)** are separated by **grain boundaries**. The *atomic order can vary from one domain to the next*.
- The grains are usually **100 nm - 100 microns in diameter**.
- Polycrystals with grains less than 10 nm in diameter are **nanocrystalline**



Polycrystalline
Pyrite form
(Grain)



ATOMIC ARRANGEMENT IN CRYSTALS



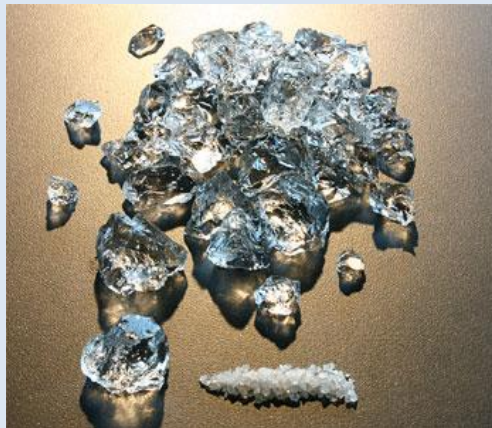
**(a) mono (or) single
crystals**

(b) polycrystalline solids

(c) amorphous solids

CRYSTALS

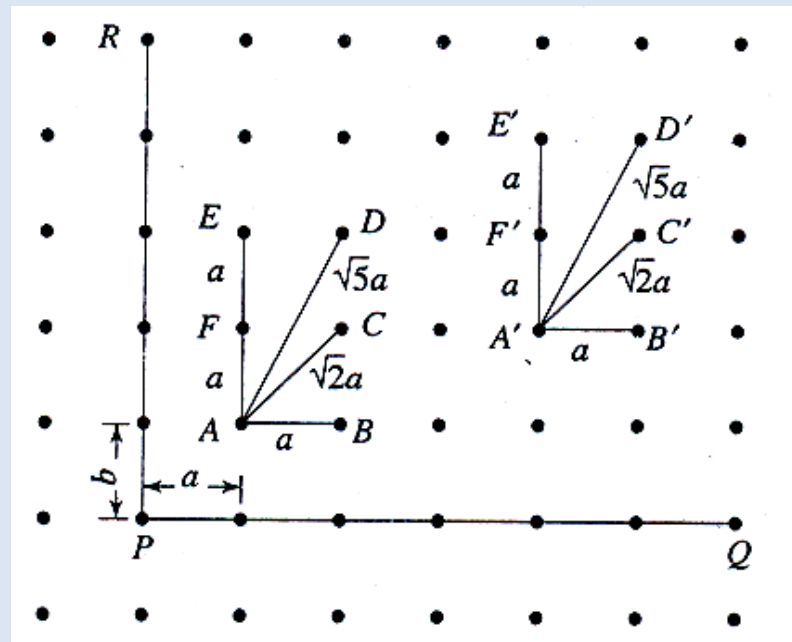
✚ It is a substance in which the constituent particles are arranged in a **systematic geometrical pattern**.



SPACE LATTICE

- ✚ A lattice is a **regular and periodic** arrangement of points in three dimension.
- ✚ It is defined as an **infinite array** of points in **three dimension** in which every point has surroundings identical to that of every other point in the array.
- ✚ The Space lattice is otherwise called the Crystal lattice

TWO DIMENSIONAL SPACE LATTICE



SPACE LATTICE

- ✚ Consider the points **P, Q and R**.
- ✚ Let us join the points P and Q by a straight line, and the point P and R by another straight line.
- ✚ The line **PQ is taken as X-axis** and the line **PR is taken as Y-axis**.
- ✚ The distance between any two successive lattice points in the X-direction is taken as '**a**'.

SPACE LATTICE

- ✚ Similarly, the distance between any two successive lattice points along the Y-direction is taken as 'b'.
- ✚ Here a and b are said to be lattice translational vectors. Consider a square lattice in which $\vec{a} = \vec{b}$.

SPACE LATTICE

✚ Consider two sets of points A, B, C, D, E, F and A', B', C', D', E', F' .

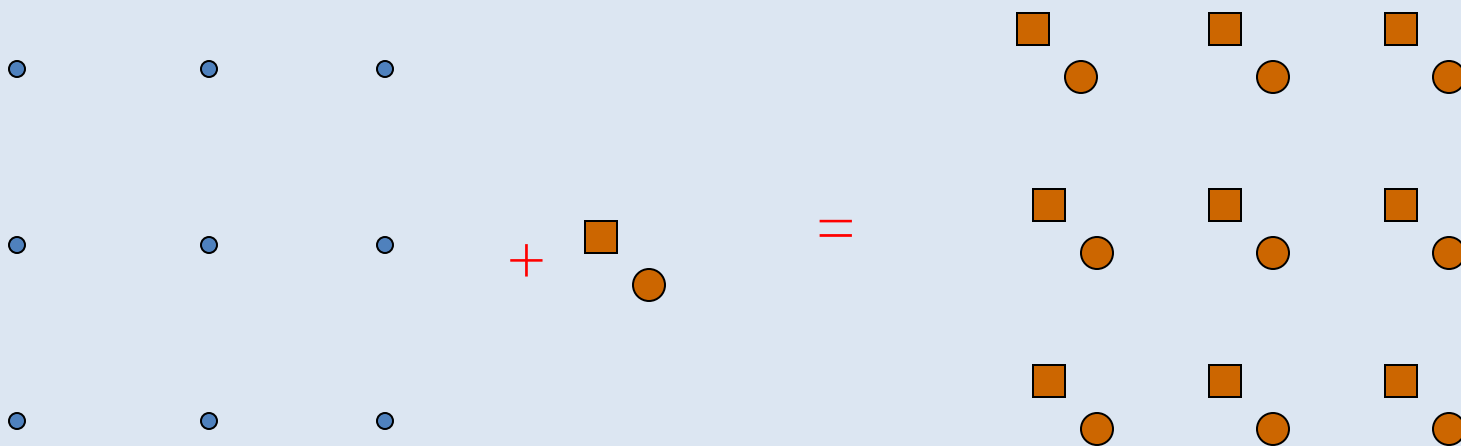
✚ In these two sets, the surrounding environment looks symmetrical; i.e. the distances AB and $A'B'$, AC and $A'C'$, AD and $A'D'$, AE and $A'E'$ and AF and $A'F'$ are equal.

✚ Therefore, in the arrangement of points, if the surrounding environment looks the same when the arrangement is viewed from different lattice points, then that arrangement is said to be a **space lattice**.

BASIS

- ✚ A crystal structure is formed by associating every lattice point with an unit assembly of atoms or molecules identical in **composition, arrangement and orientation**.
- ✚ This unit assembly is called the '*basis*'.
- ✚ When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure.
- ✚ The **crystal structure is real**, while the **lattice is imaginary**.

CRYSTAL STRUCTURE



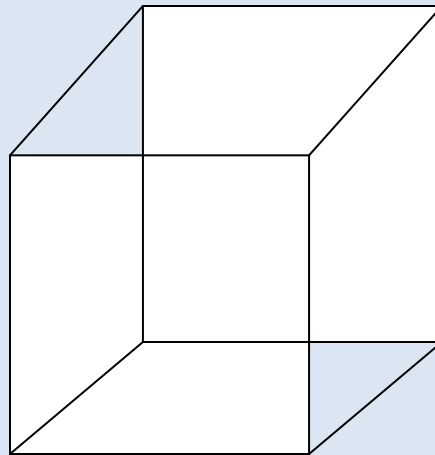
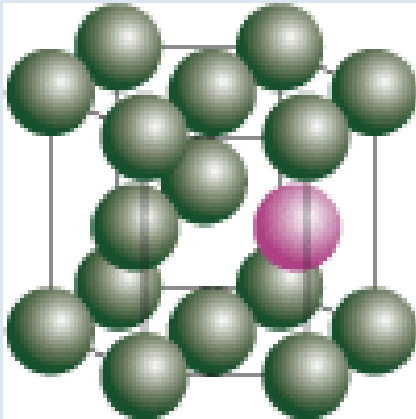
Lattice

+ Basis =

Crystal structure

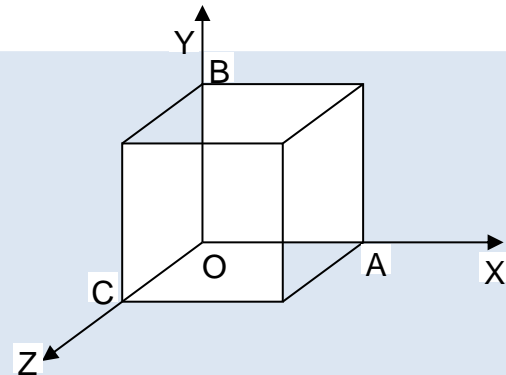
UNIT CELL

✚ A unit cell is defined as a **fundamental building block** of a crystal structure, which can generate the complete crystal by repeating its own dimensions in various directions.



CRYSTALLOGRAPHIC AXES

- ✚ Consider a unit cell consisting of three mutually perpendicular edges OA, OB and OC as shown in figure.
- ✚ Draw parallel lines along the three edges.
- ✚ These lines are taken as **crystallographic axes** and they are denoted as X, Y and Z axes.





LATTICE PARAMETERS

- ✚ Consider the unit cell as shown in figure.
- ✚ Let OA, OB and OC are the intercepts made by the unit cell along X, Y and Z axes respectively.
- ✚ These intercepts are known as *primitives*. In crystallography the intercepts OA, OB and OC are represented as \vec{a} , \vec{b} and \vec{c} .

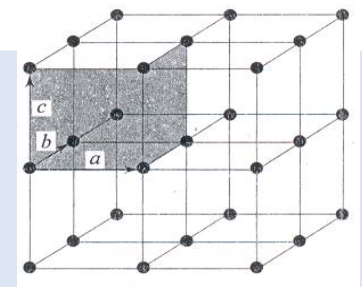


LATTICE PARAMETERS

- ✚ The angle between X and Y axes is represented as γ .
- ✚ Similarly the angles between Y and Z and Z and X axes are denoted by ' α ' and ' β ' respectively as shown in the above figure. These angles α , β and γ are called as *interaxial angles or interfacial angles*.
- ✚ To represent a lattice, the three interfacial angles and their corresponding intercepts are essential. These six parameters are said to be *lattice parameters*.

PRIMITIVE CELL

- ✚ It is the **smallest unit cell** in volume constructed by primitives. It consists of only **one full atom**
- A primitive cell is one, which has got the points or atoms only at the corners of the unit cell.
- If a unit cell consists of more than one atom, then it is not a primitive cell.
- Example for primitive cell : **Simple Cubic unit cell**
- Examples for non-primitive cell: **BCC and FCC unit cell.**










CRYSTALS SYSTEMS

- ✚ A three dimensional space lattice is generated by **repeated translation** of three translational vectors a , b and c .
- ✚ Crystals are grouped under **seven systems** on the basis of the shape of the unit cell.
- ✚ The seven crystal systems are distinguished from one another by their **lattice parameters** .

CRYSTALS SYSTEMS

The seven systems are,

-  Cubic (isometric)
-  Tetragonal
-  Orthorhombic
-  Trigonal (rhombohedral)
-  Hexagonal
-  Monoclinic and
-  Triclinic

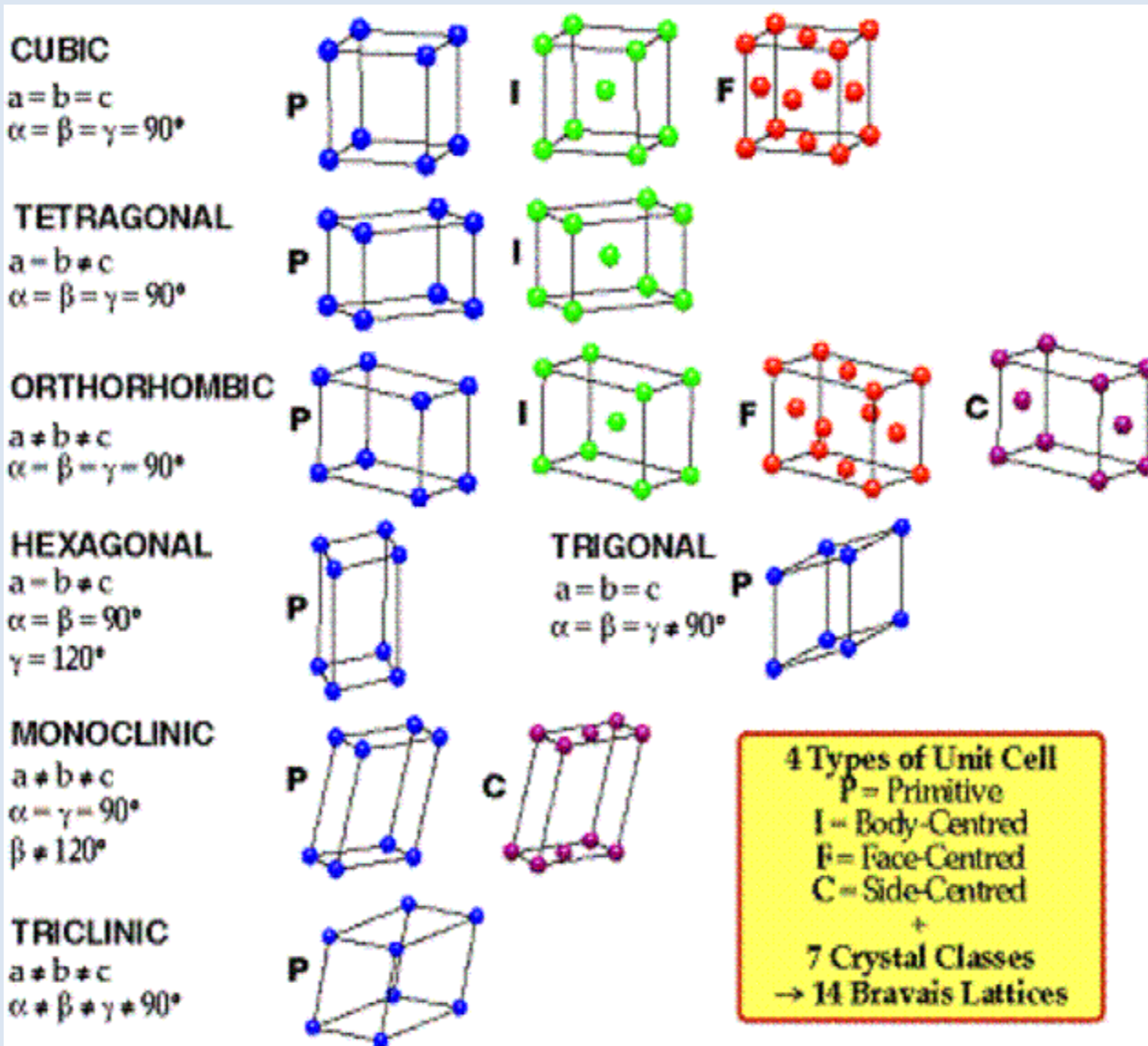
CRYSTALS SYSTEMS

The space lattices formed by unit cells are marked by the following symbols.

