

Material Science and Engg.-BME303

Crystal Structure

Module-1

Structure of Materials

Introduction: Classification of materials, crystalline and non-crystalline solids, atomic bonding: Ionic Bonding and Metallic Bonding.

Crystal Structure: Crystal Lattice, Unit Cell, Planes and directions in a lattice, Planar Atomic Density, Coordination number, atomic Packing Factor of all the Cubic structures and Hexagonal Close Packed structure. Classification and Coordination of voids, Bragg's Law.

Imperfections in Solids: Types of imperfections, Point defects: vacancies, interstitials, line defects, 2-D and 3D-defects, Concept of free volume in amorphous solids. Slip, Twinning.

Material Science is primarily concerned with the search for basic knowledge about processing of materials.

Materials engineering is mainly concerned with the use of fundamental and applied knowledge of materials so that the materials can be converted into products necessary or desired by the Society.

There are several ways of classifying engineering materials. One way of classifying them is into five groups.

1. Metallic materials. *Example: steels, Cast irons, Al, copper, silver gold, brass Bronzes etc.*

2. Polymeric materials. *Examples: Plastics, Polyethylene, PVC, Nylon etc.*

3. Ceramic materials. *Examples: MgO, ZnO, SiC, Silica, Nitrides, etc.*

4. Composite materials. *Examples: PMC, MMC and CMC etc.,*

5. Electronic materials. *Examples: Semiconductors*

Materials science restricts itself to solid materials, which help engineers to build machines, structures, automobiles, electronic gadgets and a wide variety of other products useful to mankind.

Solid materials may be broadly classified into two groups based on the regularity with which atoms or molecules are arranged with respect to one another.

1. Crystalline solids

2. Amorphous solids

These two types of solids are based on their structural units which make up their building blocks.

Crystalline solids

The basic structural unit is a crystal and a number of crystals come together to form a crystalline solid. Each of these crystals contain a number of repetitive blocks called unit cells which are arranged neatly in an order.

Density of crystalline solids are generally high since unit cells can be packed in an orderly manner in a given unit space.

Their structure is stable and materials are stronger. They also have higher melting point and strength.

Examples: metals, alloys, some salts like NaCl, KCl, many oxides, ceramics etc.

Amorphous Solids

In amorphous solids- the basic structural unit here is a molecule and chains of these molecules come together to form an amorphous solid. These chains of molecules are random within the solid and occur in no particular order.

They are irregular and lack of symmetry unlike crystalline solids. Density of amorphous solids is low and their structure is unstable.

Examples: Glass, polymers, elastomers (Rubber).

Although all materials can be classified as either crystalline or non-crystalline, there are certain materials which can occur as both.

Example: Silicate can occur as crystalline solid (quartz) or as a non-crystalline solid as (silicate glass).

Crystal Structure

Unit Cell:

Unit cell is a smallest repeatable unit of a crystalline solid.

In other words, every unit cell in a crystalline solid consists of a group of atoms arranged in a definite order. The shape of the unit cell and the atomic arrangements within them can themselves be of different types.

