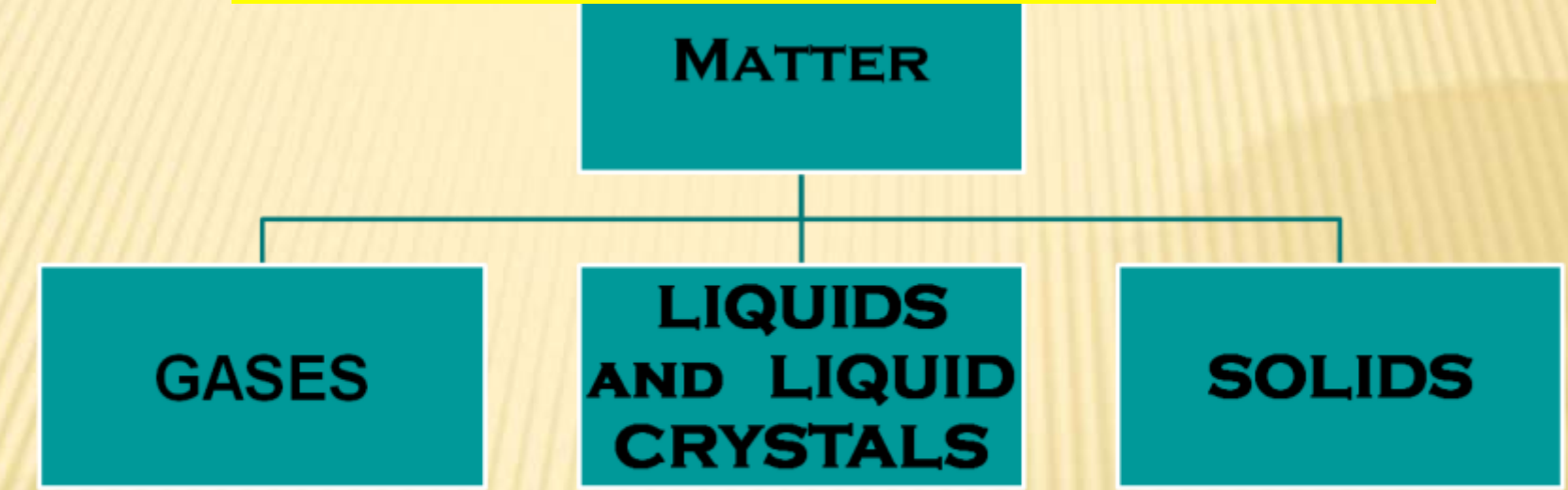
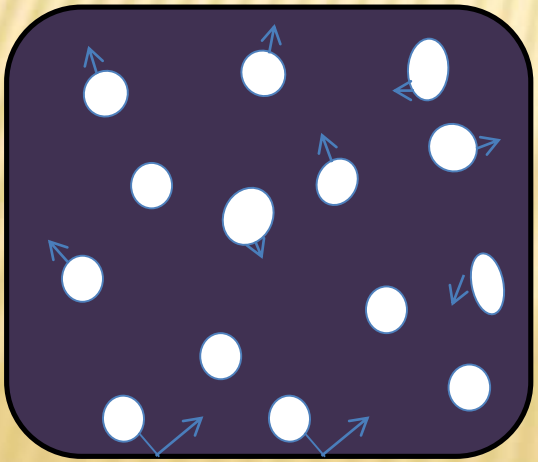
Unit-I

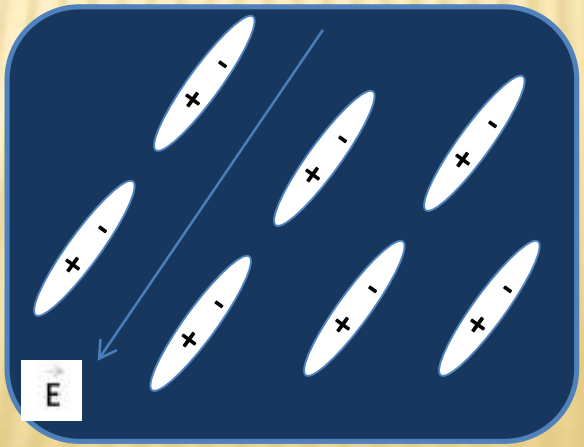
Elements of Crystallography

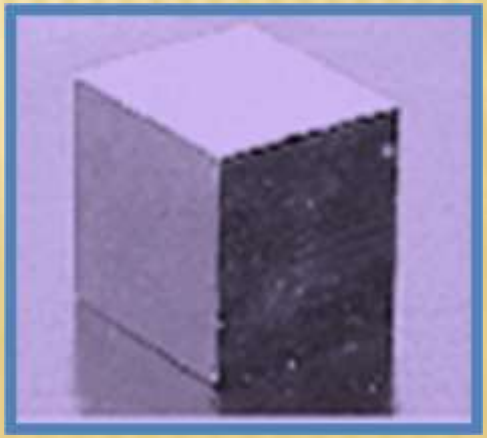
- **INTRODUCTION TO CRYSTAL PHYSICS**
- **CRYSTALLINE AND NON-CRYSTALLINE SOLIDS**
- **SPACE LATTICE**
- **CRYSTAL STRUCTURE**
- **LATTICE PARAMETERS**
- **CRYSTAL SYSTEMS**
- **BRAVAIS LATTICES**

INTRODUCTION TO CRYSTAL PHYSICS









What is Crystal Physics

- physical properties of crystalline solids

- determination of their actual structure by using

X-rays, neutron beams and electron beams.-

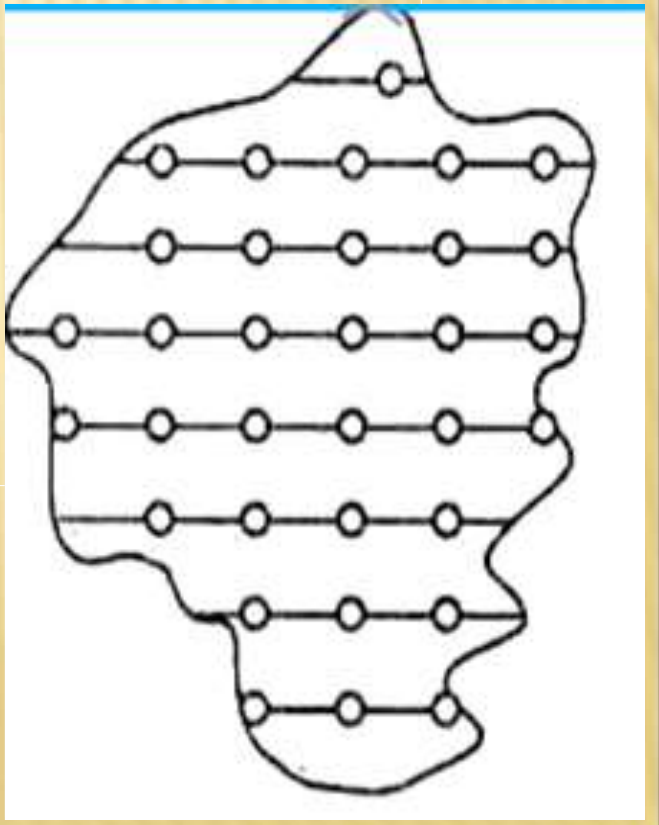
CLASSIFICATION OF SOLIDS

SOLID MATERIALS

- CRYSTALLINE
  - Single Crystal
- POLYCRYSTALLINE
- AMORPHOUS (NON-CRYSTALLINE)

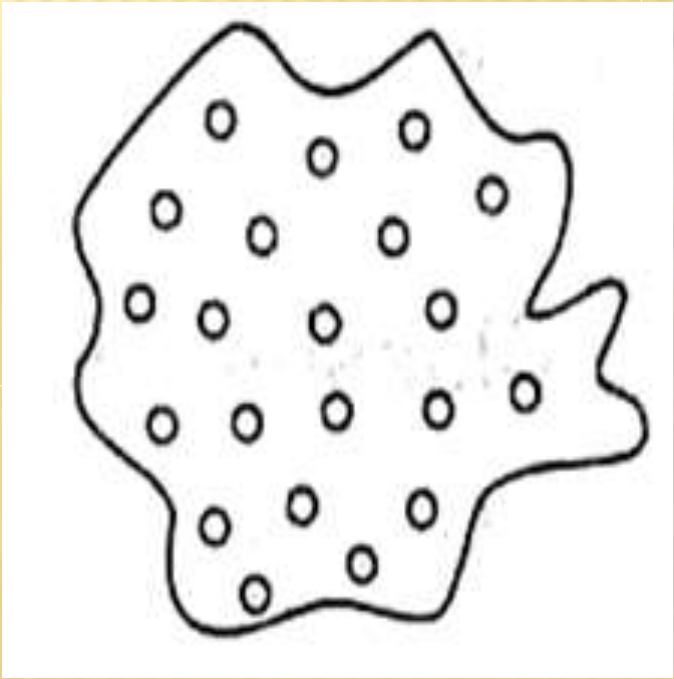
CRYSTALLINE SOLIDS

- arrangement of units of matter is regular and periodic.
- anisotropic substance.
- sharp melting point.
- possesses a regular shape
- **Ex: Iron, Copper, Carbon, Germanium**



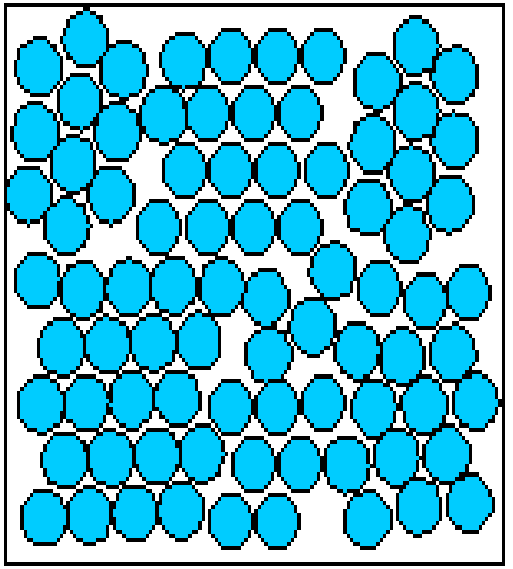
NON CRYSTALLINE SOLIDS

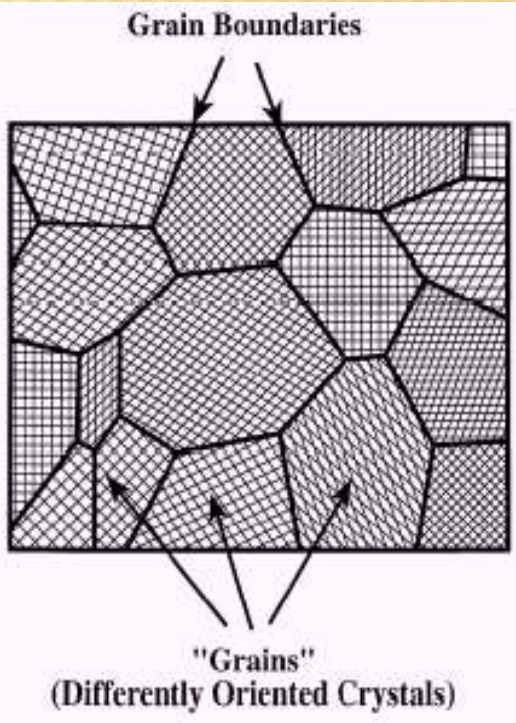
- amorphous solids
- particles are randomly distributed.
- `isotropic' substances.
- have wide range of melting point
- **Examples: Glass, Plastics, Rubber etc.,**



POLYCRYSTALLINE SOLIDS

- aggregate of **many small single crystals**
- high degree of order over many atomic or molecular dimensions.
- **grain boundaries.**
- grains are usually **100 nm - 100 microns in diameter**.
- Polycrystals with grains < 10 nm in diameter are **nanocrystalline**
- Examples : Inorganic solids, Most of the metals and Ceramics