- ✚ **Primitive lattice: P** → having lattice points only at the corners of the unit cell.
- ✚ **Body centred lattice: I** → having lattice points at the corners as well as at the body centre of the unit cell.
- ✚ **Face centred lattice :F** → having lattice points at the corners as well as at the face centres of the unit cell.
- ✚ **Base centred lattice: C** → having lattice points at the corners as well as at the top and bottom base centres of the unit cell.

BRAVAIS LATTICE

Bravais in 1948 showed that 14 types of unit cells under seven crystal systems are possible. They are commonly called as '*Bravais lattice*'.



14 Bravais Lattices divided into 7 Crystal Systems

A Symmetry based concept

'Translation' based concept

	Crystal System	Shape of UC	Bravais Lattices			
			P	I	F	C
1	Cubic	Cube	✓	✓	✓	
2	Tetragonal	Square Prism (general height)	✓	✓		
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓
4	Hexagonal	120° Rhombic Prism	✓			
5	Trigonal	Parallopiped (Equilateral, Equiangular)	✓			
6	Monoclinic	Parallogramic Prism	✓			✓
7	Triclinic	Parallopiped (general)	✓			

P	Primitive
I	Body Centred
F	Face Centred
C	Base- Centred

 **MILLER INDICES**

 **PROCEDURE FOR FINDING MILLER INDICES**

 **DETERMINATION OF MILLER INDICES**

 **IMPORTANT FEATURES OF MILLER INDICES**

 **CRYSTAL DIRECTIONS**

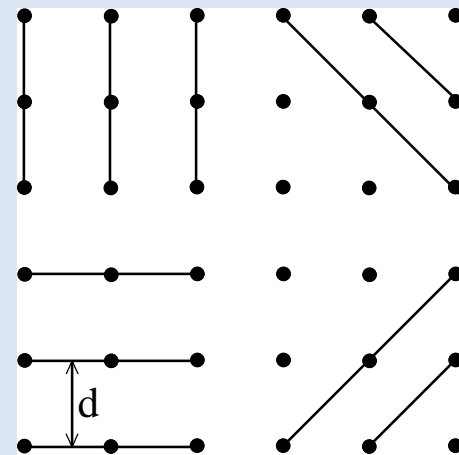
 **SEPARATION BETWEEN LATTICE PLANES**

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MILLER INDICES

- ✚ The crystal lattice may be regarded as made up of an infinite set of parallel equidistant planes passing through the lattice points which are known as lattice planes.
- ✚ In simple terms, the planes passing through lattice points are called '*lattice planes*'.
- ✚ For a given lattice, the lattice planes can be chosen in a different number of ways.

DIFFERENT LATTICE PLANES



MILLER INDICES

✚ Miller indices is defined as the **reciprocals** of the **intercepts** made by the plane on the **three crystallographic axes** which is **used to designate plane in the crystal**.

Miller indices are set of three possible integers represented as $(h\ k\ l)$ which is used to designate plane in the crystal, is the reciprocal of the intercept made by the planes on the crystallographic axes.

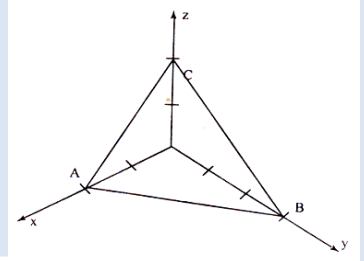
MILLER INDICES

Procedure for finding Miller Indices

- ✚ **Step 1:** Determine the **intercepts** of the plane along the axes X, Y and Z in terms of the lattice constants a, b and c .
- ✚ **Step 2:** Determine the **reciprocals** of these numbers.
- ✚ **Step 3:** Find the least common denominator (lcd) and multiply each by this lcd .
- ✚ **Step 4:** The result is written in paranthesis. This is called the '**Miller Indices**' of the plane in the form $(h\ k\ l)$.
- ✚ This is called the '**Miller Indices**' of the plane in the form $(h\ k\ l)$.

ILLUSTRATION

PLANES IN A CRYSTAL



- ✚ Plane ABC has intercepts of **2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.**

DETERMINATION OF 'MILLER INDICES'

Step 1: The intercepts are **2, 3 and 2** on the three axes.

Step 2: The reciprocals are **$1/2$, $1/3$ and $1/2$.**

Step 3: The least common denominator is '6'. Multiplying each reciprocal by lcd, we get, **3, 2 and 3.**

Step 4: Hence **Miller indices for the plane ABC is (3 2 3)**

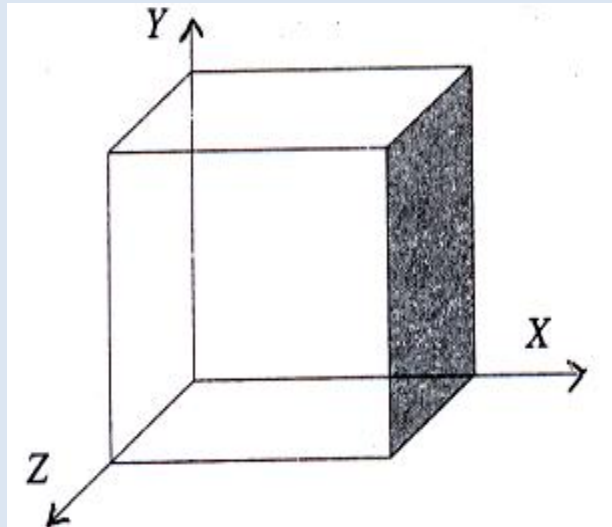
MILLER INDICES

IMPORTANT FEATURES OF MILLER INDICES

For the cubic crystal especially, the important features of Miller indices are,

- ✚ A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞). Therefore the Miller index for that axis is zero; i.e. for an intercept at infinity, the corresponding index is zero.

EXAMPLE



(1 0 0) plane

Plane parallel to Y and Z axes

EXAMPLE

- ✚ In the above plane, the intercept along X axis is 1 unit.
- ✚ The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are ' ∞ '.
- ✚ Now the intercepts are 1, ∞ and ∞ .
- ✚ The reciprocals of the intercepts are = $1/1$, $1/\infty$ and $1/\infty$.
- ✚ Therefore the Miller indices for the above plane is (1 0 0).

MILLER INDICES

IMPORTANT FEATURES OF MILLER INDICES

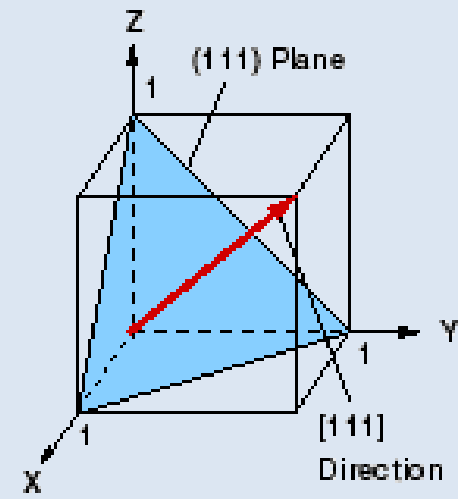
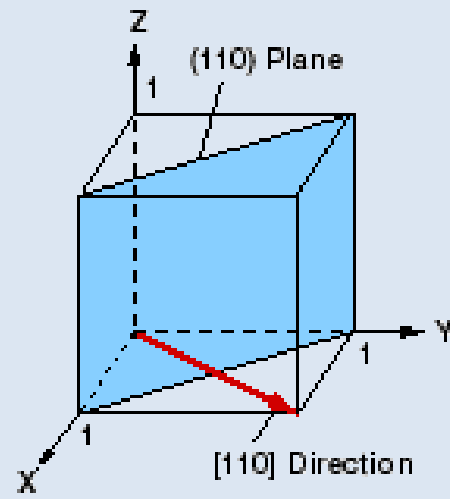
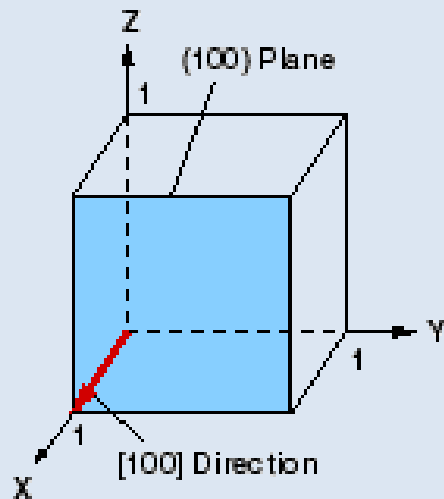
- ✚ A plane passing through the origin is defined in terms of a parallel plane having non zero intercepts.
- ✚ All equally spaced parallel planes have same 'Miller indices' i.e. The Miller indices do not only define a particular plane but also a set of parallel planes. Thus the planes whose intercepts are 1, 1,1; 2,2,2; -3,-3,-3 etc., are all represented by the same set of Miller indices.

MILLER INDICES

IMPORTANT FEATURES OF MILLER INDICES

- ✚ It is only the ratio of the indices which is important in this notation. The $(6\ 2\ 2)$ planes are the same as $(3\ 1\ 1)$ planes.
- ✚ If a plane cuts an axis on the negative side of the origin, corresponding index is negative. It is represented by a bar, like $(\bar{1}\ 0\ 0)$. i.e. Miller indices $(1\ 0\ 0)$ indicates that the plane has an intercept in the $-ve\ X$ $-axis$.

MILLER INDICES OF SOME IMPORTANT PLANES



PROBLEMS

Worked Example:

A certain crystal has lattice parameters of 4.24, 10 and 3.66 Å on X, Y, Z axes respectively. Determine the Miller indices of a plane having intercepts of 2.12, 10 and 1.83 Å on the X, Y and Z axes.

Lattice parameters are = 4.24, 10 and 3.66 Å

The intercepts of the given plane = 2.12, 10 and 1.83 Å

i.e. The intercepts are, 0.5, 1 and 0.5.

Step 1: The Intercepts are $1/2$, 1 and $1/2$.

Step 2: The reciprocals are 2, 1 and 2.

Step 3: The least common denominator is 2.

Step 4: Multiplying the lcd by each reciprocal we get, 4, 2 and 4.

Step 5: By writing them in parenthesis we get (4 2 4)

Therefore the Miller indices of the given plane is (4 2 4) or (2 1 2).

PROBLEMS

Worked Example:

Calculate the miller indices for the plane with intercepts $2a$, $-3b$ and $4c$ the along the crystallographic axes.

The intercepts are 2, -3 and 4

Step 1: The intercepts are 2, -3 and 4 along the 3 axes

Step 2: The reciprocals are $\frac{1}{2}$, $\frac{1}{-3}$ and $\frac{1}{4}$

Step 3: The least common denominator is 12.

Multiplying each reciprocal by lcd, we get 6 -4 and 3

Step 4: Hence the Miller indices for the plane is $(6 \bar{4} 3)$

CRYSTAL DIRECTIONS

- ✚ In crystal analysis, it is essential to indicate certain directions inside the crystal.
- ✚ A direction, in general may be represented in terms of three axes with reference to the origin. In crystal system, the line joining the origin and a lattice point represents the **direction of the lattice point**.

DESIRABLE FEATURES OF MILLER INDICES

- ✚ The relation between the interplanar distance and the interatomic distance is given by,

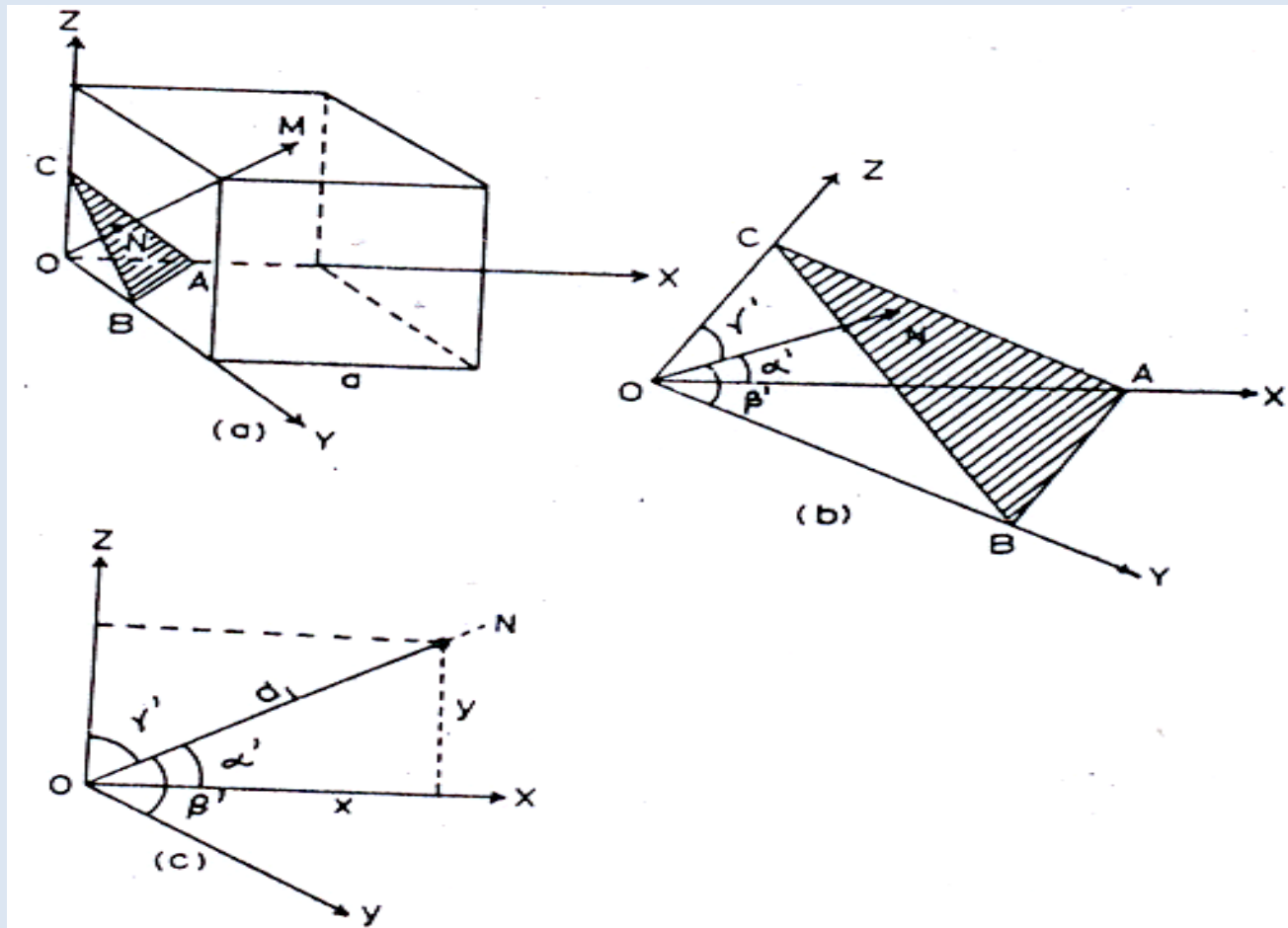
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{for cubic crystal.}$$

- ✚ If (h k l) is the Miller indices of a crystal plane then the intercepts made by the plane with the crystallographic axes are given as $\frac{a}{h}$, $\frac{b}{k}$ and $\frac{c}{l}$ where a, b and c are the primitives.