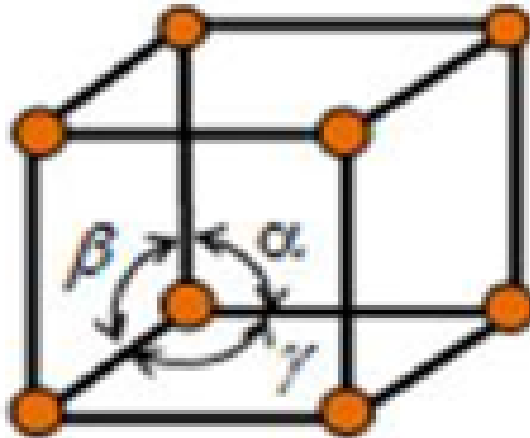
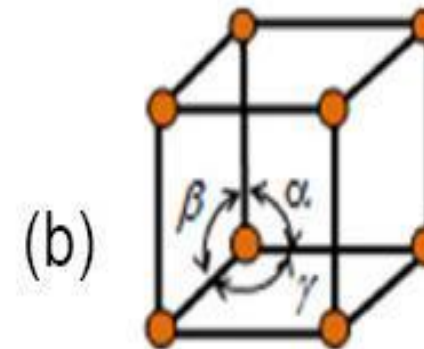
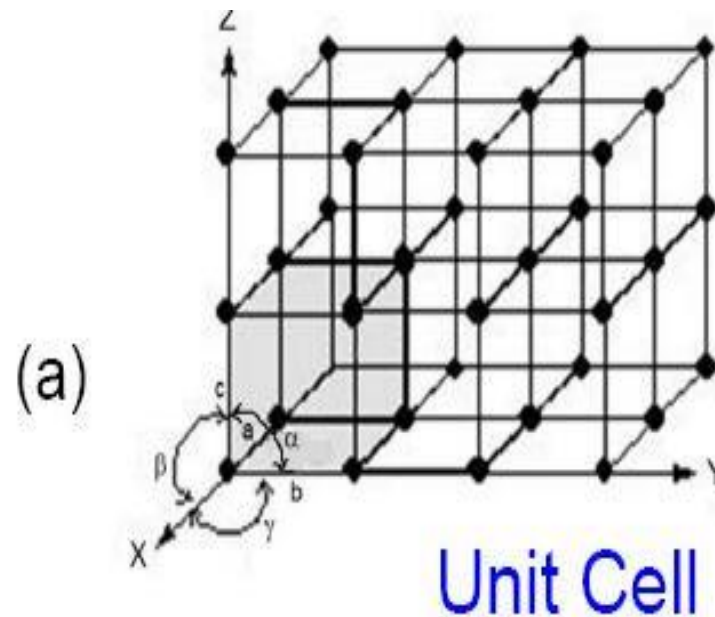
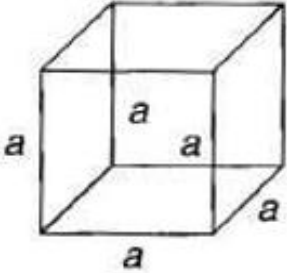
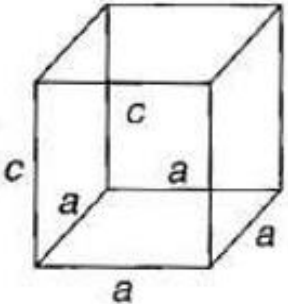
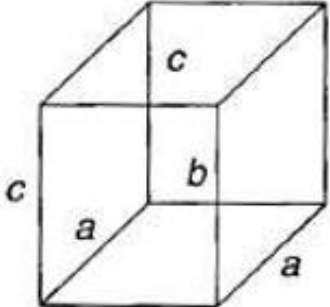


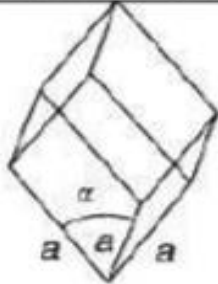
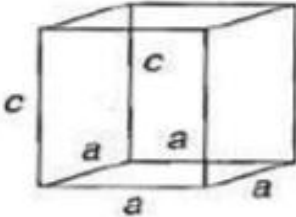
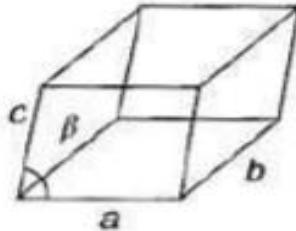
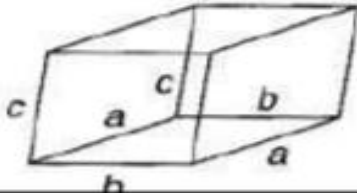
Fig.(a) This cell is known as unit cell (Fig. b) which when repeated in the three dimensions generates the crystal structure.