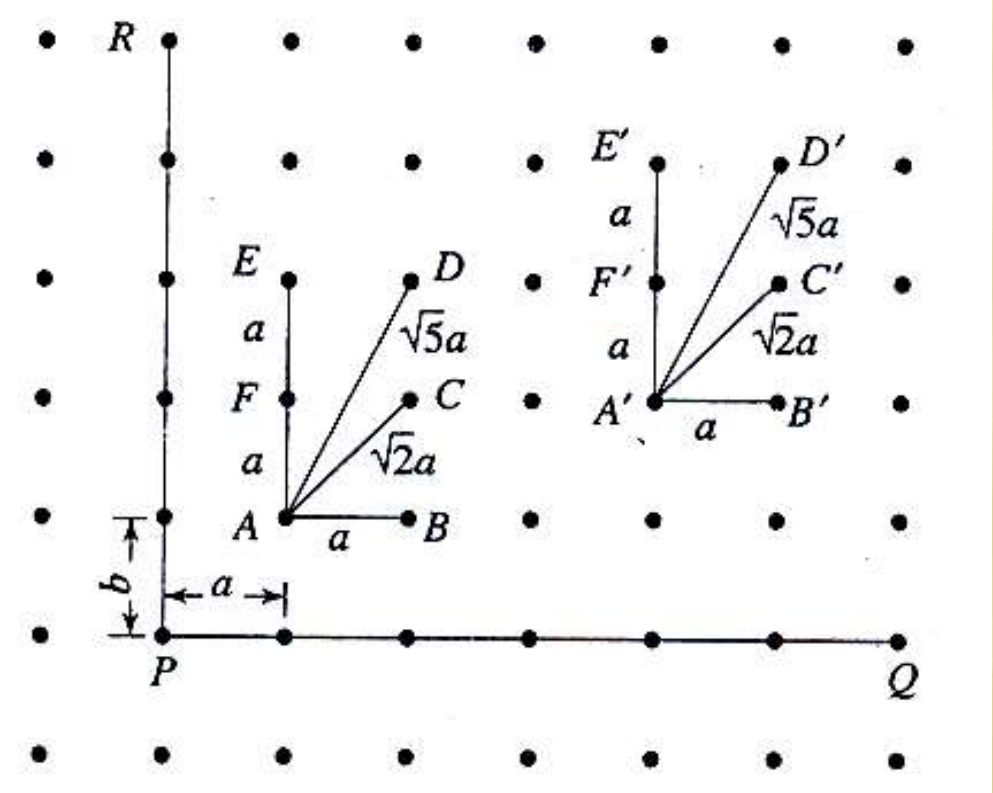


CRYSTALLOGRAPHIC TERMS

- SPACE LATTICE
- LATTICE POINTS
- LATTICE LINES
- LATTICE PLANES
- BASIS or MOTIF
- CRYSTAL STRUCTURE
- UNIT CELL
- LATTICE PARAMETERS

SPACE LATTICE

- regular and periodic arrangement of points in three dimension.
- identical surroundings to that of every other point in the array.

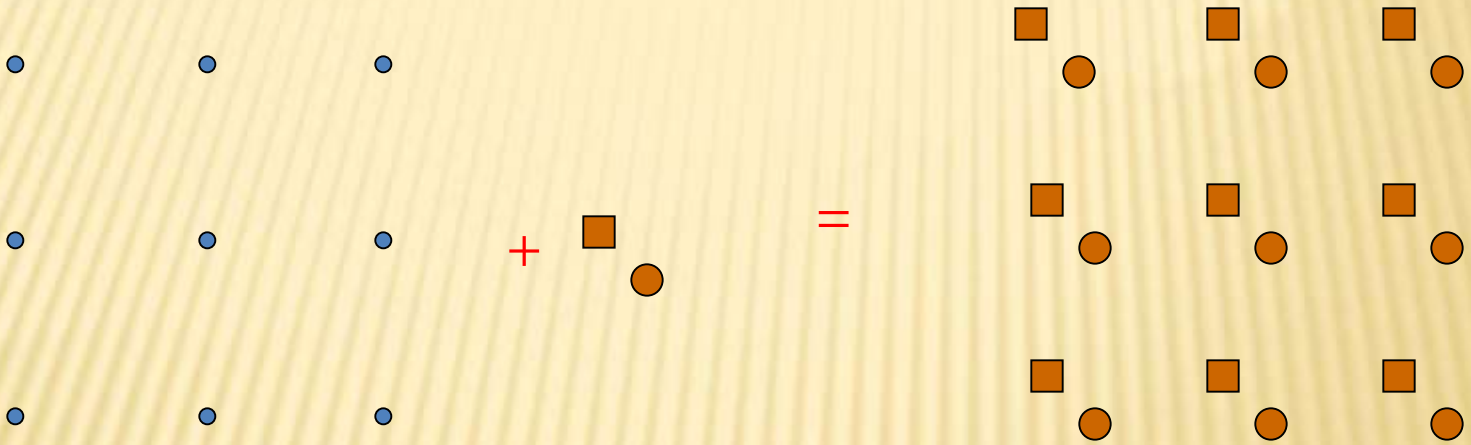


BASIS

- a unit assembly of atoms or molecules identical in composition, arrangement and orientation.
- repeatation of basis correct periodicity in all directions
- The crystal structure is real, while the lattice is imaginary.

Examples	No. of atoms in Basis
Aluminim	01
Barium	01
NaCl	02
KCl	02
CaF_2	03

CRYSTAL STRUCTURE

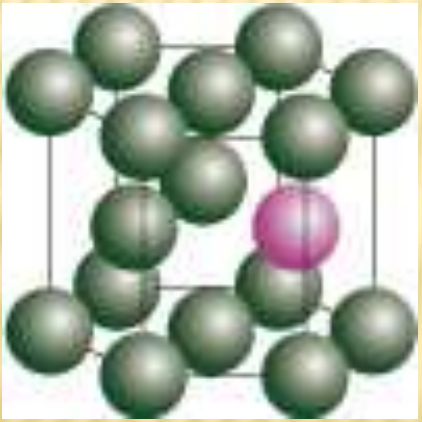


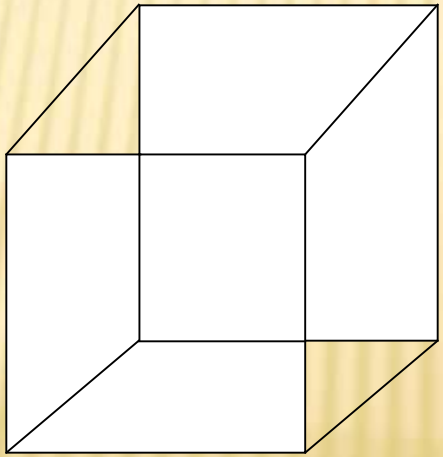
Lattice + Basis = Crystal structure

UNIT CELL

- a fundamental building block

- repeating its own dimensions in various directions gives crystal structure

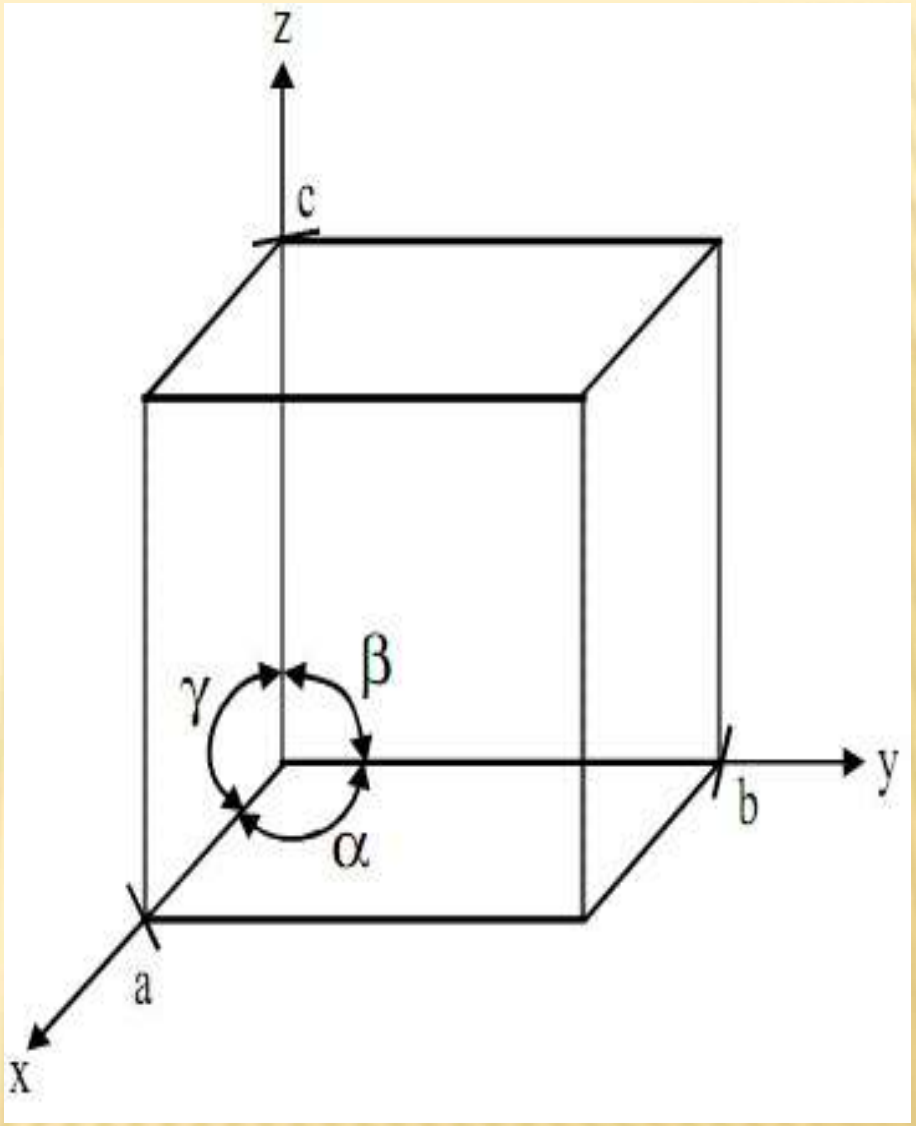




Lattice parameters

x, y and ***z*** *are* crystallographic axes

Length of the unit cell along the *x*, *y*, and *z* direction are ***a, b***, and ***c***



Interaxial angles:

α = the angle between *a* and *b*

β = the angle between *b* and *c*

γ = the angle between *c* and *a*

a, b, c, α, β, γ are collectively known as the **lattice parameters**

PRIMITIVE CELL

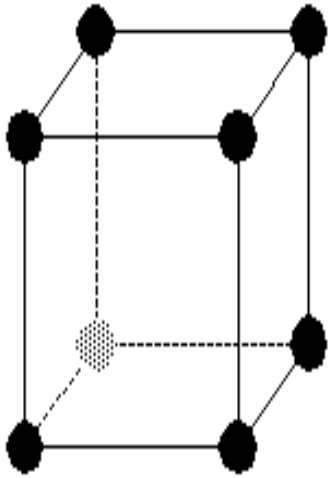
- A unit cell consists of only one full atom
- A primitive cell got the points or atoms only at the corners
- If a unit cell consists more than one atom, then it is not a primitive cell.

- Example for primitive cell :

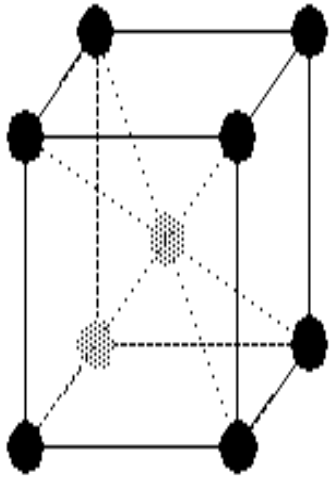
Simple Cubic(SC)

- Examples for non-primitive cell :

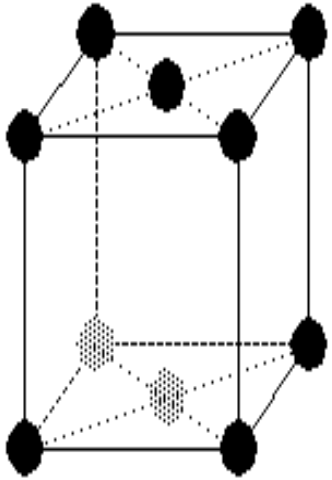
BCC and FCC unit cell.