SEPARATION BETWEEN LATTICE PLANES

- ✚ Consider a **cubic crystal** of side 'a', and a plane ABC.
- ✚ This plane belongs to a family of planes whose Miller indices are (h k l) because **Miller indices represent a set of planes**.
- ✚ Let $ON = d$, be the perpendicular distance of the plane A B C from the origin.

SEPARATION BETWEEN LATTICE PLANES



SEPARATION BETWEEN LATTICE PLANES

✚ Let α' , β' and γ' (different from the interfacial angles α , β and γ) be the angles between co-ordinate axes X,Y,Z and ON respectively.

✚ The intercepts of the plane on the three axes are,

$$OA = \frac{a}{h}, \quad OB = \frac{a}{k} \quad \text{and} \quad OC = \frac{a}{l} \longrightarrow (1)$$

SEPARATION BETWEEN LATTICE PLANES

From the figure, we have,

$$\cos \alpha^1 = \frac{d_1}{OA}, \cos \beta^1 = \frac{d_1}{OB} \text{ and } \cos \gamma^1 = \frac{d_1}{OC} \longrightarrow (2)$$

From the property of direction of cosines,

$$\cos^2 \alpha^1 + \cos^2 \beta^1 + \cos^2 \gamma^1 = 1 \longrightarrow (3)$$

SEPARATION BETWEEN LATTICE PLANES

Using equation 1 in 2, we get,

$$\cos\alpha^1 = \frac{d_1 h}{a}, \cos\beta^1 = \frac{d_1 k}{a}, \quad \text{and} \quad \cos\gamma^1 = \frac{d_1 l}{a} \quad (4)$$

Substituting equation (4) in (3), we get,

$$\left(\frac{d_1 h}{a}\right)^2 + \left(\frac{d_1 k}{a}\right)^2 + \left(\frac{d_1 l}{a}\right)^2 = 1$$

$$\frac{d_1^2 h^2}{a^2} + \frac{d_1^2 k^2}{a^2} + \frac{d_1^2 l^2}{a^2} = 1$$

$$\frac{d_1^2}{a^2} (h^2 + k^2 + l^2) = 1$$

$$d_1^2 = \frac{a^2}{(h^2 + k^2 + l^2)}$$

$$d_1 = \text{ON} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{-----(5)}$$

i.e. the perpendicular distance between the origin

and the 1st plane ABC is, $d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

- ✚ Now, let us consider the next parallel plane.
- ✚ Let $OM=d_2$ be the perpendicular distance of this plane from the origin.
- ✚ The intercepts of this plane along the three axes are

$$OA^1 = \frac{2a}{h}, OB^1 = \frac{2a}{k}, OC^1 = \frac{2a}{l},$$

$$\therefore OM = d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}$$



SEPARATION BETWEEN LATTICE PLANES

- Therefore, the interplanar spacing between two adjacent parallel planes of Miller indices $(h \ k \ l)$ is given by, $NM = OM - ON$

i.e. Interplanar spacing

$$d = (d_2 - d_1) = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (6)$$



PROBLEMS

Worked Example

The lattice constant for a unit cell of aluminum is 4.031\AA . Calculate the interplanar space of $(2\ 1\ 1)$ plane.

$$a = 4.031\text{\AA}$$

$$(h\ k\ l) = (2\ 1\ 1)$$

Interplanar spacing

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{4.031 \times 10^{-10}}{\sqrt{2^2 + 1^2 + 1^2}}$$

$$\therefore d = 1.6456\text{\AA}$$



PROBLEMS

Worked Example:

Find the perpendicular distance between the two planes indicated by the Miller indices (1 2 1) and (2 1 2) in a unit cell of a cubic lattice with a lattice constant parameter 'a'.

We know the perpendicular distance between the origin and the plane is (1 2 1)

$$d_1 = \frac{a}{\sqrt{h_1^2 + k_1^2 + l_1^2}} = \frac{a}{\sqrt{1^2 + 2^2 + 1^2}} = \frac{a}{\sqrt{6}}$$

and the perpendicular distance between the origin and the plane (2 1 2),

$$d_2 = \frac{a}{\sqrt{h_2^2 + k_2^2 + l_2^2}} = \frac{a}{\sqrt{2^2 + 1^2 + 2^2}} = \frac{a}{\sqrt{9}} = \frac{a}{3}$$



PROBLEMS

The perpendicular distance between the planes (1 2 1) and (2 1 2) are,

$$d = d_1 - d_2 = \frac{a}{\sqrt{6}} - \frac{a}{3} = \frac{3a - \sqrt{6}a}{3\sqrt{6}} = \frac{a(3 - \sqrt{6})}{3\sqrt{6}}$$

(or) **$d = 0.0749 a.$**

Characteristics of unit cell

- Number of atoms per unit cell
- Coordination number
- Atomic radius
- Atomic Packing factor or Packing Density

- **Number of atoms per unit cell:** The number of atoms present in the unit cell .
- **Coordination number:** The number of equidistant nearest neighbouring atoms surrounding the particular atom considered.
- **Atomic Radius (r) :** It is defined as half the distance between the nearest neighbouring atoms in a crystal.
- **Atomic Packing factor or Packing Density:** It is the ratio of the volume occupied by the atoms in an unit cell (v) to the volume of the unit cell (V). It is also called packing fraction or packing density.

 **SIMPLE CUBIC STRUCTURE**

 **BODY CENTRED CUBIC STRUCTURE**

 **FACE CENTERED CUBIC STRUCTURE**

 **HEXAGONAL CLOSED PACKED STRUCTURE**

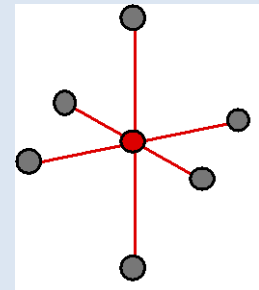
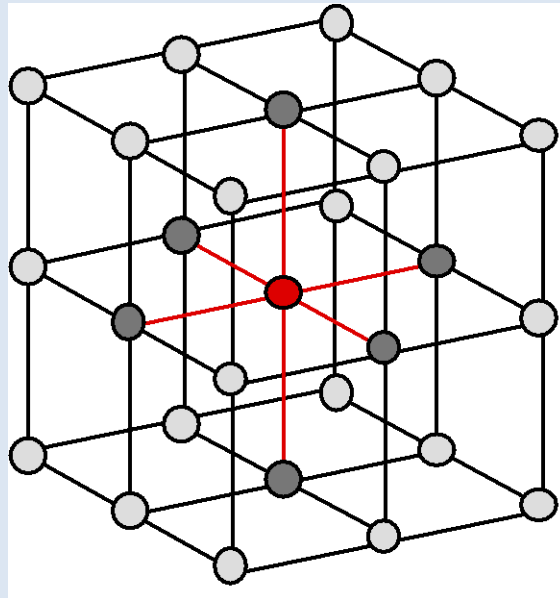
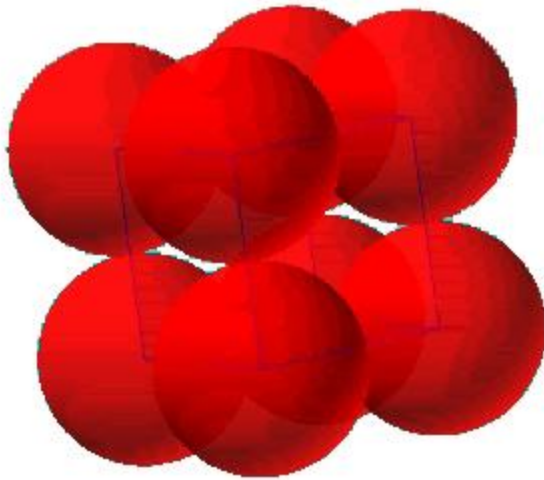
 **PROBLEMS**

Simple Cubic Structure (SC)

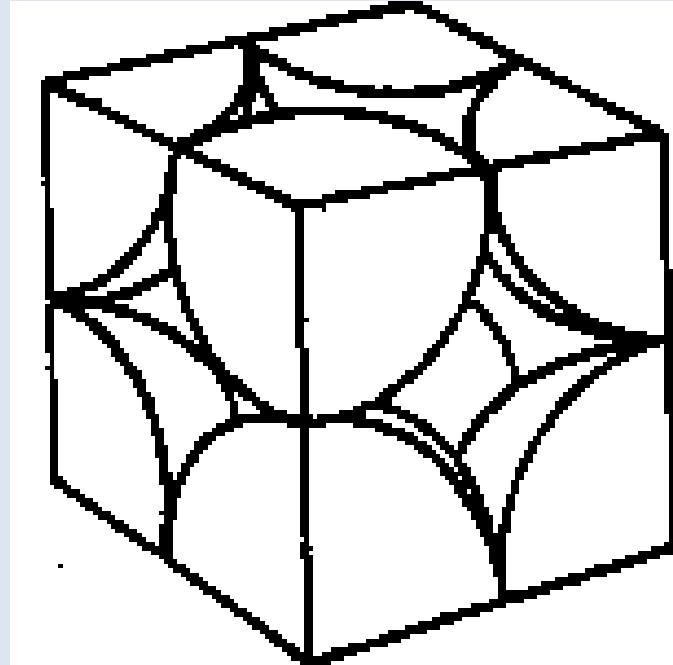
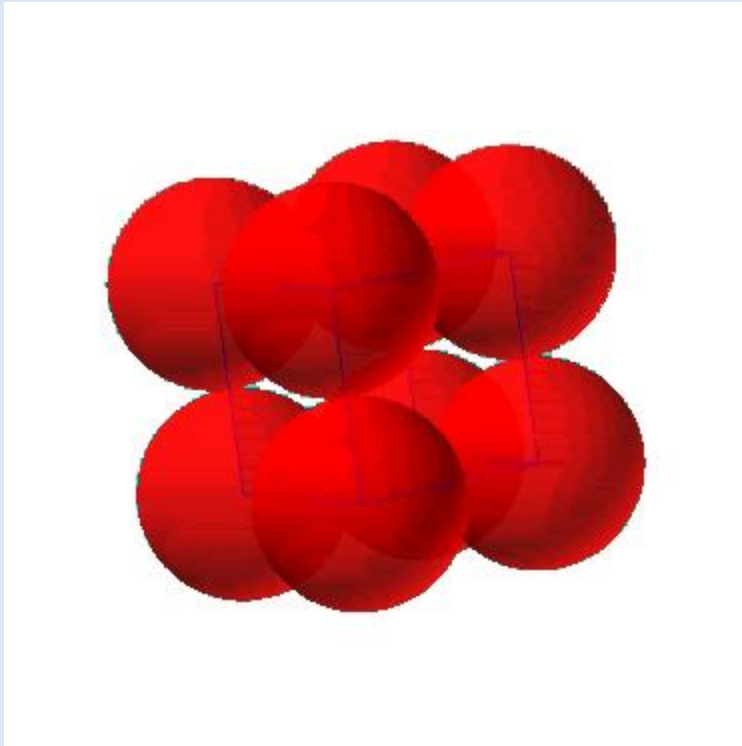
- Rare due to poor packing (only Po has this structure)
- **Close-packed directions** are cube edges.

Coordination # = 6
(# nearest neighbors)

1 atom/unit cell



One atom per unit cell



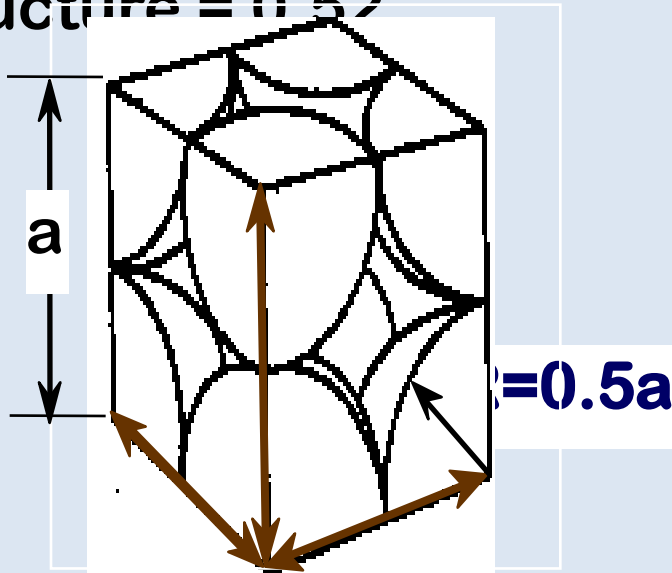
$$\frac{1}{8} \times 8 = 1$$

Atomic Packing Factor

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52

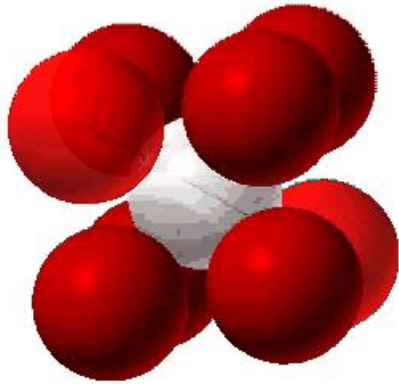


$$APF = \frac{\begin{array}{c} \text{atoms} \\ \text{unit cell} \end{array} \cdot \begin{array}{c} \text{Volume of an atom} \\ \frac{4}{3} \pi (0.5a)^3 \end{array}}{\begin{array}{c} \text{Volume of unit cell} \\ a^3 \end{array}}$$

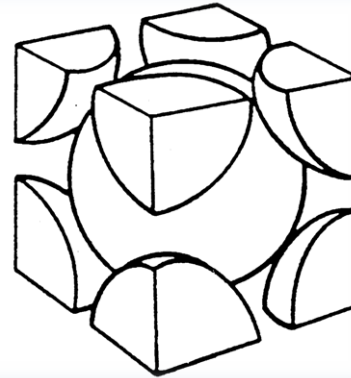
Body Centered Cubic Structure (BCC)

How is 'a' and 'R' related for an BCC?
[a= unit cell dimension, R = atomic radius].