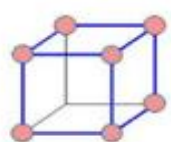


Space lattice

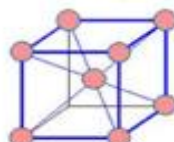
- A space lattice can be defined as a three-dimensional array of points, each of which has identical surroundings.
- There are 14 possible types of space lattices are called “Bravias” space lattices they fall under 7 crystal systems.

System	Lattice constants and angles	Unit cell geometry
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	

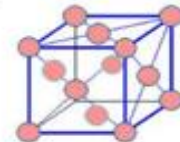
System	Axial lengths and angles	Unit cell geometry
Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \neq \beta$	
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	



Simple cubic

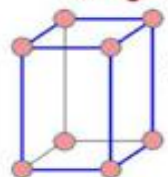


Body-centered cubic (BCC)

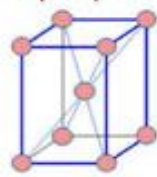


Face-centered cubic (FCC)

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

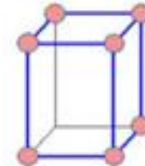


Simple Tetragonal

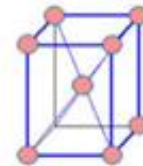


Body-centered Tetragonal (BCT)

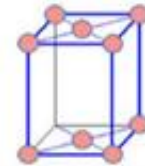
Orthorhombic: $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



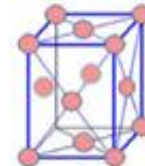
Simple



Body-centered

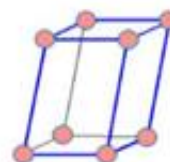


Base-centered

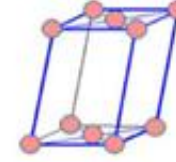


Face-centered

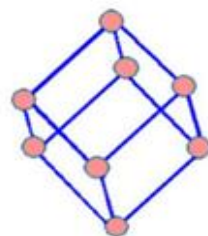
Monoclinic: $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$



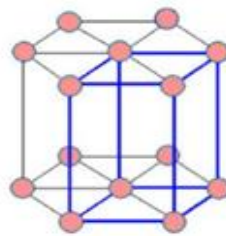
Simple monoclinic



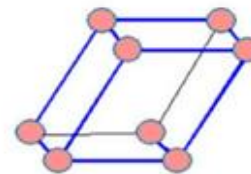
Base-centered monoclinic



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



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



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

Example of the materials:

- Cubic unit cell: Mn, Polonium (Po) NaCl.
- Body Centred Cubic: Na, V, Cr, Mo, W, Fe, alfa-iron, delta-iron
- FCC: Ni, Cu, Ag, Pb, Au, Pt (platinum)
- Tetragonal: (a) ST (b) BCT
ST-Pa (protactinium) and for BCT—Martensite and tin (Sn)
- Orthorhombic: (a) SO (b) ECO (c) BCO (d) FCO Examples: Ar (Arsenic) Bi (Bismuth) Sb (Antimony)
BCO- example: Cementite
FCO- example: S (sulphur), Ga (Gallium)
- Rhombohedral: Example: B (Boron), CaCO_3 , SiO_2
- Hexagonal: Example: Mg, Ti, Zr, CO, Zn Be (Beryllium)
- Monoclinic: (1) SM and (2) ECM Example: CaSO_4 , NaSO_4
- Triclinic: (1) ST Example: CuSO_4

Unit cells of the some of the common space lattices of crystalline solids are:

1. Simple cubic
2. Face centred cubic
3. Body centred cubic
4. Hexagonal close packed

Coordination number is the number of nearest neighbour to a particular atom in the crystal.

The coordination number (CN) of a crystal structure is defined as the number of nearest and equidistant neighbouring atoms that the each atom has in a space lattice.