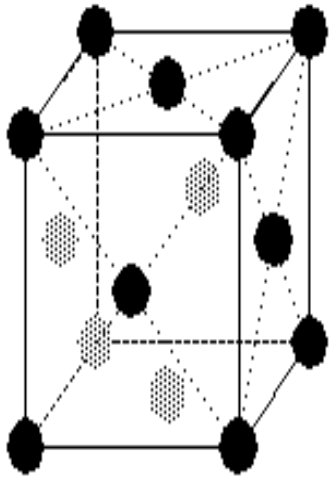
Primitive



Body-Centered (bcc)



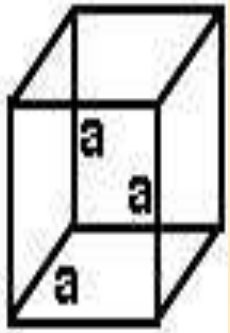
Side-Centered



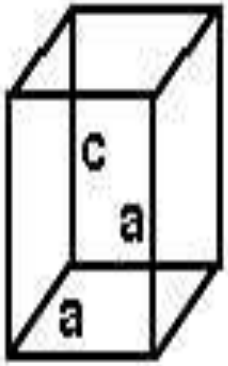
Face-Centered (fcc)

Seven crystal systems

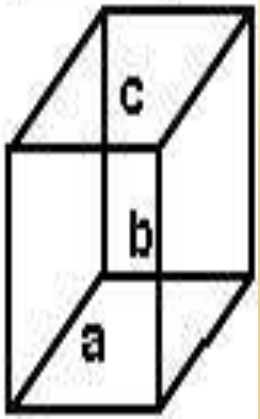
Cubic $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$



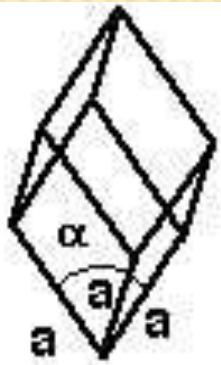
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



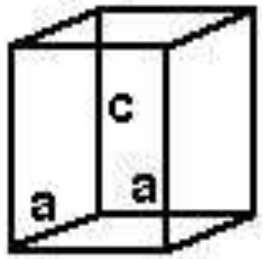
Orthorhombic $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



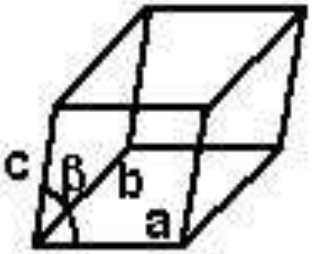
Rhombohedral $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$



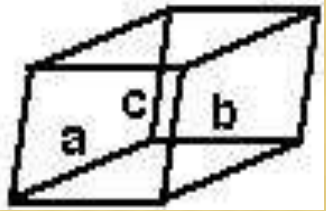
Hexagonal $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$



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



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

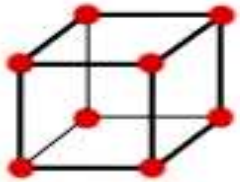


Seven crystal systems and its lattice Parameters

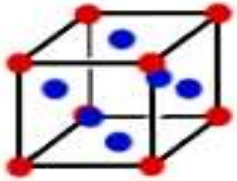
Sr. No.	Crystal System	Axial length of Unit Cell	Inter axial angles	Number of Lattice in the system
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	2
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	4
4	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^0 \neq \gamma$	2
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	1
6	Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^0, \neq 90^0$	1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0$, and $\gamma = 120^0$	1

BRAVAIS LATTICE

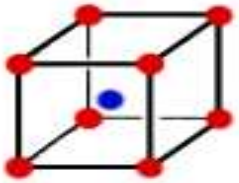
Bravais in 1948 showed that **14 types of unit cells under seven crystal systems** are possible.



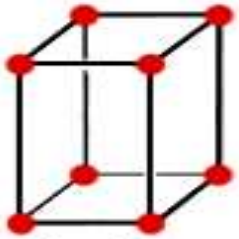
Simple cubic



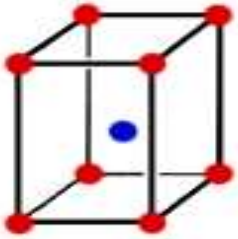
Face-centered cubic



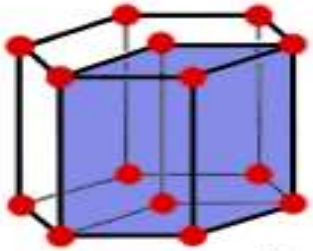
Body-centered cubic



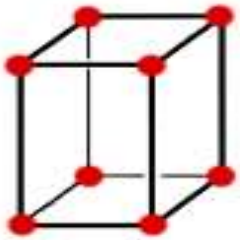
Simple tetragonal



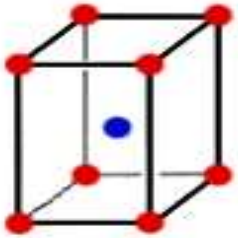
Body-centered tetragonal



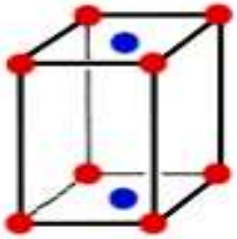
Hexagonal



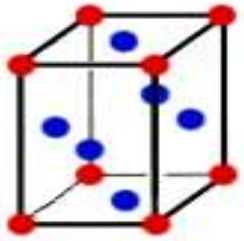
Simple orthorhombic



Body-centered orthorhombic

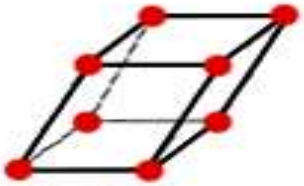


Base-centered orthorhombic

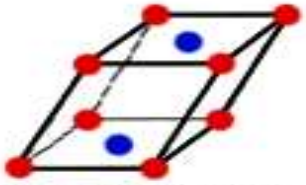


Face-centered orthorhombic

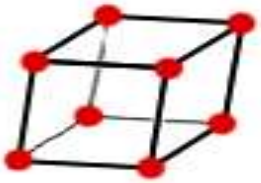
Rhombohedral



Simple Monoclinic



Base-centered monoclinic



Triclinic

14 Bravais Lattices divided into 7 Crystal Systems

	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

Characteristics of unit cell

- **Number of atoms / unit cell**

- **Coordination number**

  No. of equidistant nearest neighbouring atoms to a particular atom

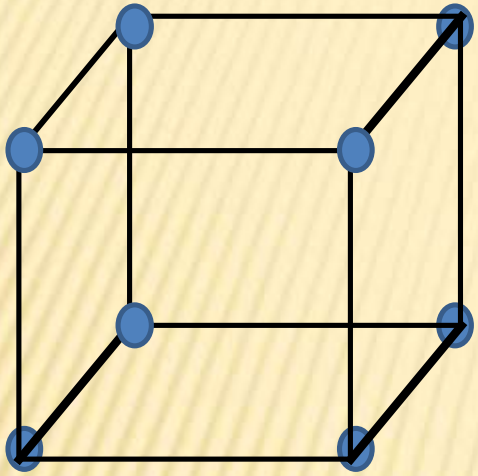
- **Atomic Radius (r)**

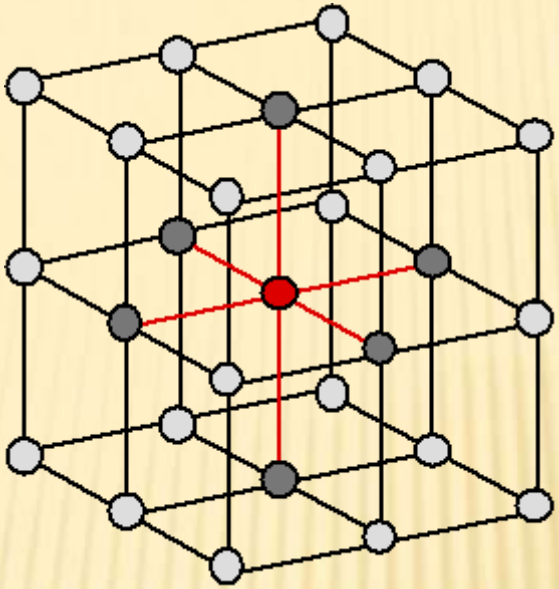
  half the distance between the nearest neighbouring atoms

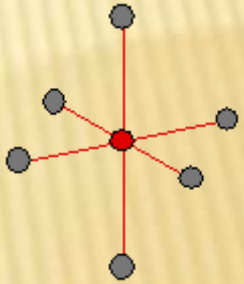
- **Atomic Packing factor or Packing Density**

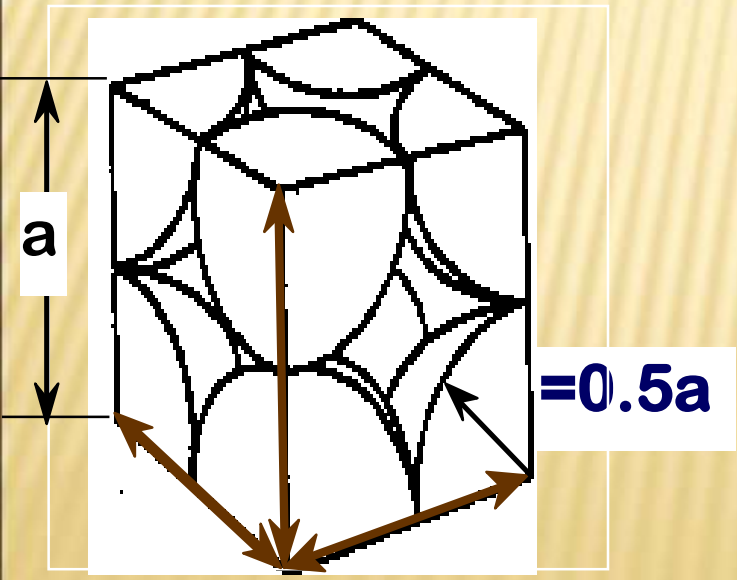
  ratio of the volume occupied by the atoms in an unit cell (v) to the volume of the unit cell (V)

Simple Cubic Structure (SC)