All atoms are identical

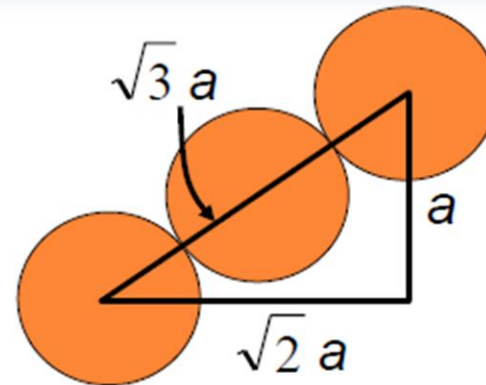
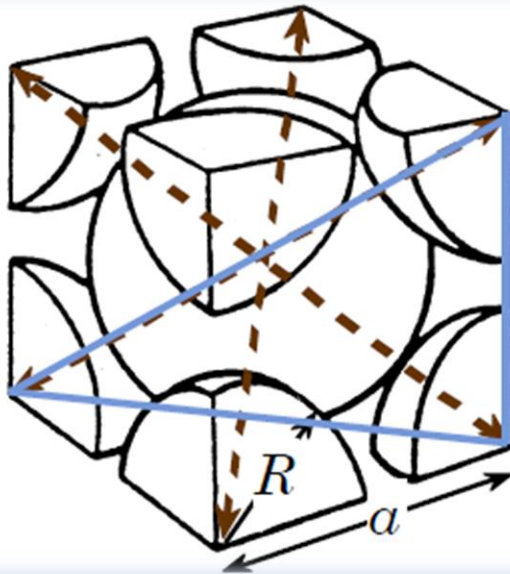


2 atoms/unit cell



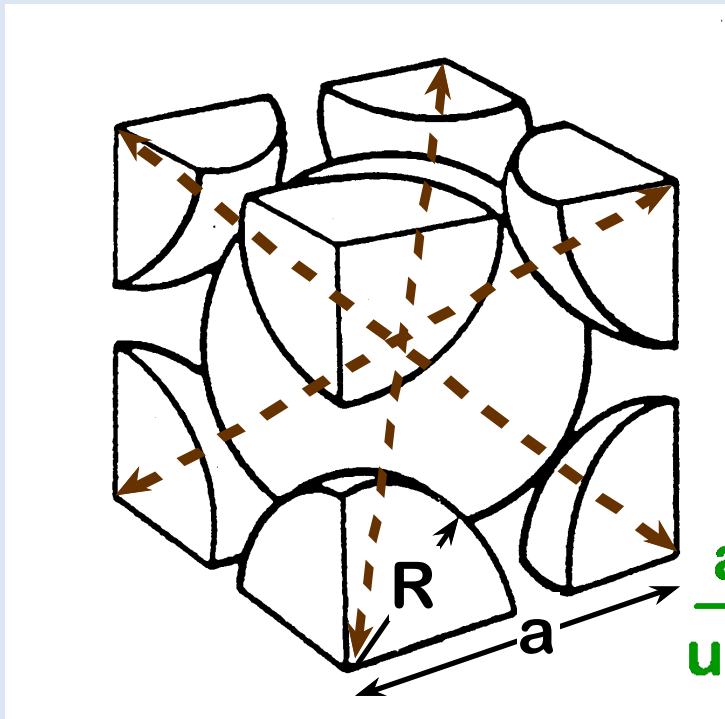
- Exhibited by Cr, Fe, Mo, Ta, W
- Close packed directions are cube diagonals.
- Coordination number = 8

Body Centered Cubic Structure (BCC)



Close-packed directions:
length = $4R = \sqrt{3}a$

ATOMIC PACKING FACTOR: BCC



- APF for a body-centered cubic structure = 0.68

Close-packed
direction - diagonal

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

atoms
unit cell

$$2 \frac{4}{3} \pi (\sqrt{3}a/4)^3$$

volume
atom

APF =

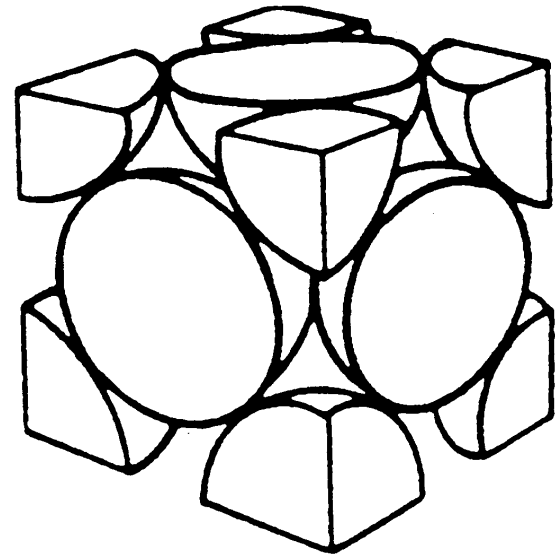
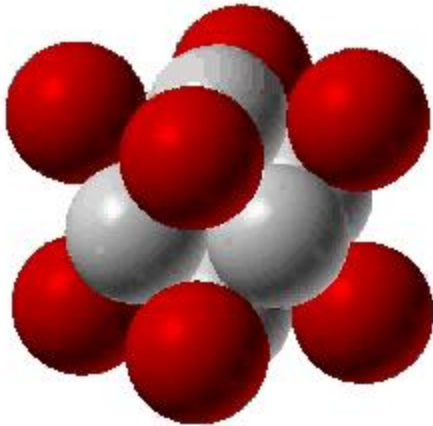
$$a^3$$

volume
unit cell

Face Centered Cubic Structure (FCC)

- Exhibited by Al, Cu, Au, Ag, Ni, Pt
- Close packed directions are face diagonals.
- Coordination number = 12
- 4 atoms/unit cell

All atoms are identical



$$6 \times (1/2 \text{ face}) + 8 \times 1/8 (\text{corner}) = 4 \text{ atoms/unit cell}$$

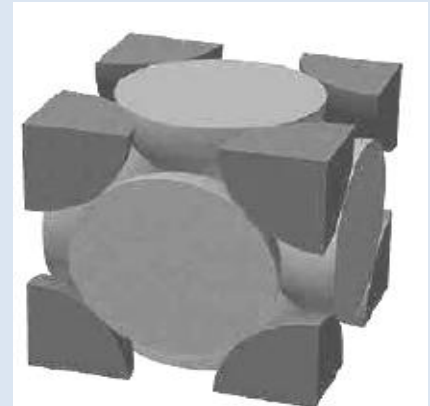
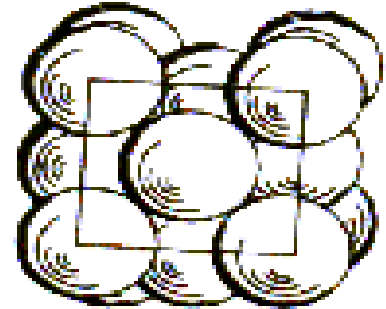
FACE CENTERED CUBIC STRUCTURE

■ The atoms in a FCC unit cell touches along the face diagonal.

■ Each and every corner atom is shared by eight adjacent unit cells.

■ Therefore each and every corner atom contributes $1/8$ of its part to one unit cell.

■ So the total number of atoms contributed by the corner atoms is $\left(\frac{1}{8}\right) \times 8 = 1$.





FACE CENTERED CUBIC STRUCTURE

- Two unit cells share each and every face centered atom.
- Therefore, the contribution of a face centered atom to unit cell is $1/2$.
- So, the total number of atoms contributed by the face centred atoms = $1/2 \times 6 = 3$.
- The total number of atoms present in a FCC unit cell = $1+3 = 4$.



FACE CENTERED CUBIC STRUCTURE

COORDINATION NUMBER

- In its own plane it touches **four face centered** atoms. The face centered atoms are its nearest neighbors.
- In a plane, which lies just above this corner atom, it has **four more face centered atoms** as nearest neighbors.
- Similarly, in a plane, which lies just below this corner atom it has yet four more face centered atoms as its nearest neighbors.



FACE CENTERED CUBIC STRUCTURE

Therefore the number of nearest neighbours i.e., co-ordination number for FCC unit cell = $4+4+4 = 12$

ATOMIC RADIUS (R)

Consider the figure, $AB = AC = 'a'$
and $AC = 4r$.

From the triangle ABC,

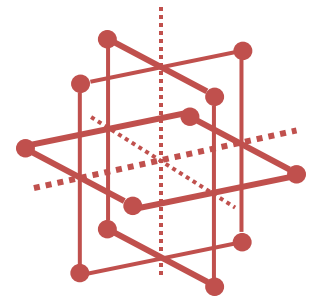
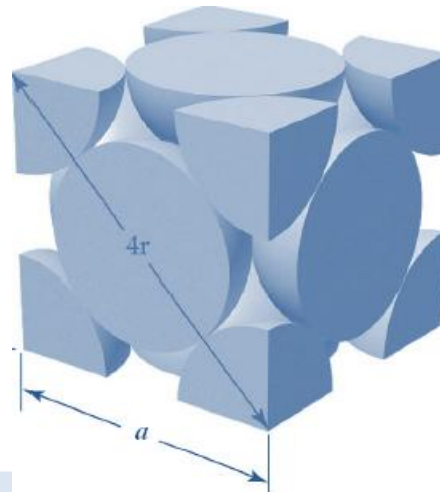
$$AC^2 = AB^2 + BC^2$$

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

$$AC^2 = 2a^2; AC = \sqrt{2}a$$

$$\text{i.e. } 4r = \sqrt{2}a$$

$$\text{Therefore atomic radius} = \frac{\sqrt{2}a}{4}$$



FACE CENTERED CUBIC STRUCTURE

Atomic Packing Factor

$$APF = \frac{v}{V}$$

$$v = 4 \times \frac{4}{3} \pi r^3 \quad V = a^3$$

$$APF = \frac{4 \times \frac{4}{3} \pi r^3}{a^3}$$

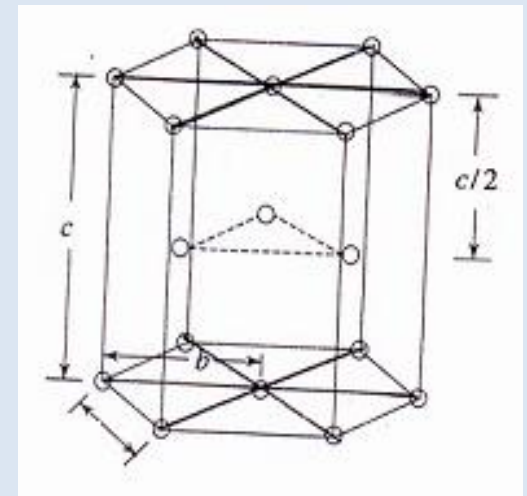
$$\text{Substituting } r = \frac{\sqrt{2}a}{4}, \quad \text{we get,}$$

$$APF = \frac{4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4} \right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Thus 74 percent of the volume of the FCC unit cell is occupied by atoms and the remaining 26 percent volume of the unit cell is vacant or void space.

HEXAGONAL CLOSED PACKED STRUCTURE

- It consists of three layers of atoms.
- The bottom layer has six corner atoms and one face centred atom.
- The middle layer has three full atoms.
- The upper layer has six corner atoms and one face centred atom.
- Each and every corner atom contributes $1/6$ of its part to one unit cell.
- The number of total atoms contributed by the corner atoms of both top and bottom layers is $1/6 \times 12 = 2$.





HEXAGONAL CLOSED PACKED STRUCTURE

- The face centred atom contributes $\frac{1}{2}$ of its part to one unit cell.
- Since there are 2 face centred atoms, one in the top and the other in the bottom layers, the number of atoms contributed by face centred atoms is $\frac{1}{2} \times 2 = 1$.
- Besides these atoms, there are 3 full atoms in the middle layer.
- Total number of atoms present in an HCP unit cell is $2 + 1 + 3 = 6$.

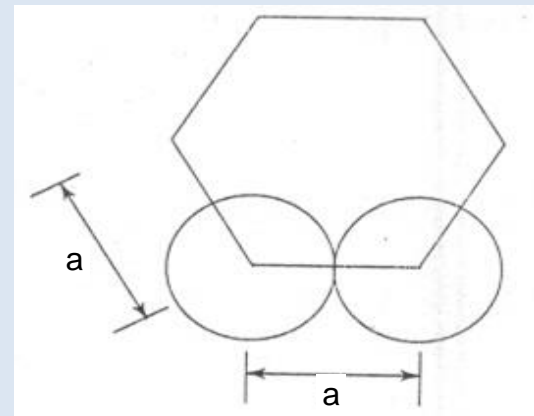
HEXAGONAL CLOSED PACKED STRUCTURE

CO-ORDINATION NUMBER (CN)

- ❖ The face centered atom touches **6 corner atoms** in its plane.
- ❖ The **middle layer has 3 atoms**.
- ❖ There are **three more atoms**, which are in the middle layer of the unit cell.
- ❖ Therefore the total number of nearest neighbours is **$6+3+3=12$** .