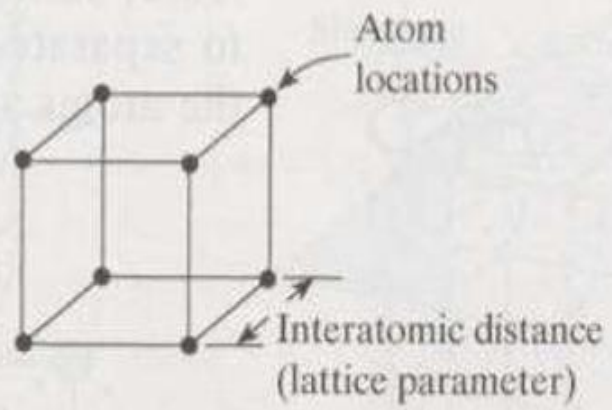
The coordination number (CN) of a few types of crystal structure are:

Simple cubic: 6

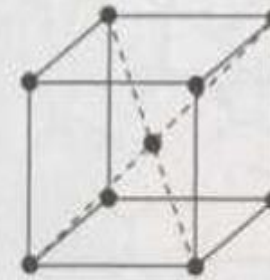
BCC: 8

FCC: 12 (4+4+4)

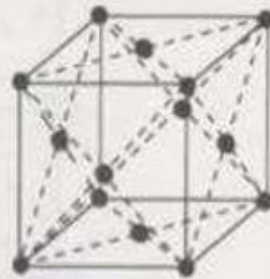
HCP: 12 (3+6+3)



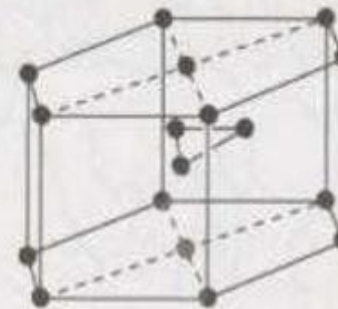
(a) Simple cubic



(b) Body-centered cubic

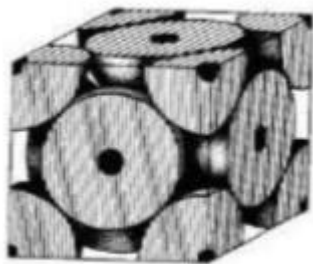
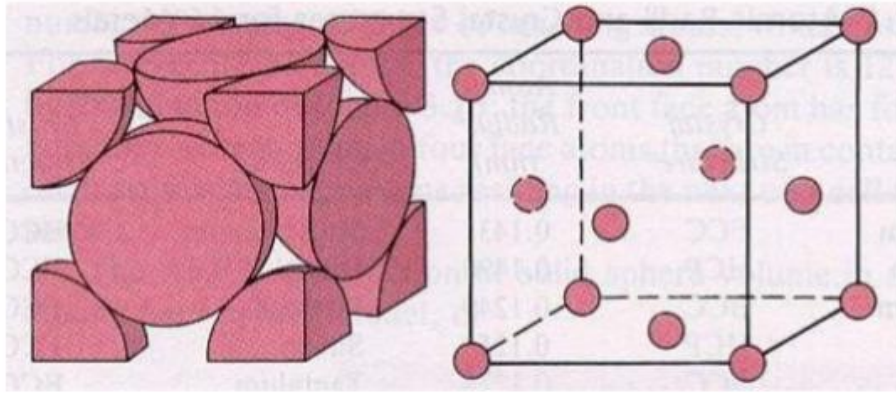


(c) Face-centered cubic



(d) Hexagonal close-packed

FCC (face centered cubic): Atoms are arranged at the corners and center of each cube face of the cell.