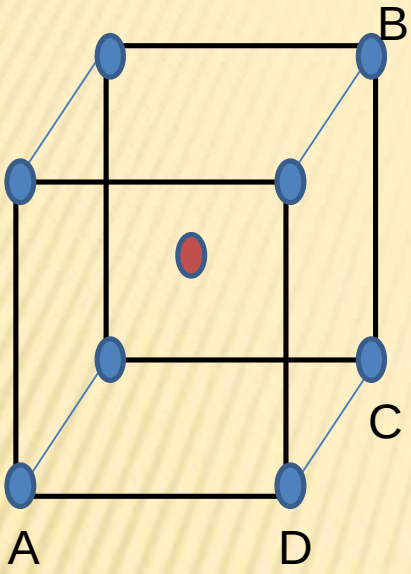


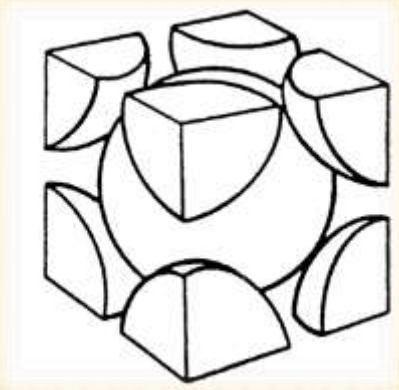


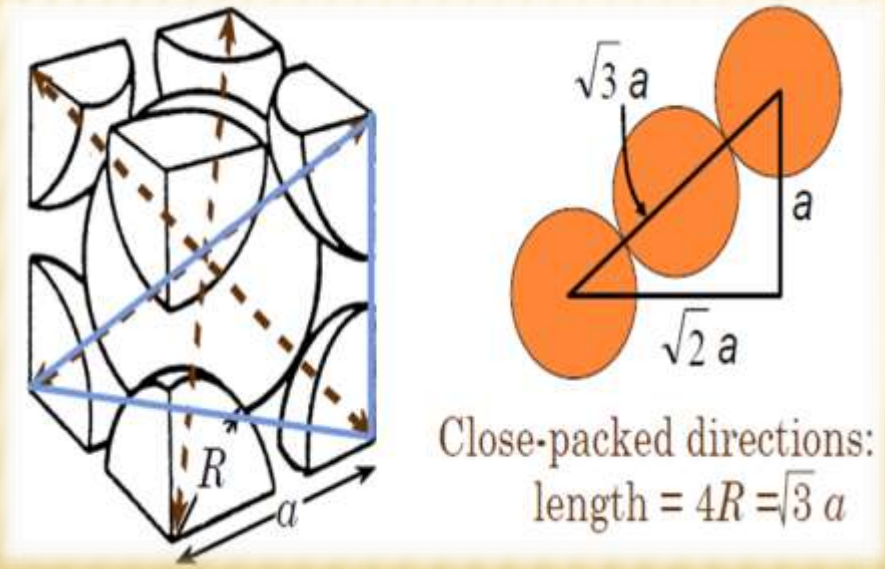


No. of atoms/unit cell	1
Atomic Radius	a/2
Coordination No.	6
APF	0.52

Body Centered Cubic Structure (BCC)

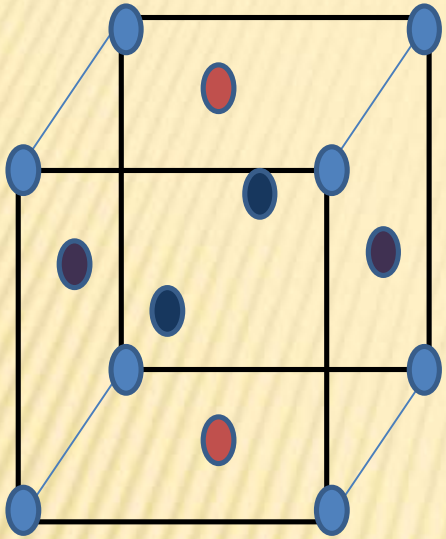


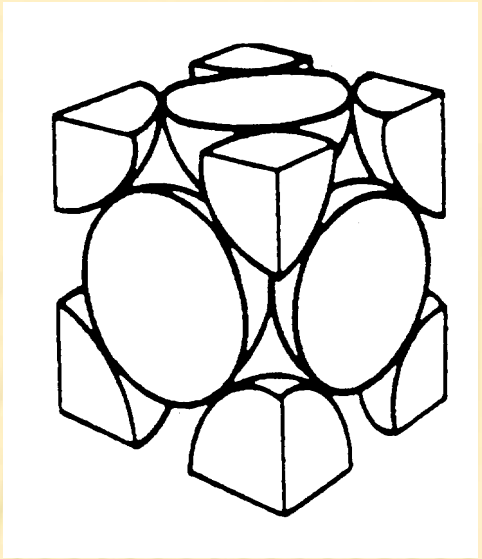


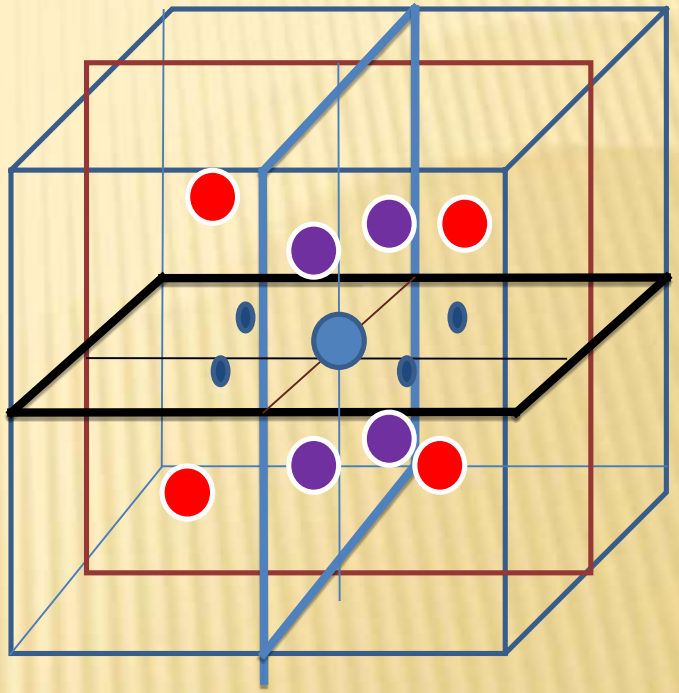


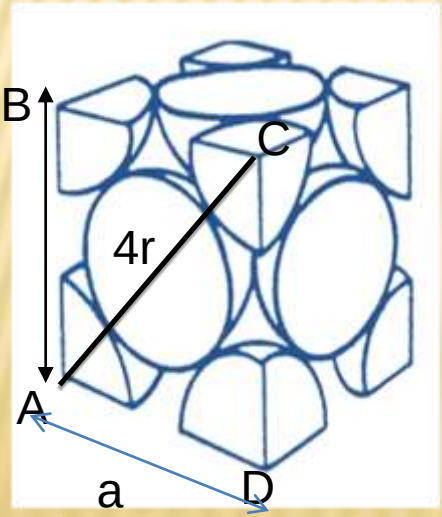
No. of atoms/unit cell	2
Atomic Radius	√3 a/4
Coordination No.	8
APF	√3π/8 or 0.68

Face Centered Cubic Structure (FCC)



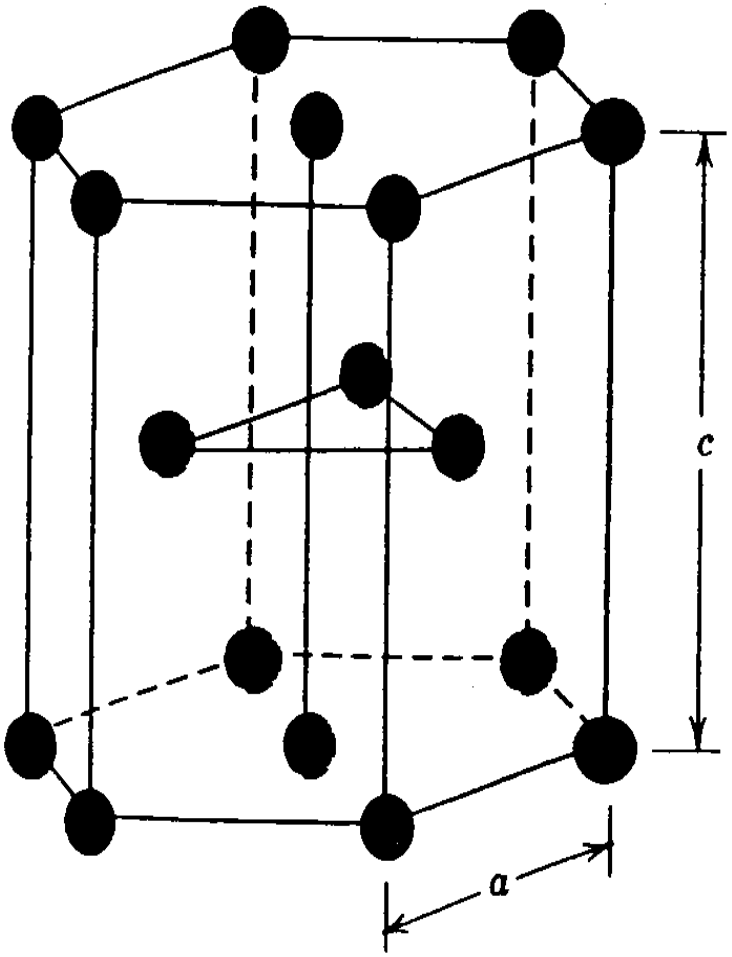




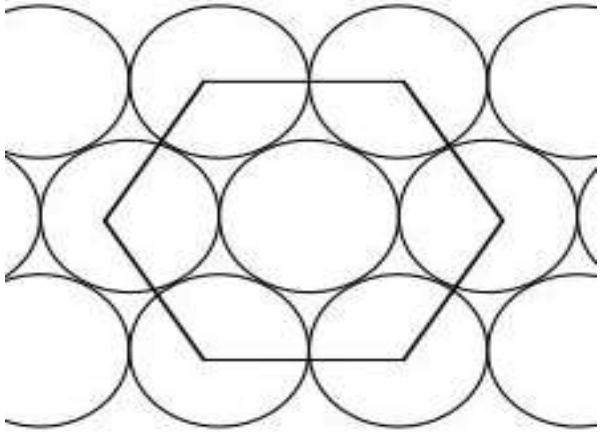


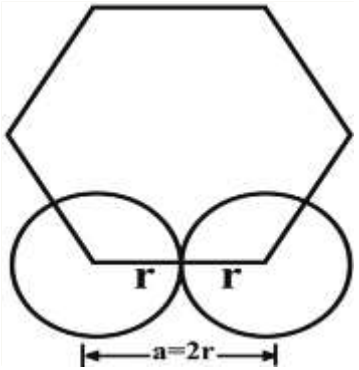
No. of atoms/unit cell	4
Atomic Radius	√2a/4
Coordination No.	12
APF	π /(3√2) or 0.74

HEXAGONAL CLOSED PACKED STRUCTURE

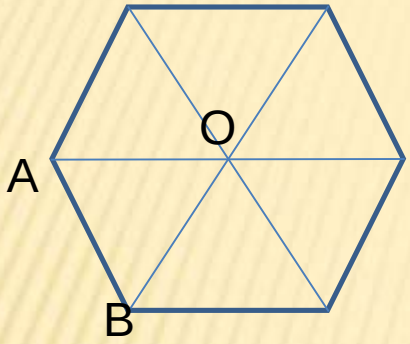


HCP





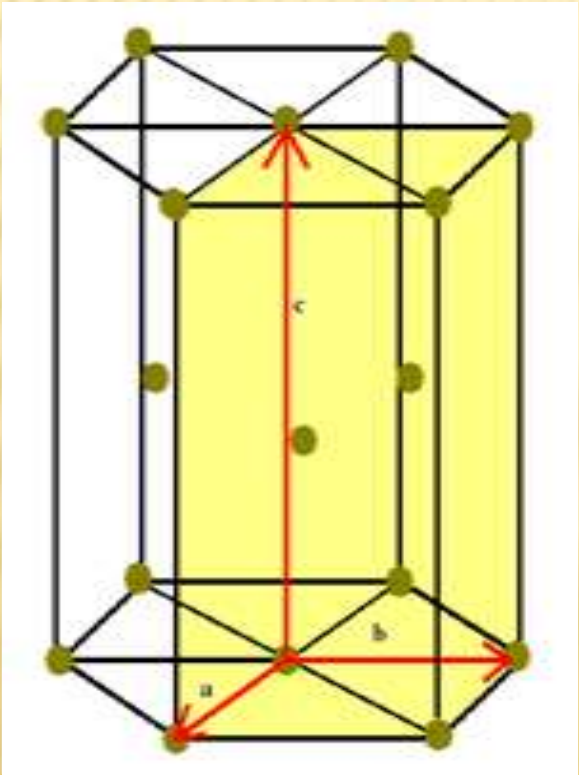
ATOMIC PACKING FACTOR (APF) of HCP



$$\text{Area of an equilateral triangle} = \frac{\sqrt{3}a^2}{4}$$

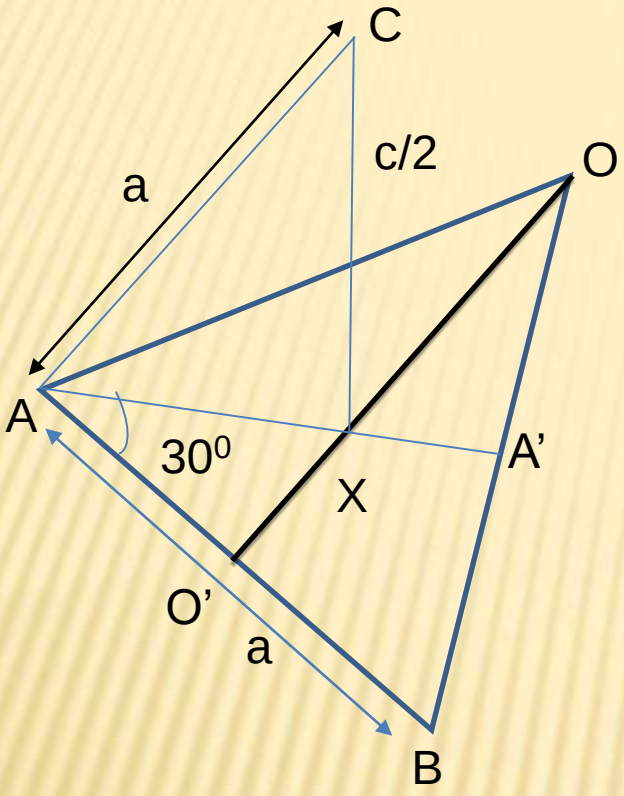
$$\text{Volume of HCP} = \text{Area of base} \times \text{height}$$