ATOMIC RADIUS (R)

- ❖ Consider any two corner atoms.
- ❖ Each and every corner atom touches each other. Therefore $a = 2r$.
i.e., The atomic radius,
 $r = a/2$



HEXAGONAL CLOSED PACKED STRUCTURE

ATOMIC PACKING FACTOR (APF)

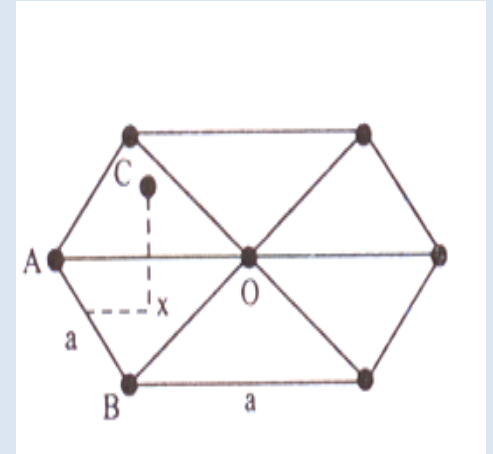
$$\text{APF} = \frac{v}{V}$$

$$v = 6 \times \frac{4}{3} \pi r^3$$

$$\text{Substitute } r = \frac{a}{2}$$

$$v = 6 \times \frac{4}{3} \pi \frac{a^3}{8}$$

$$v = \pi a^3$$



HEXAGONAL CLOSED PACKED STRUCTURE

AB = AC = BO = 'a'. CX = where c → height of the hcp unit cell.

Area of the base = 6 × area of the triangle ABO = $6 \times \frac{1}{2} \times AB \times OO'$

Area of the base = $6 \times \frac{1}{2} \times a \times OO'$

In triangle OBO' $\angle O'OB = 30^\circ$

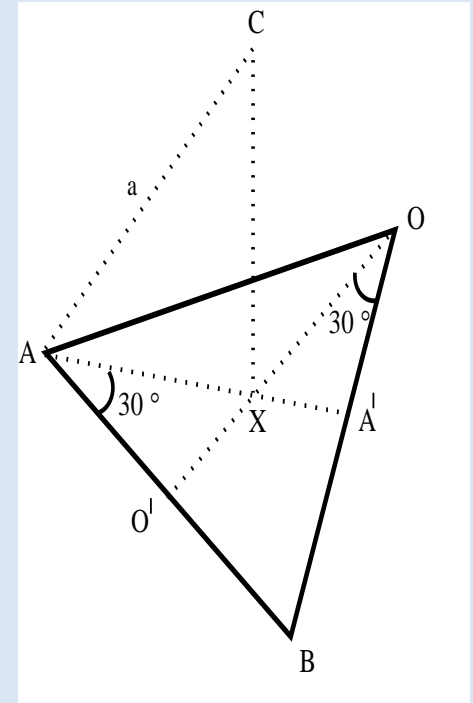
$$\cos 30^\circ = \frac{OO'}{BO} = \frac{OO'}{a}$$

$$\therefore OO' = a \cos 30^\circ = a \frac{\sqrt{3}}{2}$$

Now, substituting the value of OO',

$$\text{Area of the base} = 6 \times \frac{1}{2} \times a \times \frac{\sqrt{3}}{2} = \frac{3\sqrt{3}a^2}{2}$$

V = Area of the base × height



$$\frac{3\sqrt{3}a^2}{2}$$



HEXAGONAL CLOSED PACKED STRUCTURE

$$V = \frac{3\sqrt{3}a^2}{2} \times c$$

$$\therefore \text{APF} = \frac{v}{V} = \frac{\pi a^3}{\frac{3\sqrt{3}}{2} a^2 c}$$

$$\therefore \text{APF} = \frac{2\pi a^3}{3\sqrt{3}a^2c} = \frac{2\pi}{3\sqrt{3}} \frac{a}{c}$$



CALCULATION OF c/a RATIO

In the triangle ABA',

$$\angle A'AB = 30^\circ$$

$$\cos 30^\circ = \frac{AA'}{AB}$$

$$\therefore AA' = AB \cos 30^\circ = a \frac{\sqrt{3}}{2}$$

$$\text{But } AX = \frac{2}{3} AA' = \frac{2}{3} a \frac{\sqrt{3}}{2}$$

$$\text{i.e. } AX = \frac{a}{\sqrt{3}}$$



CALCULATION OF c/a RATIO

In the triangle AXC,

$$AC^2 = AX^2 + CX^2$$

Substituting the values of AC, AX and CX,

$$a^2 = \left(\frac{a}{\sqrt{3}} \right)^2 + \left(\frac{c}{2} \right)^2$$

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

$$\frac{c^2}{4} = a^2 - \frac{a^2}{3}$$



CALCULATION OF c/a RATIO

$$\frac{c^2}{4} = a^2 \left(1 - \frac{1}{3} \right)$$

$$\frac{c^2}{a^2} = \frac{8}{3}$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}}$$

Now substituting the value of $\frac{c}{a}$ to calculate APF of an hcp unit cell,



HEXAGONAL CLOSED PACKED STRUCTURE

$$\begin{aligned} \text{APF} &= \frac{2\pi}{3\sqrt{3}} \sqrt{\frac{3}{8}} \\ &= \frac{2\pi}{3\sqrt{3}} \frac{\sqrt{3}}{2\sqrt{2}} \end{aligned}$$

$$\therefore \text{APF} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Packing Fraction = 74%



PROBLEMS

Worked Example

Zinc has HCP structure. The height of the unit cell is 4.935\AA . Find (i). How many atoms are there in a unit cell? and (ii). What is the volume of the unit cell ?

Height of the unit cell, $c = 4.935\text{\AA} = 4.935 \times 10^{-10}\text{m}$

In HCP structure, the number of atoms present in the unit cell is 6.

We know that, the ratio $\frac{c}{a} = \sqrt{\frac{8}{3}}$

$$a = c \times \sqrt{\frac{3}{8}}, \quad a = 4.935 \times \sqrt{\frac{3}{8}} \quad a = 3.022 \text{\AA}$$



PROBLEMS

We also know that, volume of the unit cell for HCP structure is,

$$V = a^2c \text{ or } a^3$$

$$V = (3.022 \times 10^{-10})^3$$

$$V = 1.17 \times 10^{-28} \text{ m}^3$$

RELATION BETWEEN LATTICE CONSTANT (a) AND DENSITY (ρ)

Consider a cubic crystal of lattice constant 'a'

Density of the crystal = ρ

Volume of the unit cell = a^3

\therefore Mass of the unit cell = ρa^3

$$\left(\because \text{density} = \frac{\text{mass}}{\text{volume}} \right)$$

Number of atoms per unit cell = n

Atomic weight of the material = M

Avogadro's number = N

Avogadro's number is the number of atoms per kg mole of the substance.

Mass of each atom = $\frac{M}{N}$

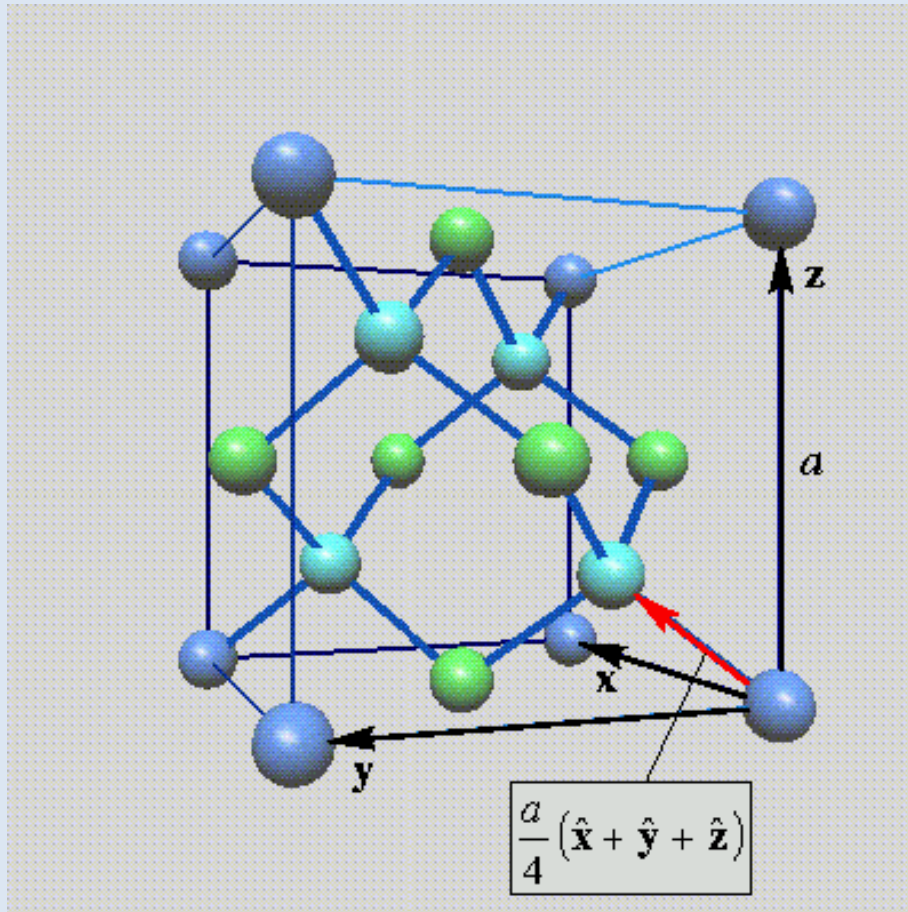
Mass of the unit cell = mass of the each atom in unit cell \times number of atoms per unit cell

$$\text{Mass of each atom} = \frac{M}{N} \times n \text{ (for n atoms per unit cell)} \quad \rho a^3 = \frac{M}{N} \times n \quad \rho = \frac{nM}{Na^3}.$$

Diamond Lattice Structure

- *Exhibited by Carbon (C), Silicon (Si) and Germanium (Ge).*
- Consists of two interpenetrating FCC lattices, displaced along the body diagonal of the cubic cell by $1/4$ the length of the diagonal.
- Also regarded as an FCC lattice with two atoms per lattice site: one centered on the lattice site, and the other at a distance of $a/4$ along all axes, ie an FCC lattice with the two-point basis.