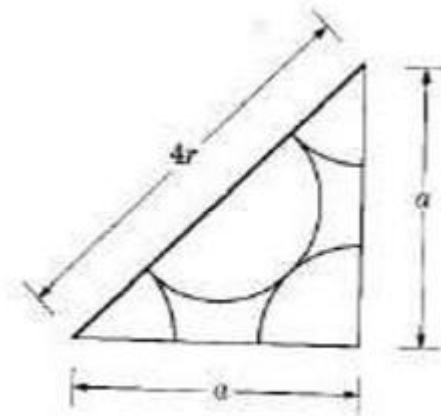


$$a = 2R\sqrt{2}$$

Close packed Plane: On each face of the cube

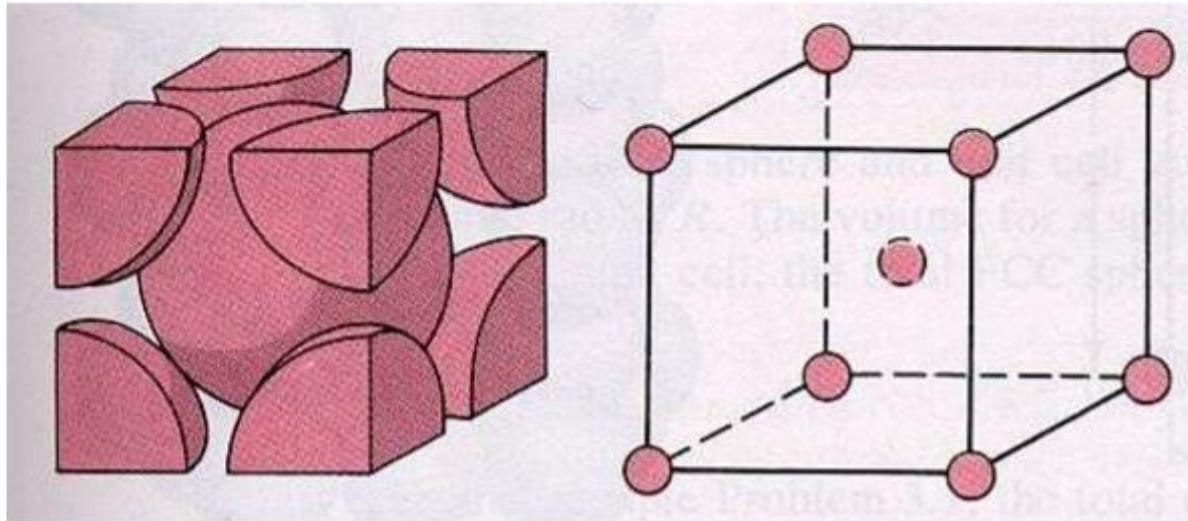
Atoms are assumed to touch along face diagonals.

4 atoms in one unit cell.