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



No. of atoms/unit cell	6
Atomic Radius	a/2
Coordination No.	12
APF	$\pi / (3\sqrt{2})$ or 0.74

C/a Ratio



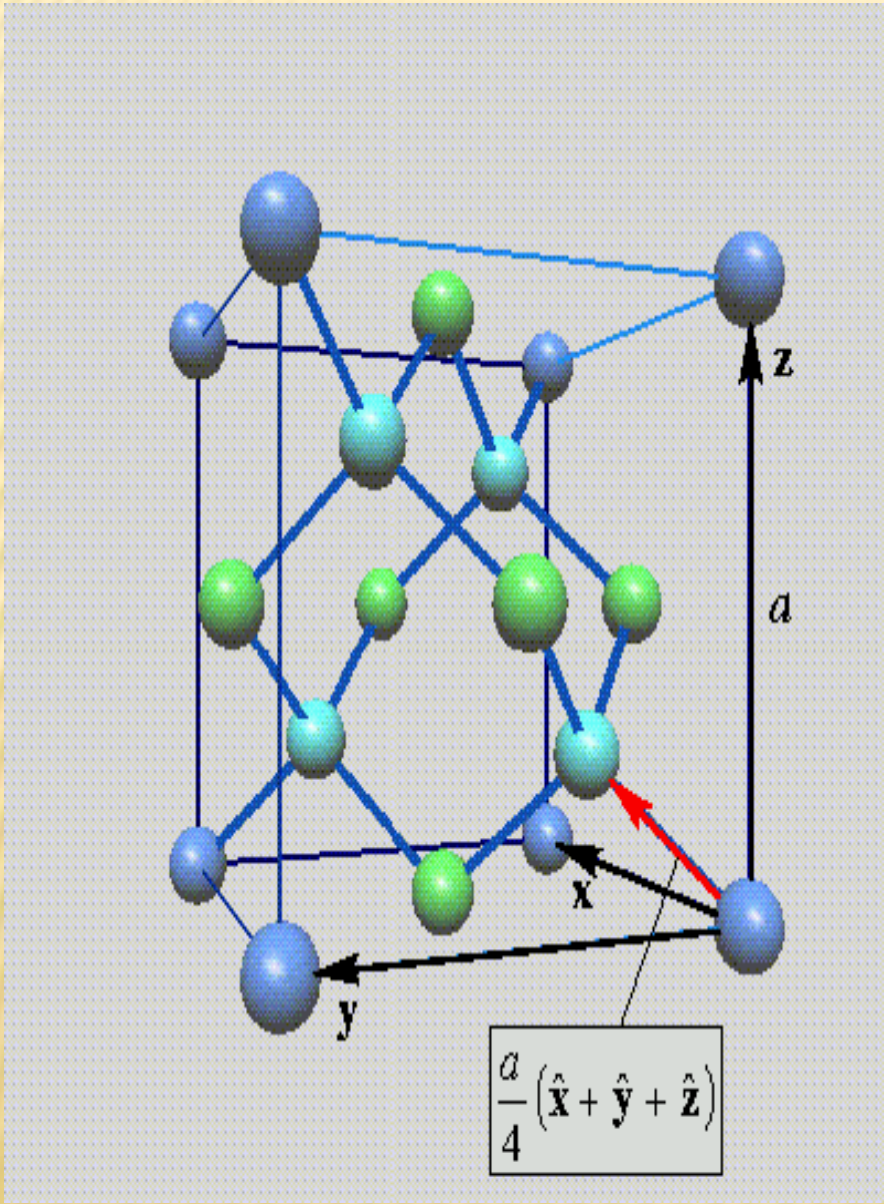
In the triangle AXC,

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

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

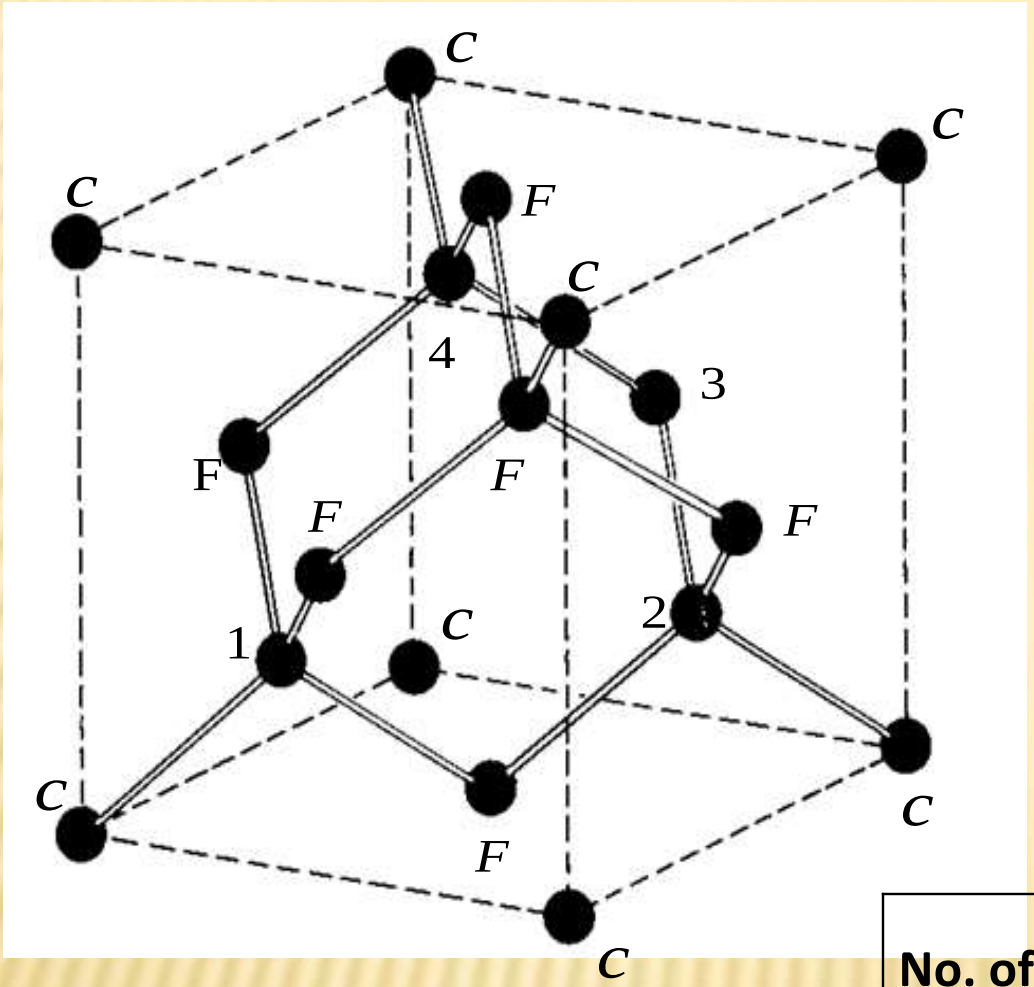
$$\frac{c}{a} = \sqrt{\frac{8}{3}}$$

Diamond Lattice Structure



- Formed by the combination of two interpenetrating FCC lattices.
- The two sub-lattices , *X and Y are* at (0,0,0) and *(a/4, a/4, a/4).*

Ex: Germanium, Silicon, Diamond



No. of atoms/unit cell	8
Atomic Radius	√3a/8
Coordination No.	4
APF	$\pi\sqrt{3}/16$ or 0.34

POLYMORPHISM & ALLOTROPHY

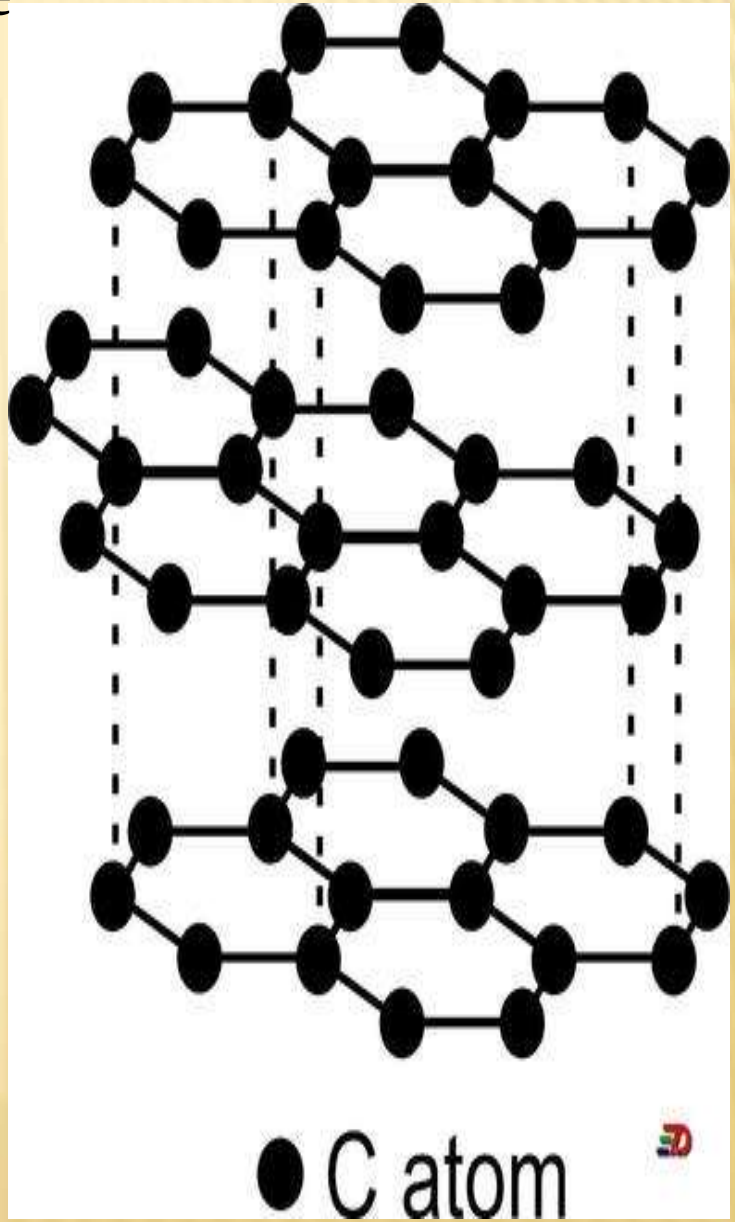
POLYMORPHISM - Ability of material to have more than one structure

ALLOTROPHY - 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
- covalently bonded with other carbons
- sheets are held together by vander waals forces
- weak bonding between sheets give softness
- Delocalized electrons



Physical properties of diamond and Graphite

S.No	Diamond	Graphite
1	high melting point (almost 4000°C).	high melting point
2	very hard	soft, slippery feel, and is used in pencils
3	does not conduct electricity.	Conducts electricity.
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	covalently bonded	covalently bonded in same plane and sheets are held together by Van der waals bonds

MILLER INDICES

- set of three possible integers represented as (h k l)
- reciprocals of the intercepts made by the plane on the three crystallographic axes
- designate plane in the crystal.