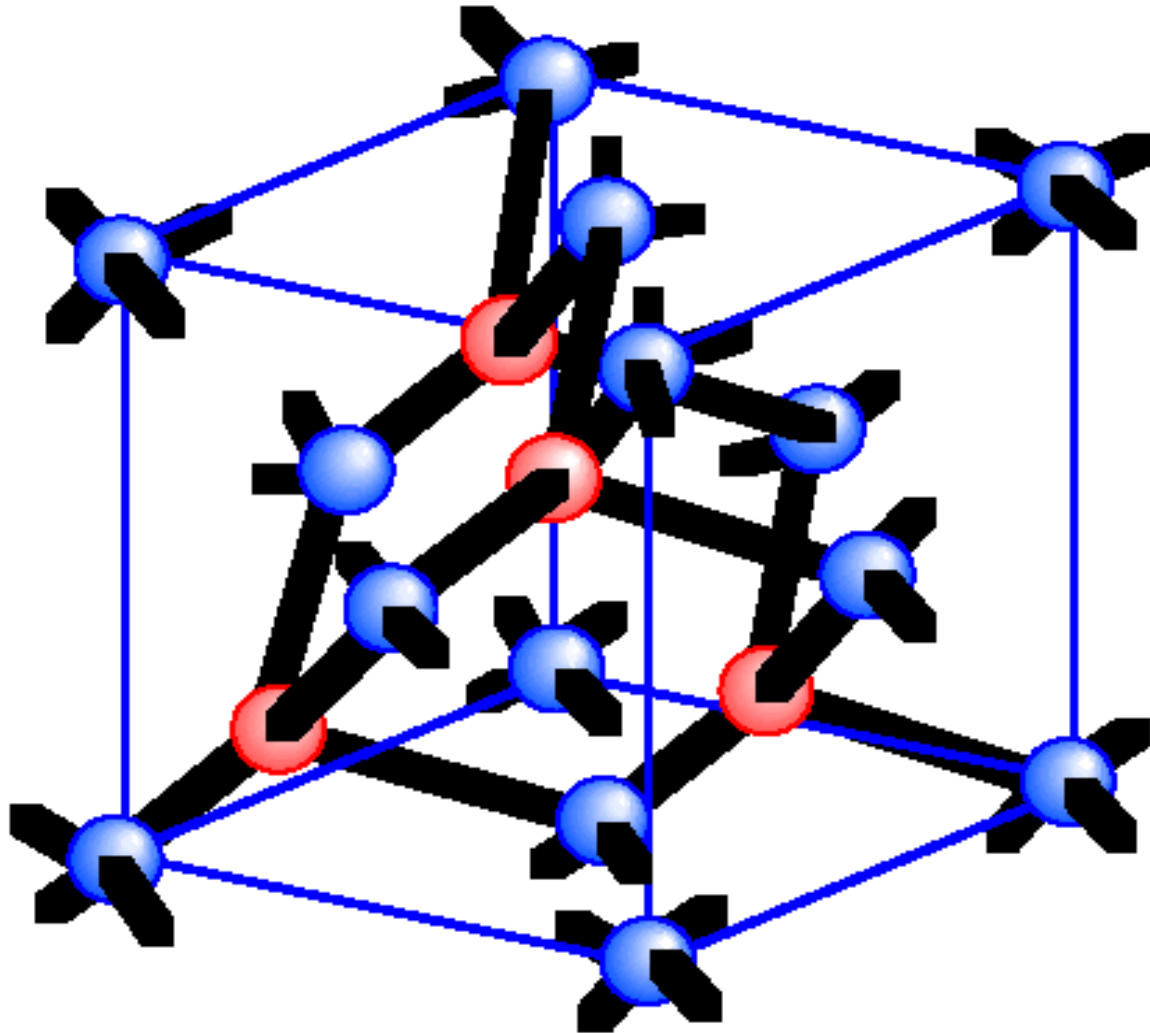
Diamond Lattice Structure



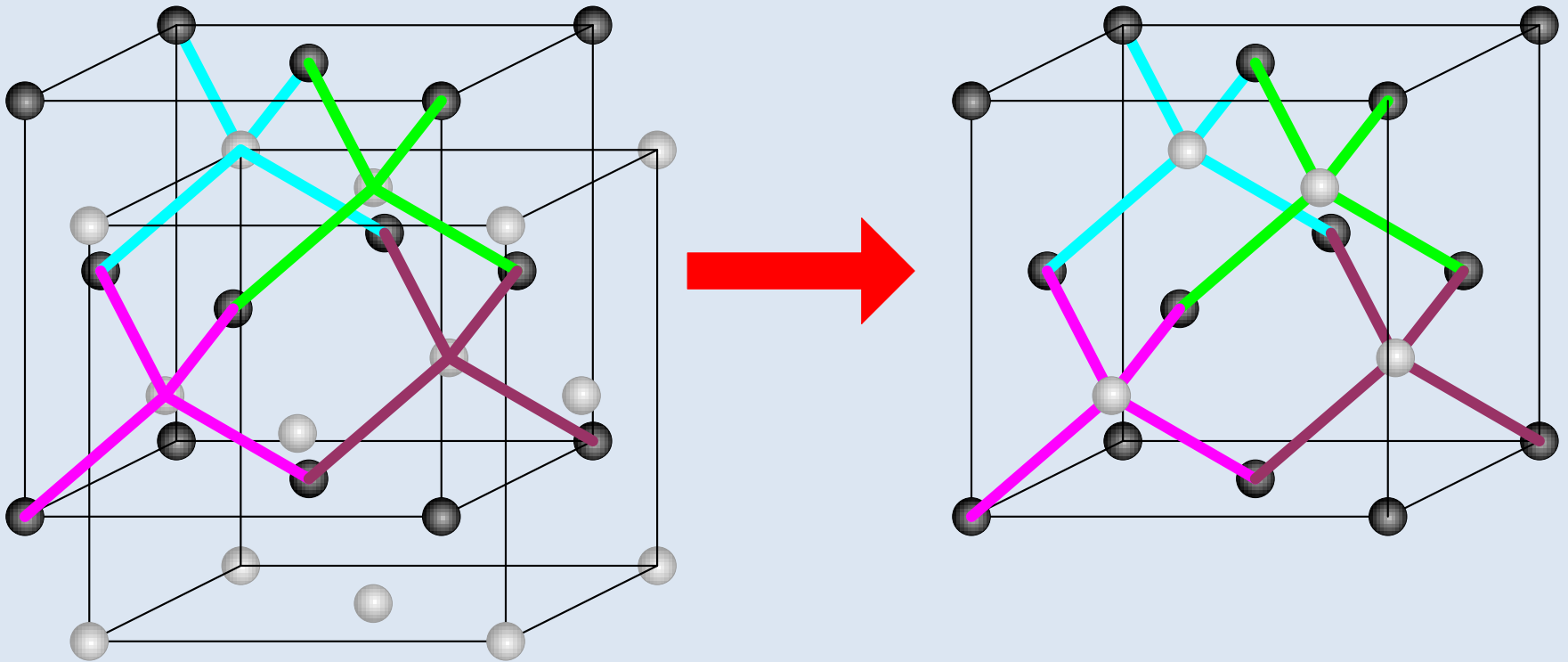
a = lattice constant

$$\mathbf{0}, \quad \frac{a}{4}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

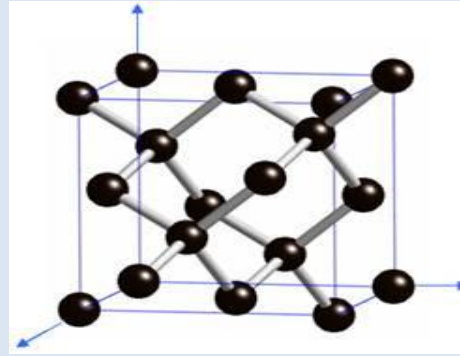
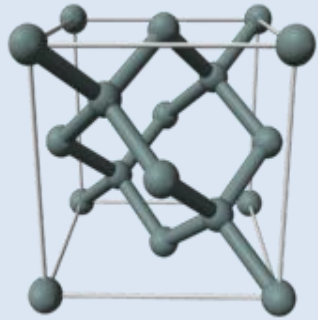
Diamond Lattice Structure



8 atoms at each corner, 6 atoms on each face, 4 atoms entirely inside the cell



DIAMOND CUBIC (DC) STRUCTURE



1. Number of atoms per unit cell

\therefore Total number of atoms per unit cell = $1 + 3 + 4 = 8$

2. Atomic radius

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

3. Coordination number

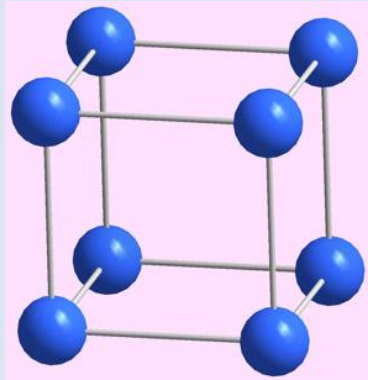
The coordination number of diamond is 4.

4. Packing factor

$$\text{Packing factor} = 0.34\%$$

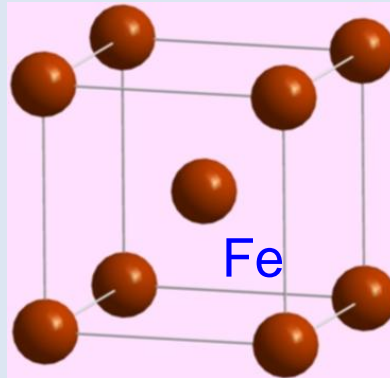
Since the packing density is very low, it is termed as very loosely packed structure.

Examples of elements with Cubic Crystal Structure



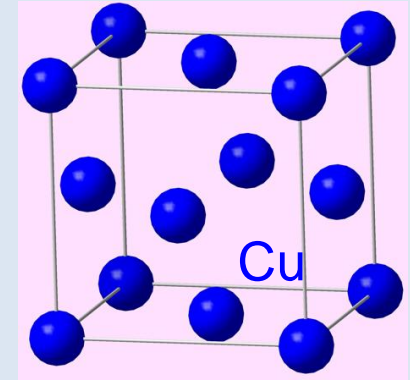
$n = 1$

SC



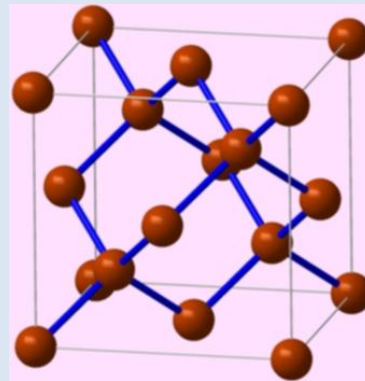
$n = 2$

BCC



$n = 4$

FCC/CCP



$n = 8$ DC

C (diamond)

	Radius	Atoms/ unit cell	Packing density
Simple cubic	$\frac{a}{2}$	1	$\frac{\pi}{6} = 52\%$
Body centered cubic	$\frac{\sqrt{3}a}{4}$	2	$\frac{\pi\sqrt{3}}{8} = 68\%$
Face centered cubic	$\frac{\sqrt{2}a}{4}$	4	$\frac{\pi\sqrt{2}}{6} = 74\%$
Diamond	$\frac{\sqrt{3}a}{8}$	8	$\frac{\pi\sqrt{3}}{16} = 34\%$

POLYMORPHISM & ALLOTROPY

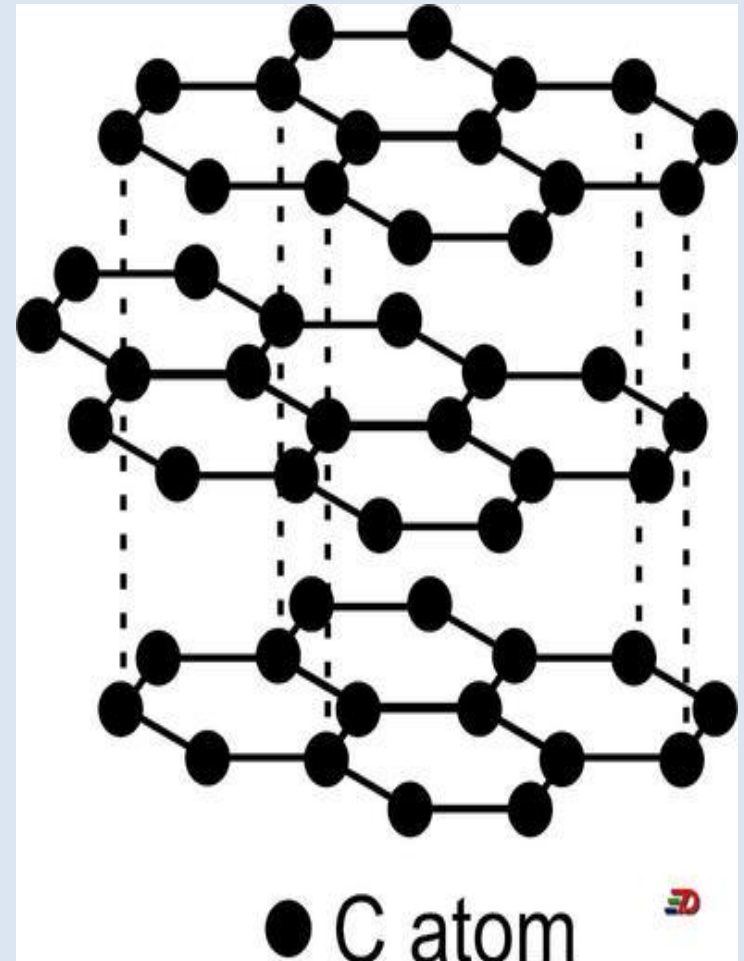
POLYMORPHISM -Ability of material to have more than one structure

ALLOTROPY - If the change in structure is reversible

Example: Cobalt at ordinary temp. -HCP and at 477°C -FCC

Graphite Structure

- Carbon atoms are arranged in layer or sheet structure
- Each carbon atoms are covalently bonded with three other carbons
- The sheets are held together by van der Waals forces
- Weak bonding between sheets give softness
- Fourth bonding electron of carbon is delocalized
- Delocalized electrons are mobile and contribute conduction



Physical properties of diamond and Graphite

S.No	Diamond	Graphite
1	high melting point (almost 4000°C).	has a high melting point
2	very hard	soft, slippery feel, and is used in pencils
3	does not conduct electricity. All the electrons are used up in bonding (held tightly between) the atoms, and are not mobile.	Conducts electricity. The delocalised electrons are free to move throughout the sheets. Hence used as lubricant
4	insoluble in water and organic solvents	insoluble in water and organic solvents
5	Transparent	Opaque
6	Crystallizes in Isometric system	Crystallizes in hexagonal system
7	Carbon atoms are covalently bonded	Carbon atoms are covalently bonded in same plane and sheets are held together by Van der waals bonds

CRYSTAL GROWTH METHOD

- Crystals are solids that form by a regular repeated pattern of molecules connecting together.
- In some solids, the arrangements of the building blocks (atoms and molecules) can be random or very different throughout the material.
- In crystals, however, a collections of atoms called the Unit Cell is repeated in exactly the same arrangement over and over throughout the entire material.

- A crystal is a substance in which the atoms, molecules, or ions which make up the substance are arranged in a regularly ordered, repeating, 3-dimensional pattern.
- A crystal or crystalline solid is a solid material whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions

METHODS OF CRYSTAL GROWTH

Crystal growth may be classified into three categories as follows,

- ❖ Solid Growth - Solid-to-Solid phase transformation
- ❖ Liquid Growth - Liquid to Solid phase transformation
- ❖ Vapour Growth - Vapour to Solid phase transformation

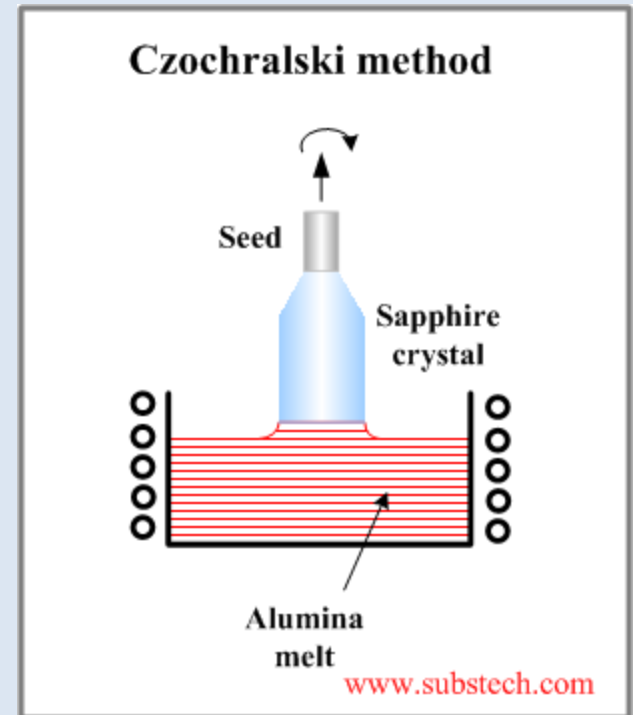
GROWTH FROM SOLUTION

- Materials, which have high solubility and have variation in solubility with temperature can be grown easily by solution method.
- There are two methods in solution growth depending on the solvents and the solubility of the solute. They are
 - High temperature solution growth
 - Low temperature solution growth

Czochralski method

Characteristics:

- charge and seed are separated at start.
- No material is added or removed (conservative process)
- charge is held at temperature slightly above melting point
- crystal grows as atoms from the melt adhere to the seed



Czochralski method

Advantages:

- Growth from free surface (stress free)
- crystal can be observed during the growth process
- Forced convection easy to impose
- Large crystals can be obtained
- High crystalline perfection can be achieved