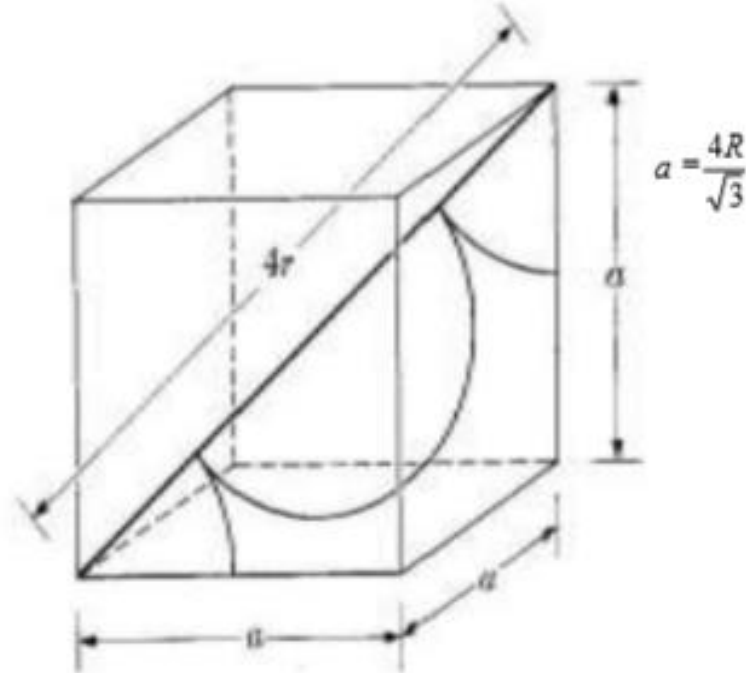
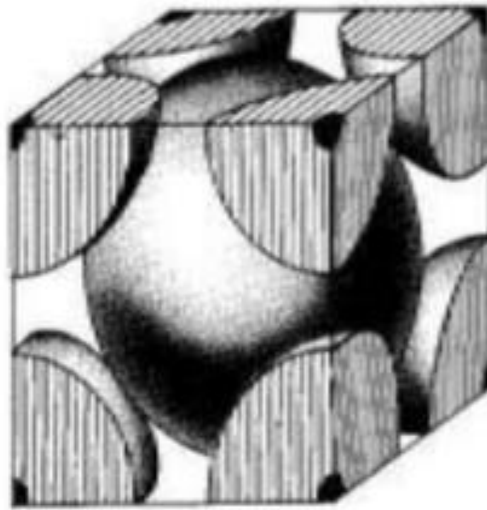


BCC: Body Centered Cubic

- Atoms are arranged at the corners of the cube with another atom at the cube center.

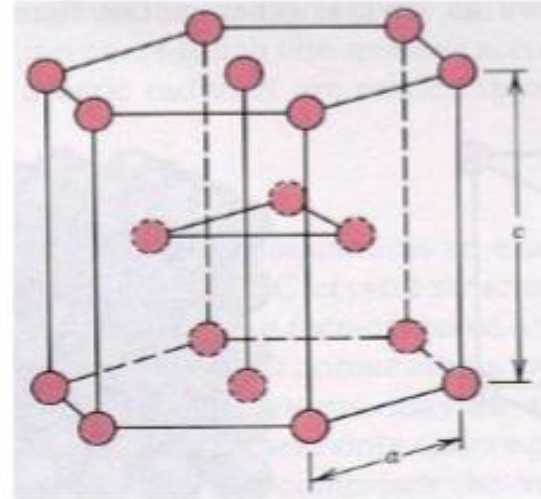


- Close Packed Plane cuts the unit cube in half diagonally
- 2 atoms in one unit cell



Hexagonal Close Packed (HCP)

- Cell of an HCP lattice is visualized as a top and bottom plane of 7 atoms, forming a regular hexagon around a central atom. In between these planes is a half-hexagon of 3 atoms.
- There are two lattice parameters in HCP, a and c , representing the basal and height parameters respectively.



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

6 atoms per unit cell

Atomic packing factor (APF) or packing efficiency indicates how closely atoms are packed in a unit cell and is given by the ratio of volume of atoms in the unit cell and volume of the unit cell