Procedure for finding Miller Indices

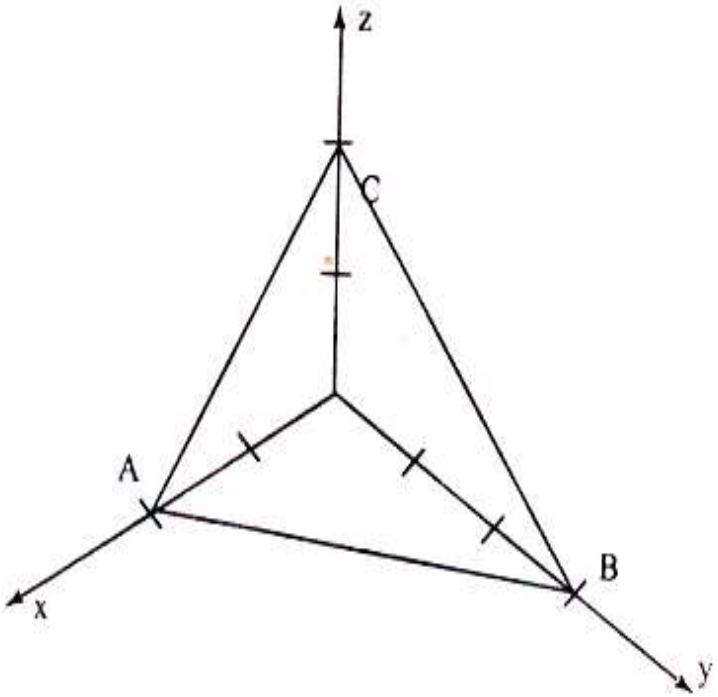
- **Step 1 :** Determine the intercepts of the plane along the axes
- **Step 2 :** Determine the reciprocals of these numbers.
- **Step 3 :** Find the ***LCD*** and multiply each by this *LCD*
- **Step 4 :** Write it in paranthesis in the form (h k l).

ILLUSTRATION

Step 1 : intercepts - **2a,3b and 2c**

Step 2 : reciprocals - **1/2, 1/3 and 1/2.**

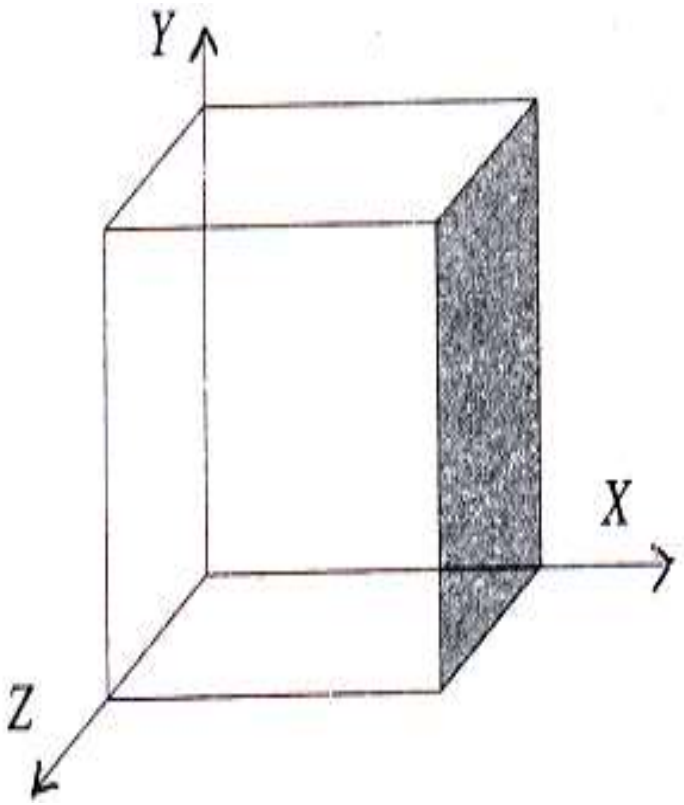
Step 3 : **LCD** is ‘6’.
Multiply each reciprocal by lcd,
we get, **3,2 and 3**.



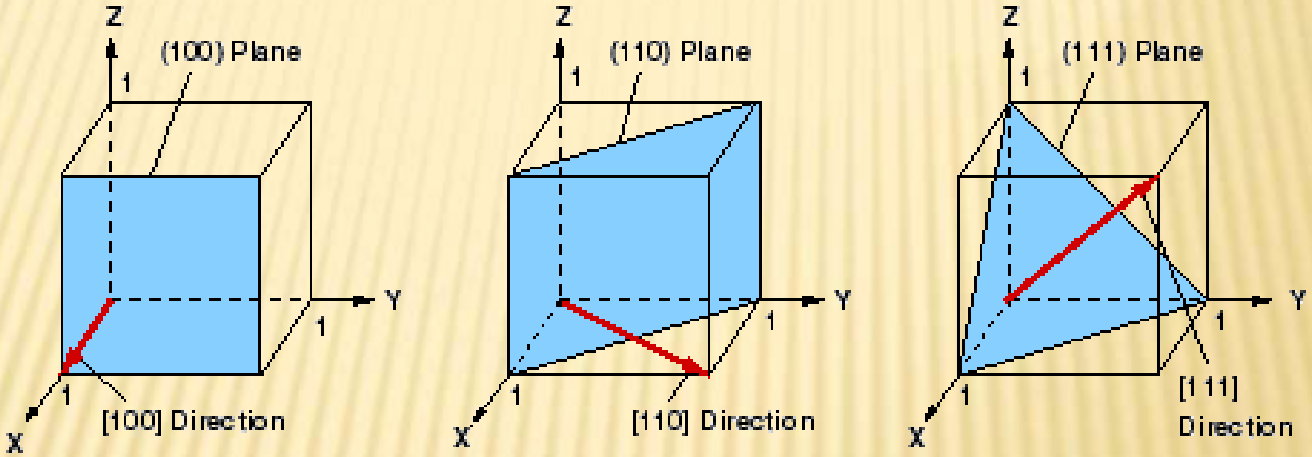
Step 4 : Miller indices for the plane
ABC is **(3 2 3)**

EXAMPLE

- intercepts are **1, ∞ and ∞.**
- reciprocals of the intercepts are **1/1, 1/∞ and 1/∞.**
- Miller indices for the plane is **(1 0 0).**



MILLER INDICES OF SOME IMPORTANT PLANES



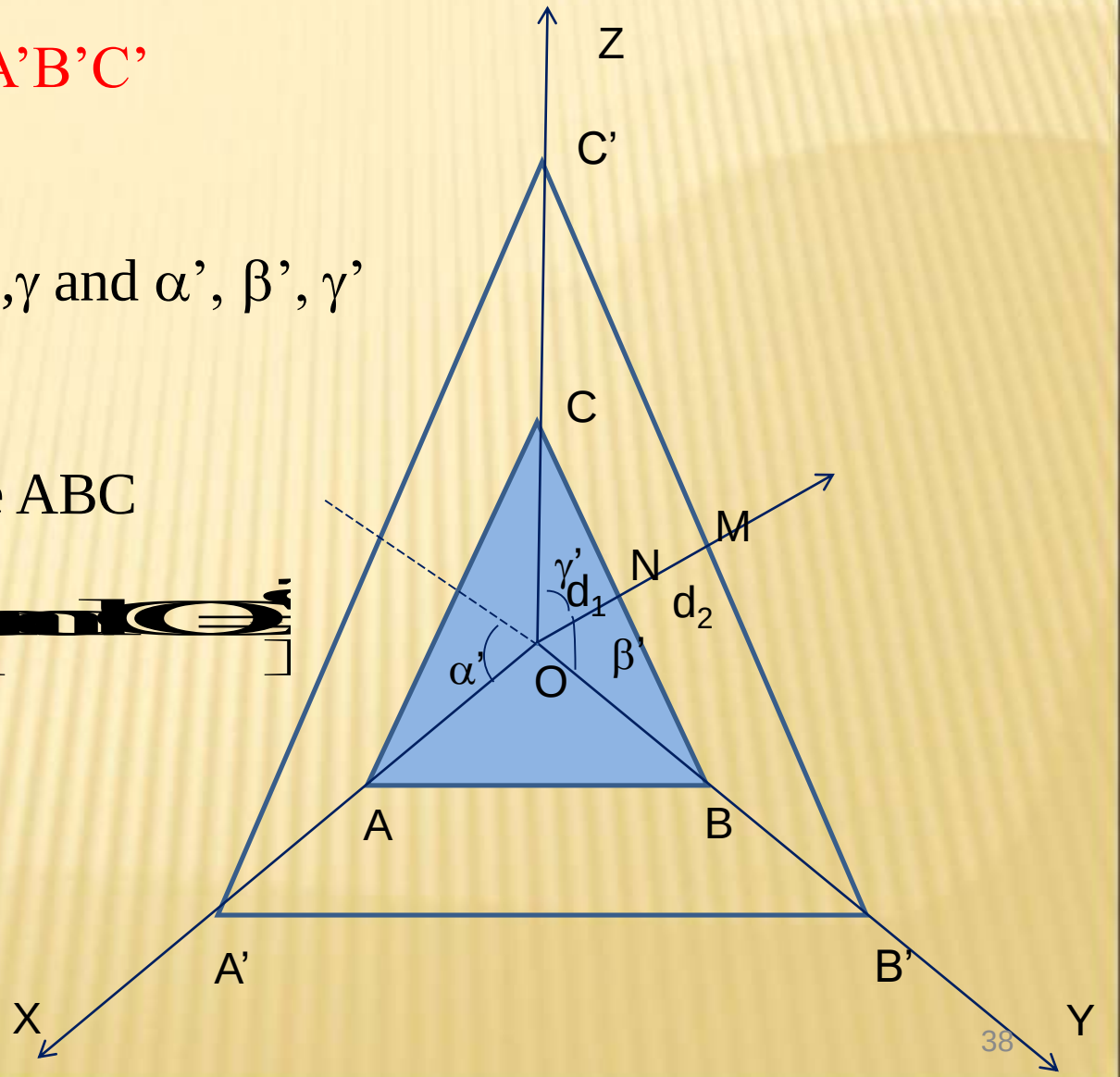
IMPORTANT FEATURES OF MILLER INDICES

- a plane parallel to the axes has an intercept of infinity (∞).
- a plane cuts an axis on the negative side of the origin, is represented by a bar, as ($\bar{1}$ 0 0).
- a plane passing through the origin have non zero intercepts
- All equally spaced parallel planes have same Miller indices

INTERPLANAR DISTANCE *or* d-Spacing

- Two planes ABC and A'B'C'
- Interfacial angles α, β, γ and α', β', γ'
- Intercepts of the plane ABC

$$\frac{a}{h} = \frac{a}{k} = \frac{a}{l}$$



From the property of direction of cosines, $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

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

Similarly , for the plane A'B'C'

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

Interplanar spacing

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

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 = $\rho\ a^3$

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

Number of atoms per unit cell = n

Atomic weight of the material = M

Avogadro's number = N

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

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

$= \frac{M}{N} \times n$ (for n atoms per unit cell)

$\rho\ a^3 = \frac{M}{N} \times n$

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

Types of bonding:

A. Primary bonding or chemical bonding
This bonding is found in solids and involves the valence electrons.
This type of bonding is strong (» 100 kJ/mol)
Examples: ionic, covalent, and metallic bonds