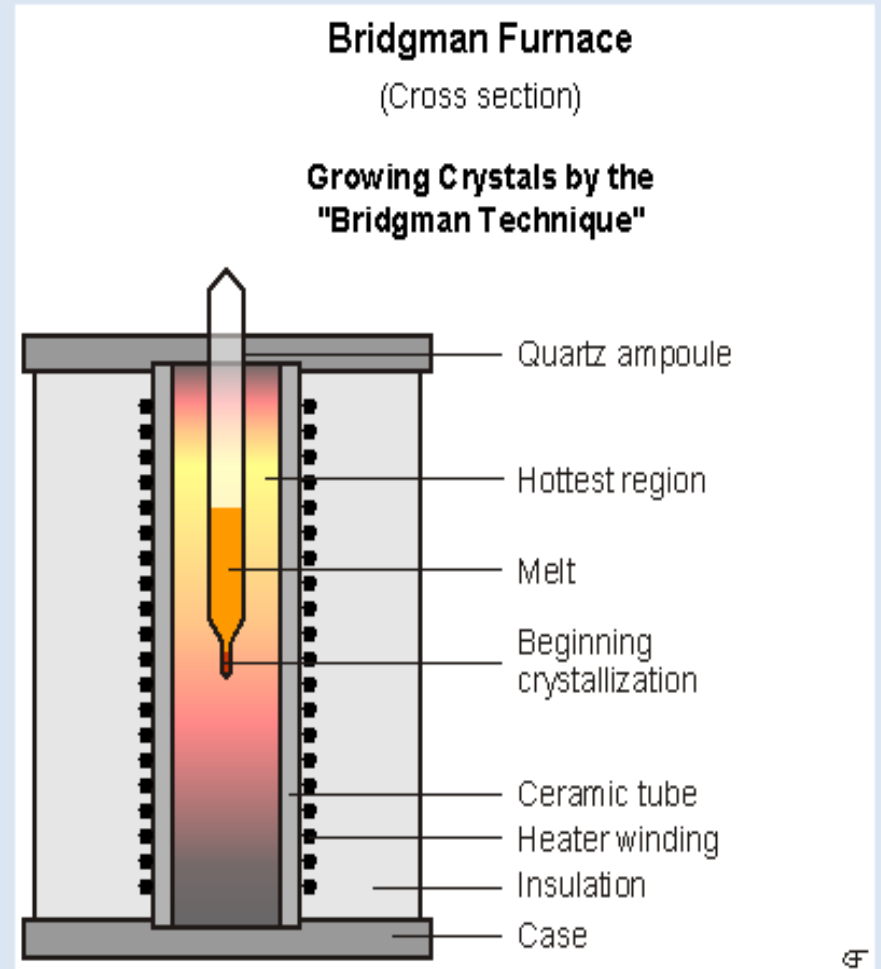
Drawbacks:

- delicate start (seeding, necking) and sophisticated further control
- delicate mechanics (the crystal has to be rotated; rotation of the crucible is desirable)
- cannot grow materials with high vapor pressure
- batch process (axial segregation, limited productivity)

Bridgman method

Characteristics:

- charge and seed are placed into the crucible
- no material is added or removed (conservative process)
- axial temperature gradient along the crucible



Bridgman method

Advantages:

- The shape of the crystal is defined by the container
- No radial temperature gradients are needed to control the crystal shape.
- low thermal stresses result in low level of stress-induced dislocations.
- crystals may be grown in sealed ampules (easy control of stoichiometry)
- easy control and maintenance

Drawbacks:

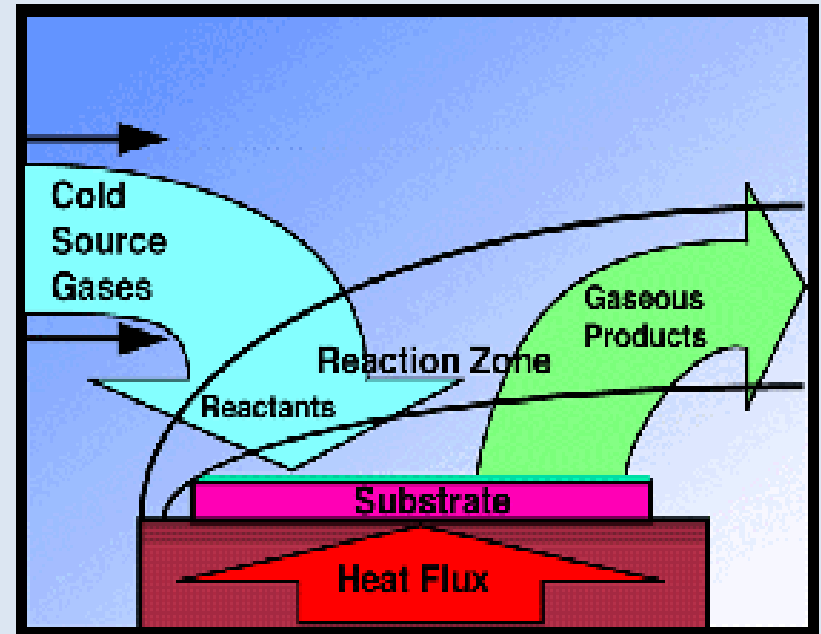
- confined growth (crucible may induce stresses during cooling)
- difficult to observe seeding and growing processes
- delicate crucible and seed preparation, sealing, etc.

CHEMICAL VAPOUR DEPOSITION & **PHYSICAL VAPOUR DEPOSITION**

CHEMICAL VAPOUR DEPOSITION

CVD is the formation of a non-volatile solid film on a **substrate** by the reaction of vapor phase chemicals (reactants) that contain the required constituents.

The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.



TYPES OF CVD

- Hot-wall thermal CVD (batch operation type)
- Plasma assisted CVD
- *Atmospheric pressure CVD* (APCVD) – CVD process at atmospheric pressure.
- *Low-pressure CVD* (LPCVD) – CVD process at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
- *Ultrahigh vacuum CVD* (UHVCVD) – CVD process at very low pressure, typically below 10^{-6} [Pa](#) ($\sim 10^{-8}$ [torr](#)). Note that in other fields, a lower division between high and [ultra-high vacuum](#) is common, often 10^{-7} Pa.

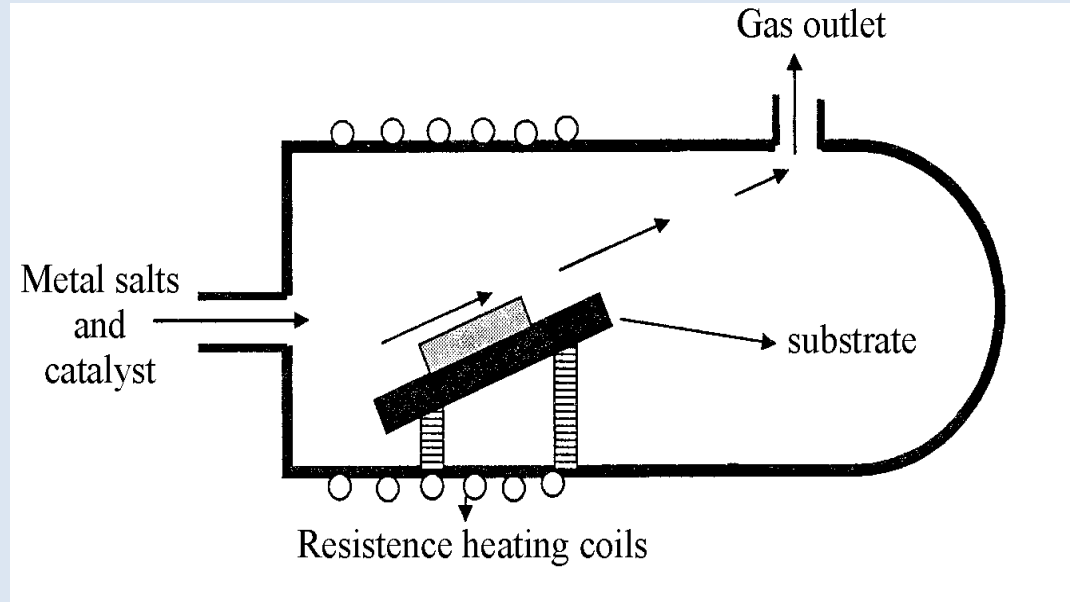
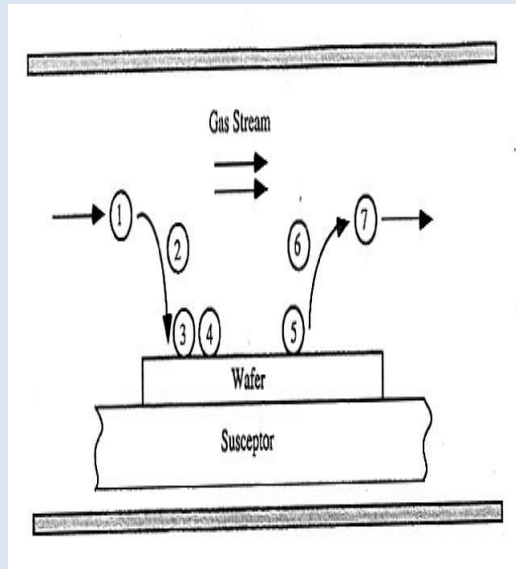
CVD APPARATUS

- **Gas delivery system** – For the supply of precursors to the reactor chamber
- **Reactor chamber** – Chamber within which deposition takes place
- **Substrate loading mechanism** – A system for introducing and removing substrates, mandrels etc.
- **Energy source** – Provide the energy/heat that is required to get the precursors to react/decompose.
- **Vacuum system** – A system for removal of all other gaseous species other than those required for the reaction/deposition.

CONTI...

- **Exhaust system** – System for removal of volatile by-products from the reaction chamber.
- **Exhaust treatment systems** – In some instances, exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.
- **Process control equipment** – Gauges, controls etc.. to monitor process parameters such as pressure, temperature and time. Alarms and safety devices would also be included in this category.

Steps involved in a CVD process (schematic)



1. Transport of reactants by forced convection to the deposition region.
2. Transport of reactants by diffusion from the main gas stream through the boundary layer to the wafer surface.

Conti.....

3. Adsorption of reactants on the wafer surface.
4. Surface processes, including chemical decomposition or reaction, surface migration to attachment sites (such as atomic-level ledges and kinks), site incorporation, and other surface reactions.
5. Desorption of byproducts from the surface.
6. Transport of byproducts by diffusion through the boundary layer and back to the main gas stream.
7. Transport of byproducts by forced convection away from the deposition region.

Advantages:

- High growth rates possible
- Can deposit materials which are hard to evaporate
- Good reproducibility
- Can grow epitaxial films

Disadvantages

- high temperatures
- complex processes
- toxic and corrosive gases

APPLICATION

➤ **Coatings –**

- Such as wear resistance,
- Corrosion resistance,
- High temperature protection,
- Erosion protection and
- Combinations thereof.

➤ **Semiconductors and related devices –**

- Integrated circuits,
- Sensors and
- Optoelectronic devices

Conti....

- **Dense structural parts** – CVD can be used to produce components that are difficult or uneconomical to produce using conventional fabrication techniques.

Dense parts produced via CVD are generally thin walled and maybe deposited onto a mandrel or former.

- **Optical Fibers** – For telecommunications.

Conti

- **Composites** – Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites. This process is sometimes called chemical vapour infiltration or CVI.
- **Powder production** – Production of novel powders and fibers
- **Catalysts**
- **Nano machines**

Physical Vapour Déposition(PVD)

- Physical vapour deposition (PVD) is fundamentally a vaporization coating technique, involving transfer of material on an atomic level.
- It is an alternative process to electroplating
- The process is similar to chemical vapour deposition (CVD) except that the raw materials/precursors,
- i.e. the material that is going to be deposited starts out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in the gaseous state.

Conti

- **Working Concept**

PVD processes are carried out under vacuum conditions. The process involved four steps:

1. Evaporation

2. Transportation

3. Reaction

4. Deposition

Evaporation

During this stage, a target, consisting of the material to be is bombarded by a high energy source such as a beam of electrons or ions. This dislodges atoms from the surface of the target, 'vaporizing' them.

Transport

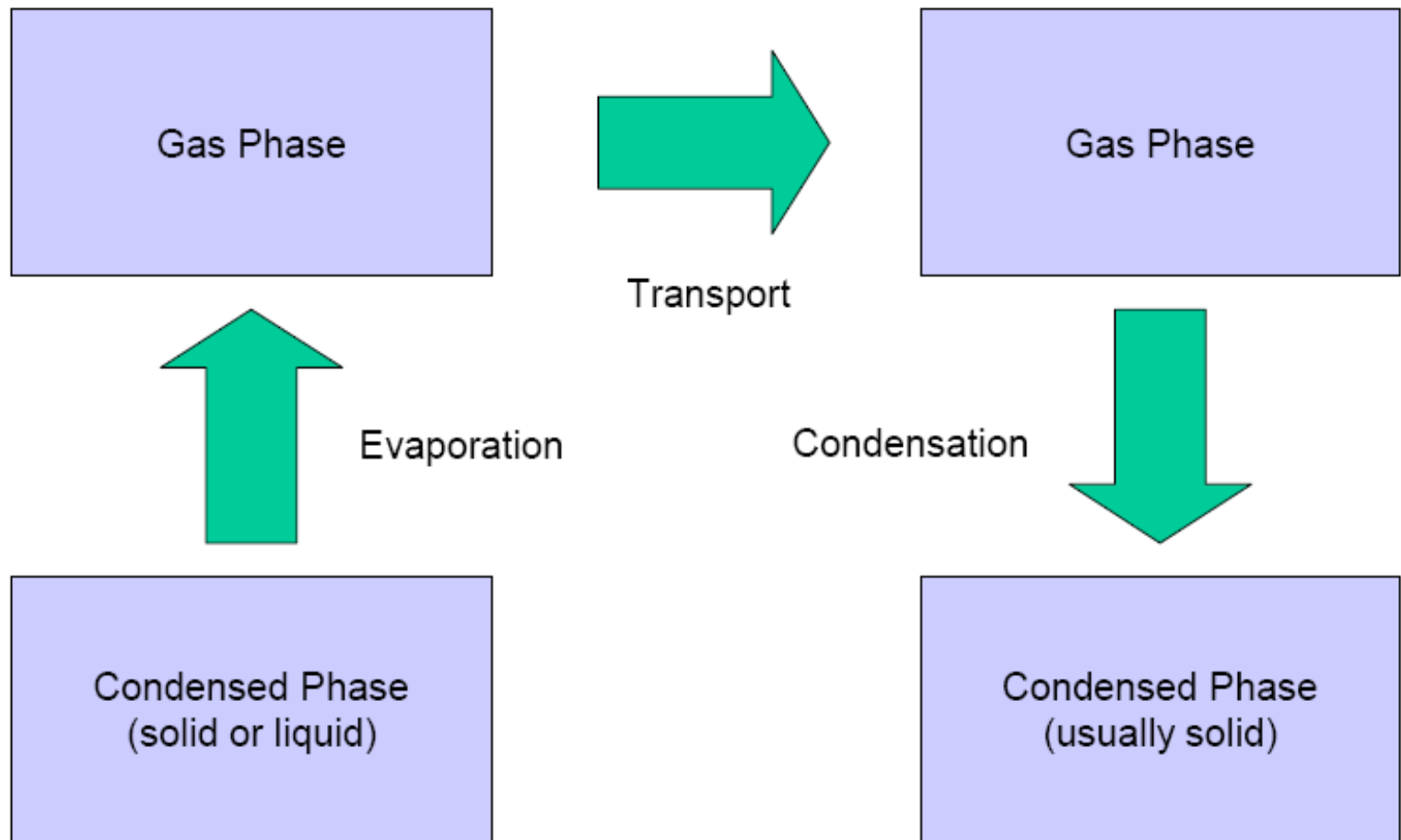
This process simply consists of the movement of 'vaporized' atoms from the target to the substrate to be coated and will generally be a straight line affair.