$$APF = \frac{\text{Volme of atoms}}{\text{Volume of unit cell}}$$

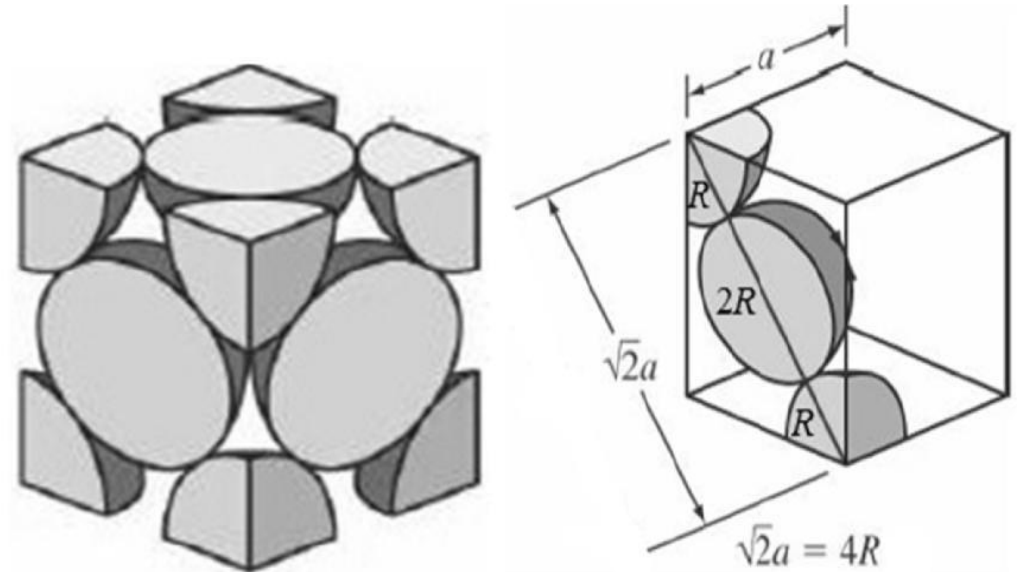
Atomic Packing Factor: FCC lattice

In the FCC unit cell effective number of atoms = 8 corner atoms \times (1/8) (each atom is shared by 8 unit cells) + 6 face centred atoms \times 1/2 (each shared by two unit cells) = 4.

Considering the atoms as hard spheres of radius R

$$\text{Total volume of atoms} = 4 \times \frac{4}{3} \pi R^3$$

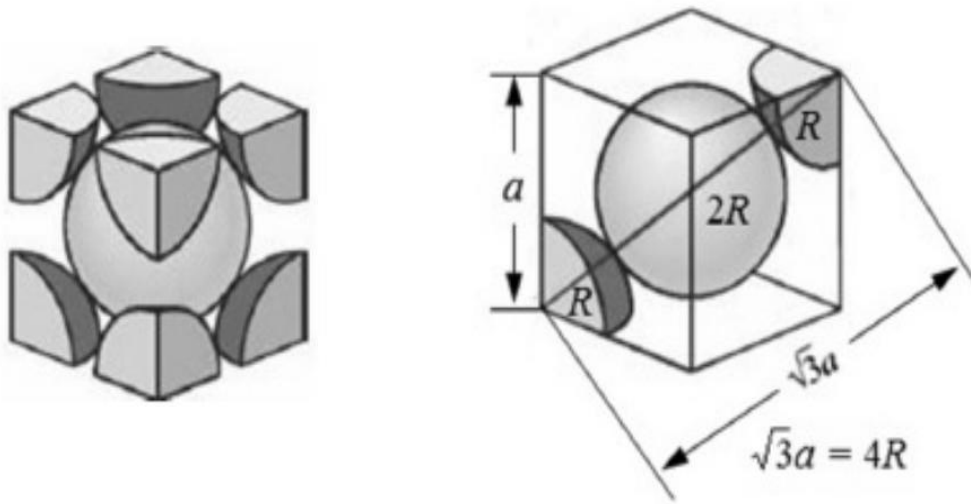
The relation between R and the FCC cell side a as shown in the figure below is $\sqrt{2}a = 4R$