B. Secondary bonding or physical bonding or van der Waals
This bonding is found in most solids and arises from atomic or molecular dipoles.
This type of bonding is weak (≅ 10kJ/mol)
Examples: fluctuating induced dipole bonds, polar molecule-Induced dipole bonds, and pemanent dipole bonds

A. Primary bonding or chemical bonding

Ionic bonding

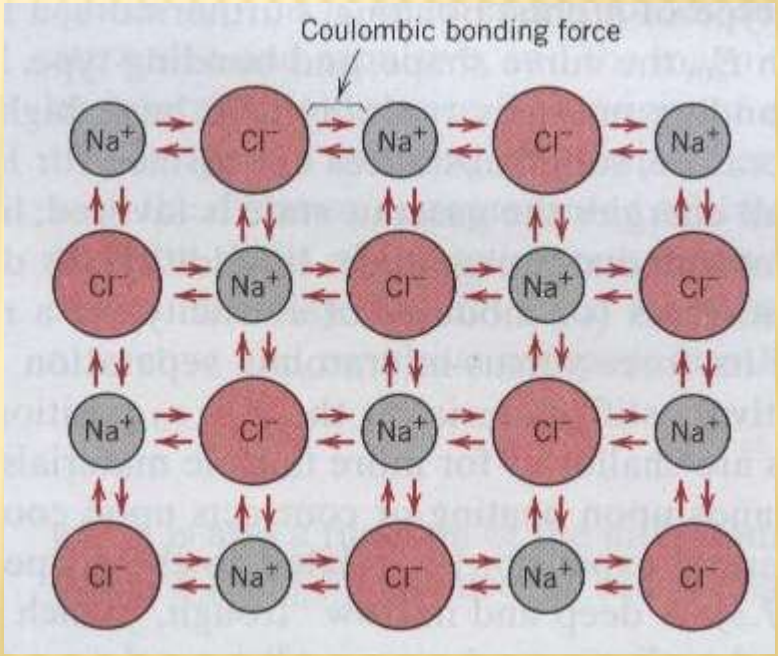
It is always found in compounds that are composed of both metallic and nonmetallic elements. Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms.
This bonding is a nondirectional bonding, the magnitude of the bond is equal in all directions around an ion.

Coulombic bonding force

Attractive energy: $E_A = -\frac{A}{r}$

Repulsive energy: $E_B = \frac{B}{r^n}$

A, B, n = constants,
n ~ 8



Callister Jr, W.D., 2005

A. Primary bonding or chemical bonding

Covalent bonding

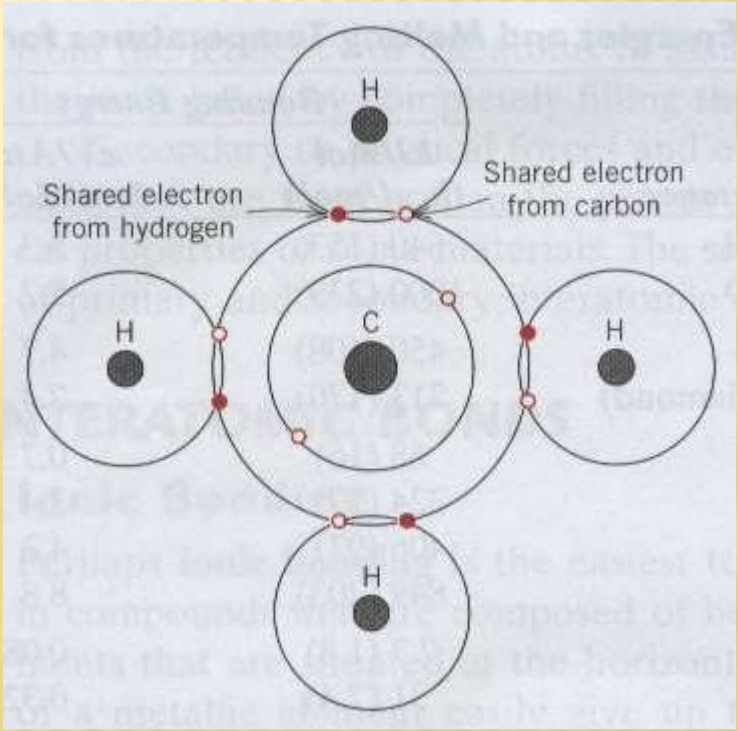
It is usually found in many nonmetallic elemental molecules (H_2, Cl_2, F_2) and molecules containing dissimilar atoms (CH_4, H_20, HNO_3, HF)
This bonding is formed on stable electron configurations by sharing of electrons between adjacent atoms.

A very strong covalent bond

Diamond with a very high melting temperature
(713 kJ/mol; 3550 ºC)

A very weak covalent bond

Bismuth with a very low melting temperature
(270 ºC)



Callister Jr, W.D., 2005

A. Primary bonding or chemical bonding

Metallic bonding

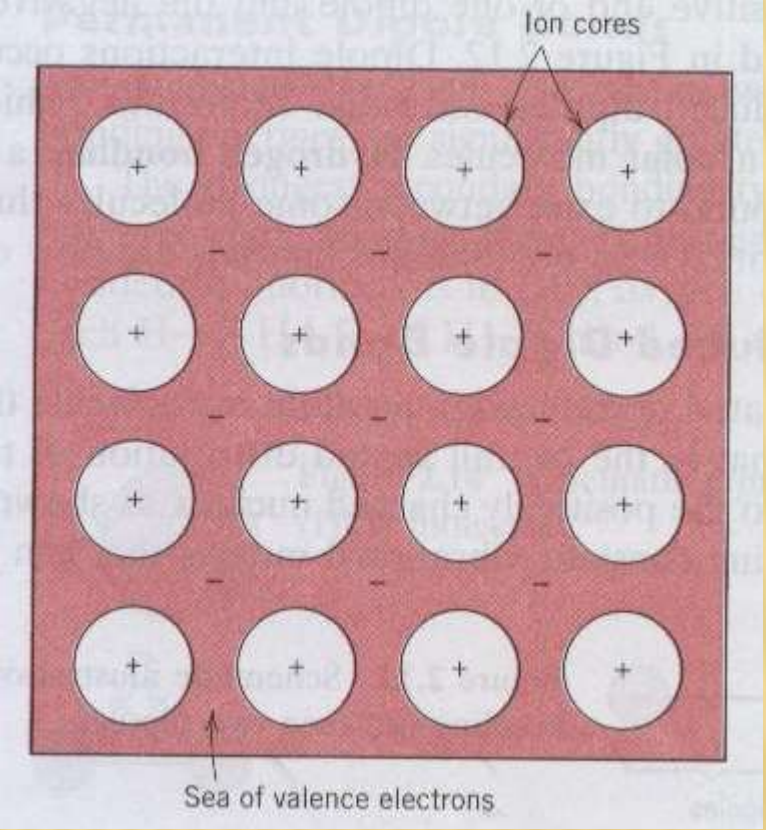
It is found in many metals and their alloys (group IA and IIA).
Metallic materials have 1, 2 or at most 3 valence electrons.
These valence electrons are not bound to any particular atom to any Particular atom in the solid and are free to drift throughout the entire metal.

→ "sea of electrons"
or "electron cloud"
Net negative charge

Ion cores
Net positive charge

Weak metallic bond
Hg (68 kJ/mol; -39 ºC)

Strong metallic bond
W (850 kJ/mol; 3410 ºC)

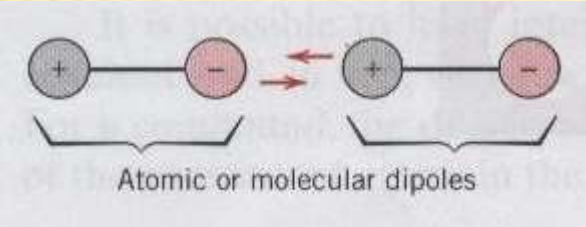


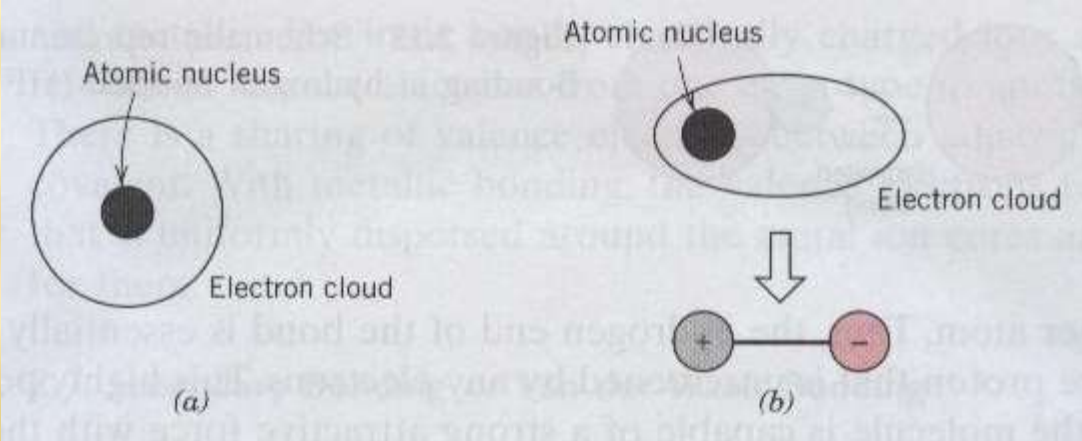
Callister Jr, W.D., 2005

B. Secondary bonding or physical bonding or van der Waals

Fluctuating induced dipole bonds

All atoms have constant vibrational motion and it causes electrical symmetry and creates small electric dipoles

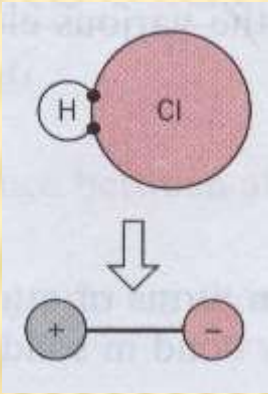




B. Secondary bonding or physical bonding or van der Waals

Polar molecule-induced dipole bonds

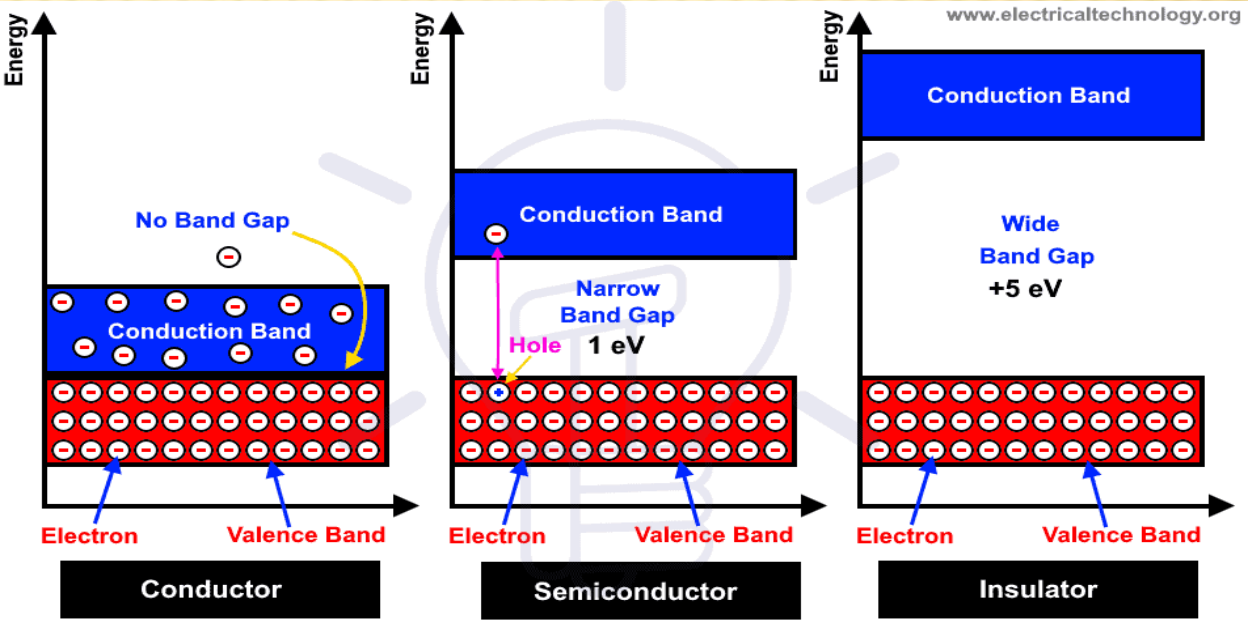
It causes by virtue of an asymmetrical arrangement of positively and negatively charged regions