Conti...

Reaction

- In some cases coatings will consist of metal oxides, nitrides, carbides and other such materials.
- In these cases, the target will consist of the metal.
- The atoms of metal will then react with the appropriate gas during the transport stage.
- For the above examples, the reactive gases may be oxygen, nitrogen and methane.
In instances where the coating consists of the target material alone, this step would not be part of the process.

Physical Vapor Deposition



Deposition

This is the process of coating build up on the substrate surface. Depending on the actual process, some reactions between target materials and the reactive gases may also take place at the substrate surface simultaneously with the deposition process.

The component that is to be coated is placed in a vacuum chamber. The coating material is evaporated by intense heat from, for example, a tungsten filament.

An alternative method is to evaporate the coating material by a complex ion bombardment technique.

The coating is then formed by atoms of the coating material being deposited onto the surface of the component being treated.

**Source
(Solid / Liquid)**

Evaporation

Gas phase

**Transport
&
Deposition**

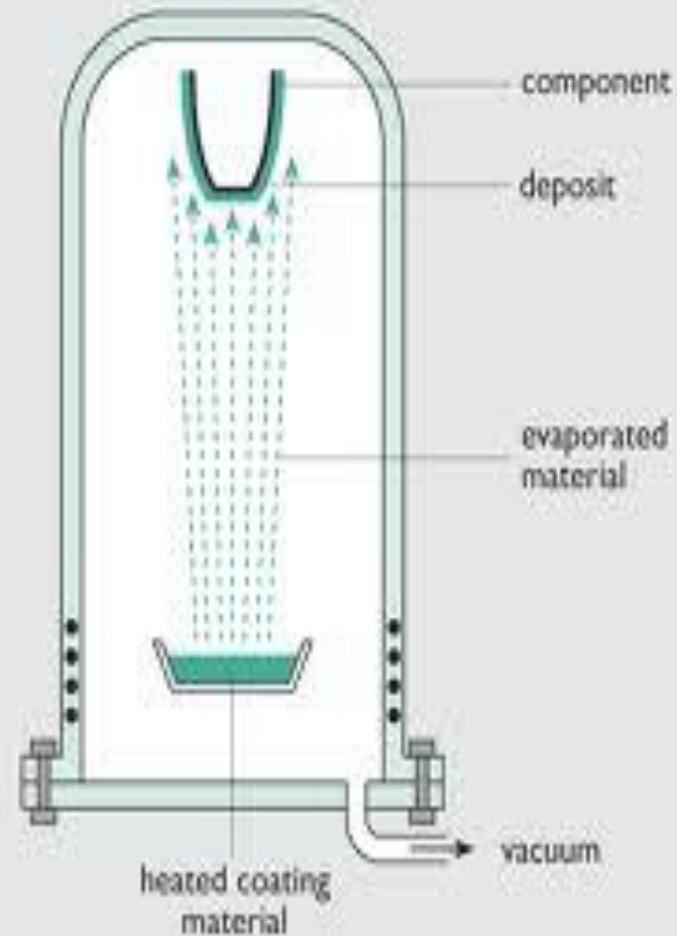
Solid phase

(Changes in physical morphology)

VARIANTS OF PVD

Evaporative Deposition

In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "high" vacuum



Importance of PVD Coatings

- PVD coatings are deposited for numerous reasons. Some of the main ones are:
- Improved **hardness and wear resistance**
- Reduced friction
- Improved **Oxidation resistance**
- The use of such coatings is aimed at improving efficiency through improved performance and longer **component life**.
- They may also allow coated components to operate in environments that the uncoated component would not otherwise have been able to perform.

Advantages

- Materials can be deposited with **improved properties** compared to the substrate material
- Almost any type of **inorganic material** can be used as well as some kinds of organic materials
- The process is more environmentally friendly than processes such as **electroplating**.

DISADVANTAGES

- It is a line of sight technique meaning that it is extremely difficult **to coat** undercuts and similar surface features
- High **capital cost**
- Some processes operate at **high vacuums** and temperatures requiring **skilled operators**
- Processes requiring large amounts of **heat** require appropriate **cooling systems**
- The **rate** of coating deposition is usually quite slow

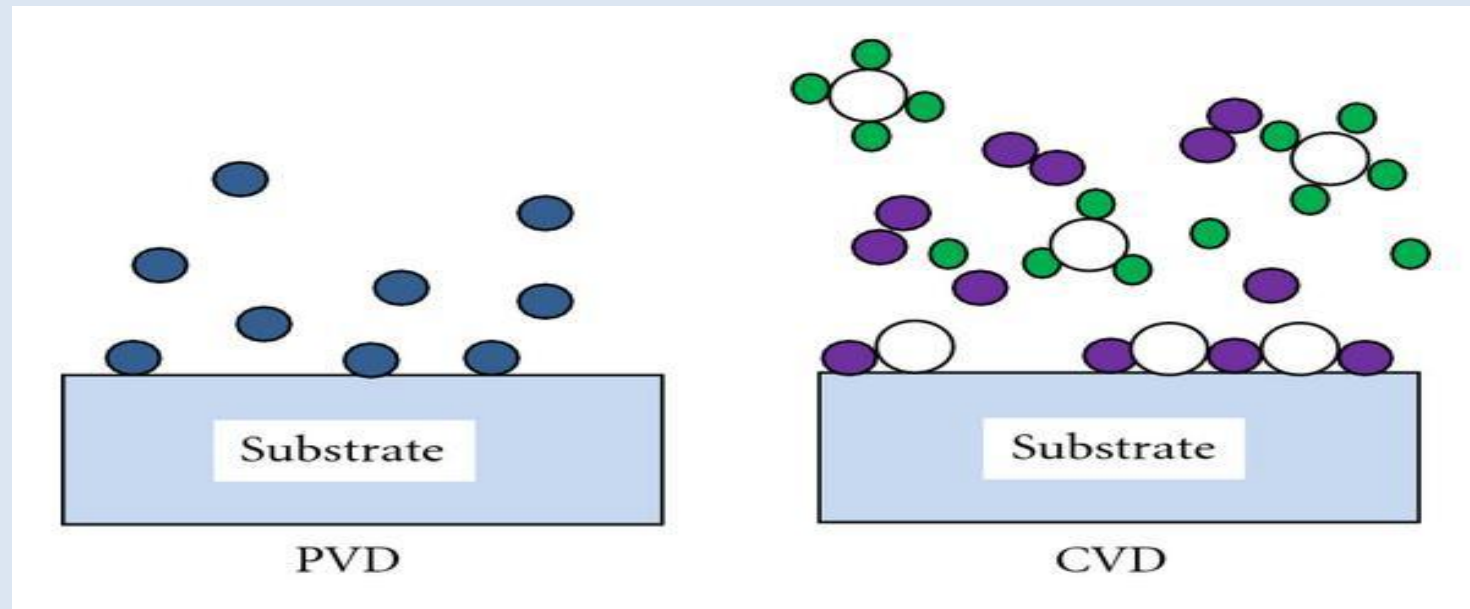
Applications

- PVD coatings are generally used to improve **Hardness, Wear Resistance And Oxidation Resistance.**
- Thus, such coatings use in a wide range of applications such as:
 - Aerospace
 - Automotive
 - Surgical/Medical
 - Dies and moulds for all manner of material processing
 - Cutting tools
 - Fire arms

DIFFERENCE BETWEEN PVD AND CVD

PVD uses Physical Processes While CVD Primarily uses Chemical processes

PVD typically uses a Pure while CVD uses a Mixed source material



UNIT-I IMPORTANT FORMULAE

✚ The relation between the interplanar distance and the interatomic distance is given by,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{for cubic crystal.}$$

✚ If (h k l) is the Miller indices of a crystal plane then the intercepts made by the plane with the crystallographic axes are given as where a, b and c are the primitives.

$$\frac{a}{h}, \quad \frac{b}{k} \quad \text{and} \quad \frac{c}{l}$$

	Radius	Atoms/ unit cell	Packing density
Simple cubic	$\frac{a}{2}$	1	$\frac{\pi}{6} = 52\%$
Body centered cubic	$\frac{\sqrt{3}a}{4}$	2	$\frac{\pi\sqrt{3}}{8} = 68\%$
Face centered cubic	$\frac{\sqrt{2}a}{4}$	4	$\frac{\pi\sqrt{2}}{6} = 74\%$
Diamond	$\frac{\sqrt{3}a}{8}$	8	$\frac{\pi\sqrt{3}}{16} = 34\%$

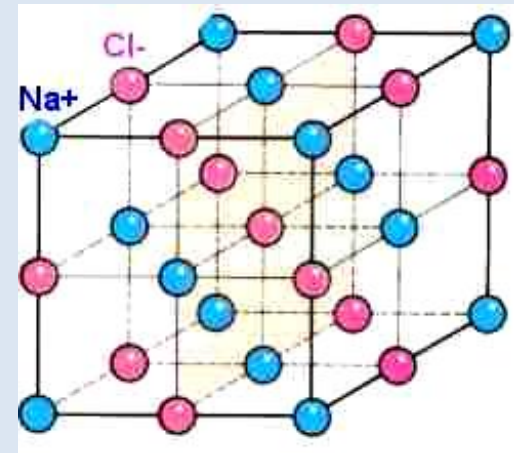
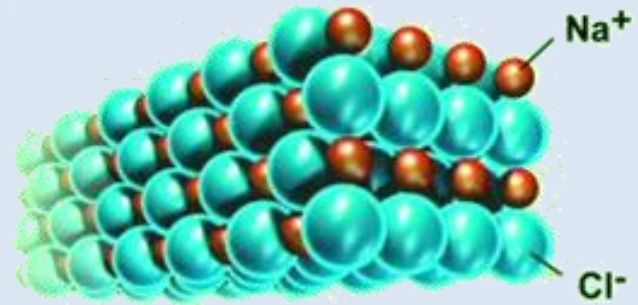
UNIT-I IMPORTANT FORMULAE

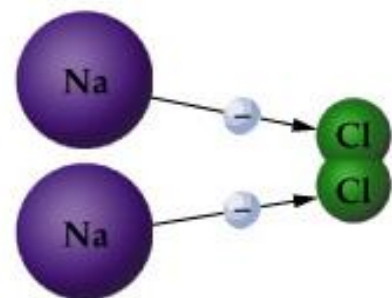
RELATION BETWEEN LATTICE CONSTANT (a) AND DENSITY (ρ)

$$\rho = \frac{nM}{Na^3}.$$

Sodium Chloride Structure

- Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.
- Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.
- Each ion has six of the other kind of ions as its nearest neighbours.

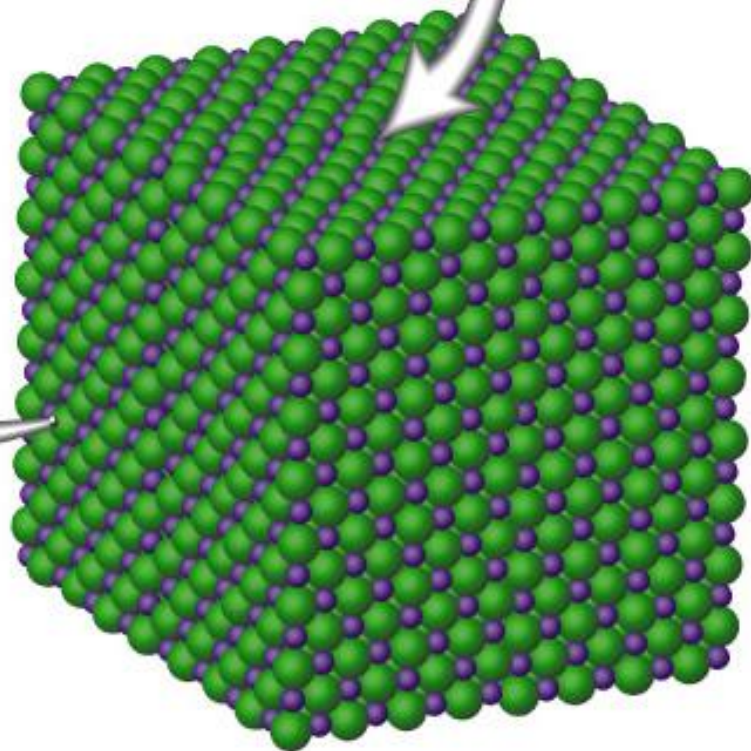
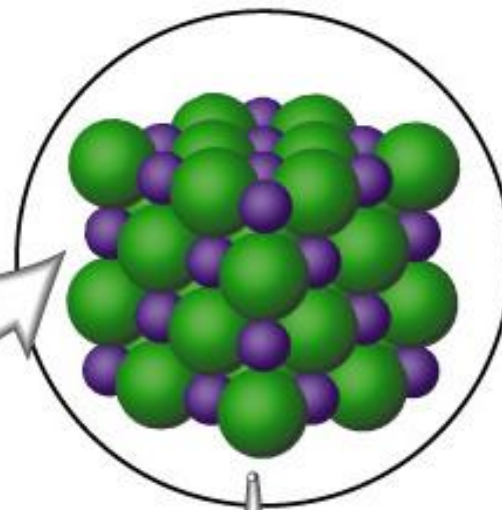




①



②





Physics is hopefully simple but Physicists are not