Callister Jr, W.D., 2005

Types of electronic materials: conductors, semiconductors, and insulators

- Conductors- Overlap of the valence band and the conduction band so that at the valence electrons can move through the material.
- Insulators- Large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band).
- Semiconductors- Have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1 eV) separating the two



Types of X-rays

There are two types of X-ray spectrum:

•**Continuous -** when high-speed electrons collide with a high-atomic-number target material, X-rays are created. The majority of the energy of the electrons is used to heat the target material in the creation of X-rays.A few fast-moving electrons penetrate deep into the interior of the target material's atoms and are drawn to their nuclei by their nuclei's attraction forces. The electrons are thrown from their initial route due to these forces. As a result, electrons slow down, and their energy reduces over time. The X-rays have a continuous frequency range up to a maximum frequency max or a minimum wavelength min. This is called Continuous X-rays. The minimum wavelength depends on the anode voltage. If *V* is the potential difference between the anode and the cathode

$eV = hv_{max} = hc / \lambda_{min}$

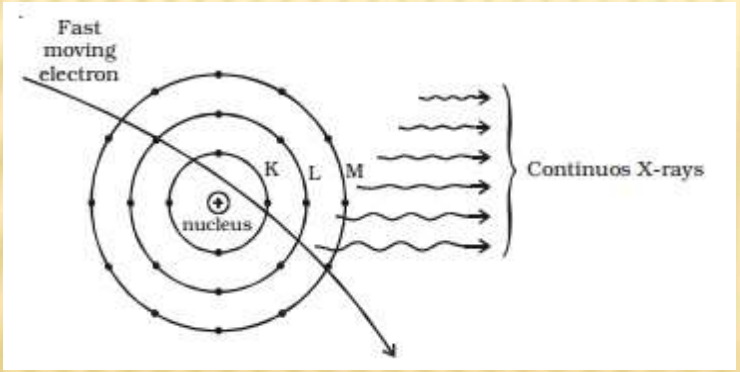
The minimum wavelength of the given radiation is,

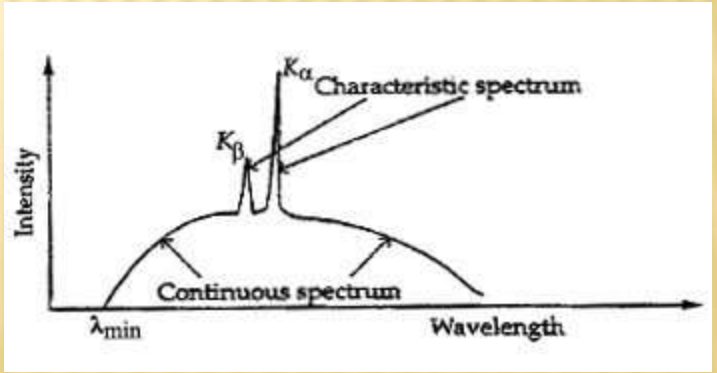
$\lambda_{min} = hc / eV$

where h is Planck's constant, c is the velocity of light and e, the charge of the electron. Substituting the known values in the above equation.

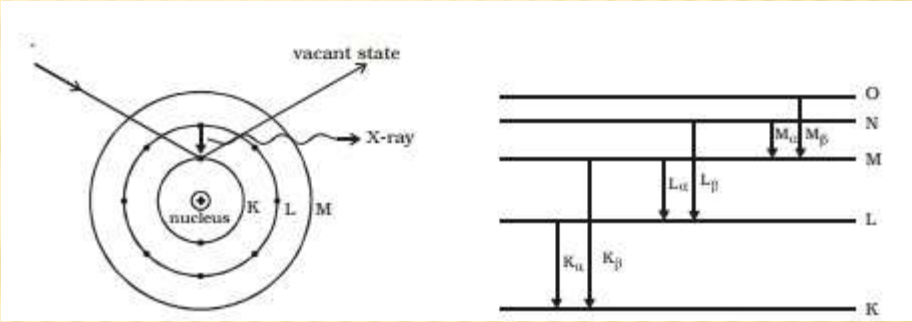
$\lambda_{min} = 12400/V$ A0

For the given operating voltage, the minimum wavelength is the same for all metals.



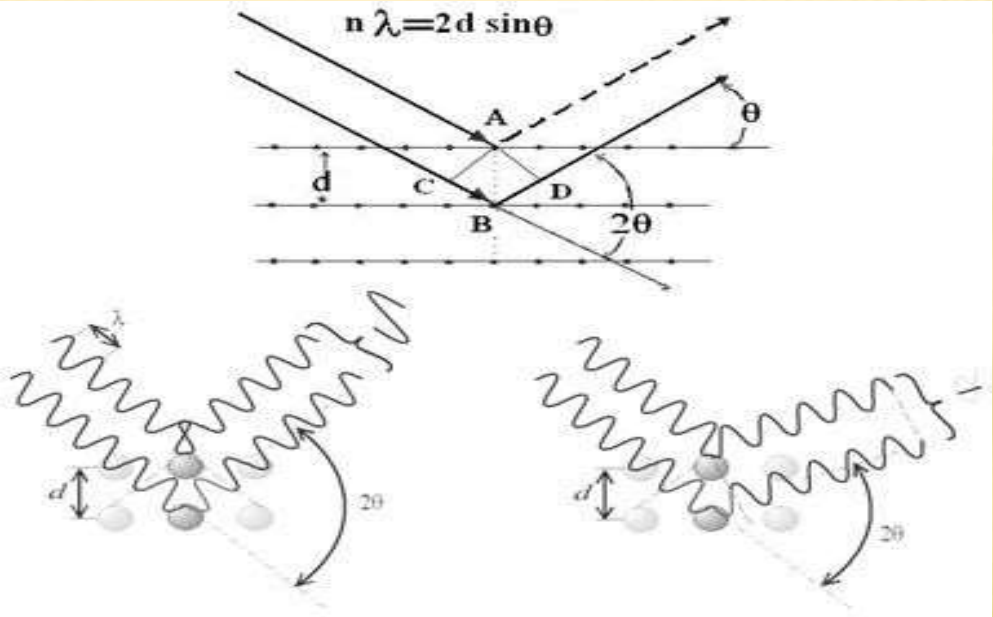


•**Characteristic X-ray -** Characteristic radiation is a sort of energy emission that is important in the creation of X-rays. When a fast-moving electron collides with a K-shell electron, the electron in the K-shell is ejected (if the incident electron's energy is larger than the K-shell electron's binding energy), leaving a 'hole' behind. An outer shell electron fills this hole (from the L-shell, M-shell, and so on) with the emission of a single X-ray photon with an energy level equal to the energy level difference between the outer and inner shell electrons engaged in the transition.



Bragg's Law:

Consider a set of parallel planes called Bragg's planes. Each atom is acting as a scattering center. The intensity of the reflected beam at certain angles will be



maximum when the path difference between two reflected waves from two adjacent planes is an integral multiple of λ.

Let'd' be the distance between two adjacent planes, 'λ' be the wavelength of the incident x-ray, 'θ' be the glancing angle. The path difference between the rays reflected at A & B is given by

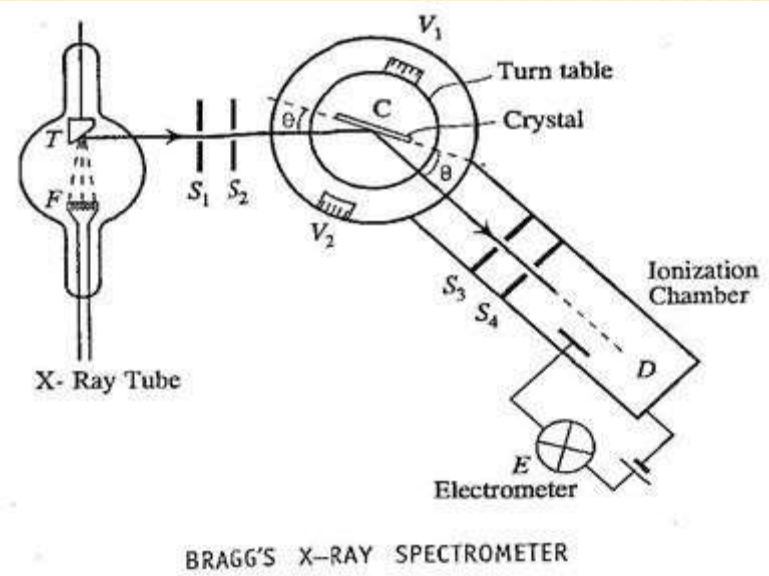
= CB + BD

= d sinθ + d sinθ = 2dsinθ

For the reflected light intensity to be maximum, the path difference 2dsinθ = nλ, where 'n' is the order of scattering. This is called Bragg's law.

Bragg's x-ray spectrometer:

The schematic diagram of Bragg's x-ray spectrometer is shown in fig. It is used to determine lattice constant and inter-planar distance'd'. It has 1) x-ray source 2) A Crystal fixed on a circular table provided with scale and vernier. 3) Ionization chamber.

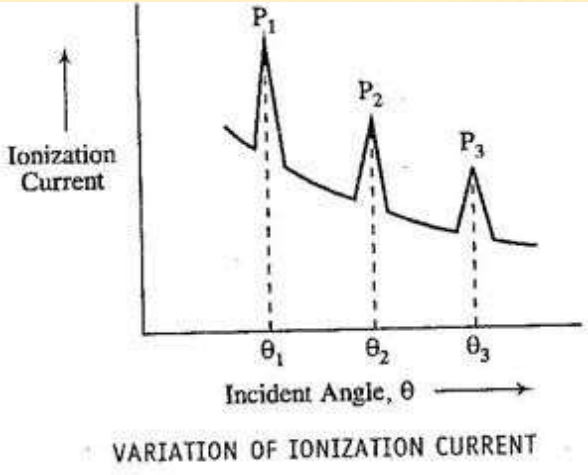


BRAGG'S X–RAY SPECTROMETER

A collimated beam of x-rays after passing the slits S_1 and S_2 is allowed to fall on a crystal C mounted on a circular table. The table can be rotated about vertical axis. Its position can be measured by vernier V_1. An ionization chamber is fixed to the longer arm attached to the table. The position of which is measured by vernier v_2. An electrometer is connected to the ionization chamber to measure the ionization current produced by diffracted x-rays from the crystal. S_3 and S_4 are the lead slits to limit the width of the diffracted beam. Here we can measure the intensity of the diffracted beam.

If x-rays incident at an angle ‘θ’ on the crystal, then reflected beam makes an angle 2θ with the incident beam. Hence the ionization chamber can be adjusted to get the reflected beam till the ionization current becomes maximum.

A plot of ionization current for different incident angles to study the x-ray diffraction spectrum is shown in fig.



VARIATION OF IONIZATION CURRENT

The rise in Ionization current for different values of ‘θ’ shows that Bragg’s law is satisfied for various values of ‘n’. i.e. $2d\sin\theta = \lambda$ or 2λ or 3λ etc. Peaks are observed at θ_1, θ_2, θ_3 etc. with intensities of P_1, P_2,P_3 etc.

i.e. $2d\sin\theta_1 : 2d\sin\theta_2 : 2d\sin\theta_3 = \lambda : 2\lambda : 3\lambda$