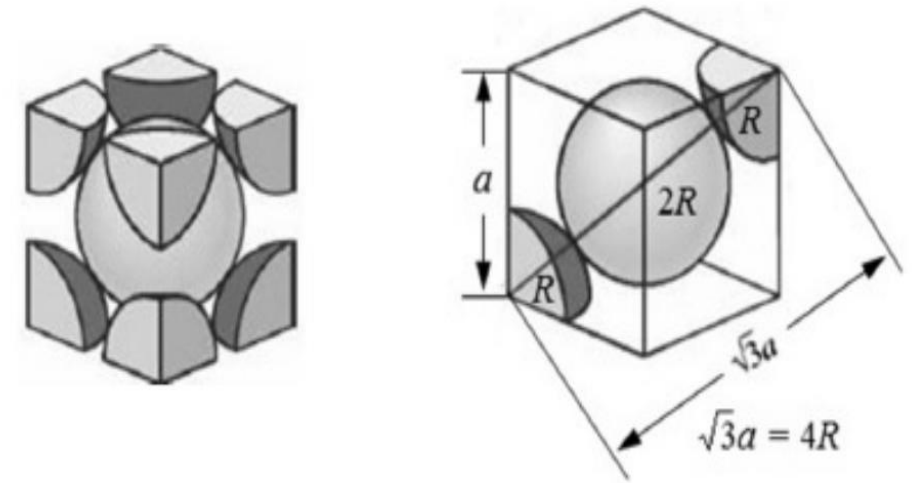
$$APF(FCC) = \frac{4 \times \frac{4}{3} \pi R^3}{a^3} = \frac{16 \times 2\sqrt{2} \pi a^3}{3 \times 64 a^3} = 0.74$$

For BCC crystals effective number of atoms per unit cell is $8 \times 1/8 + 1 = 2$ and the relation between R and a is

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



$$APF(BCC) = \frac{2 \times \frac{4}{3} \pi R^3}{a^3} = \frac{8 \times 3\sqrt{3}\pi a^3}{3 \times 64a^3} = 0.68$$



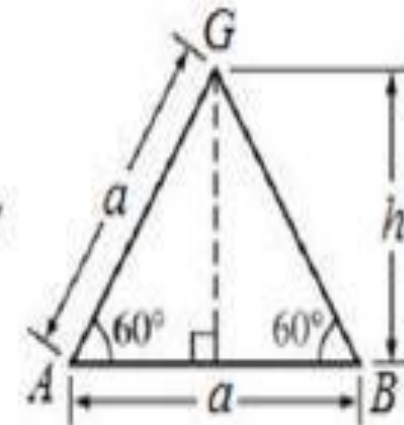
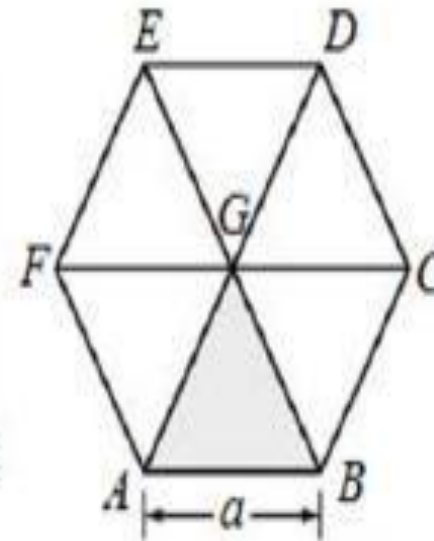
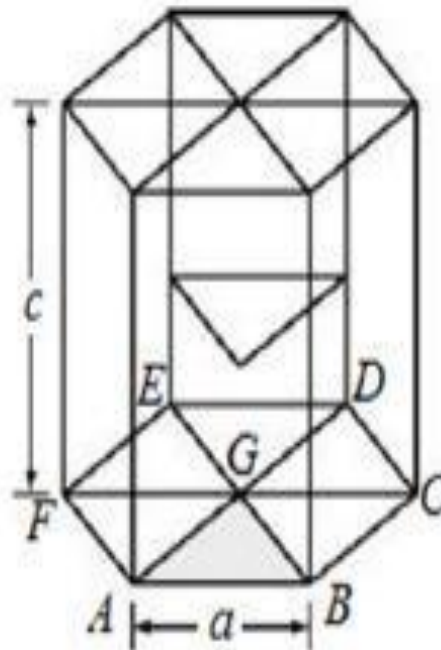
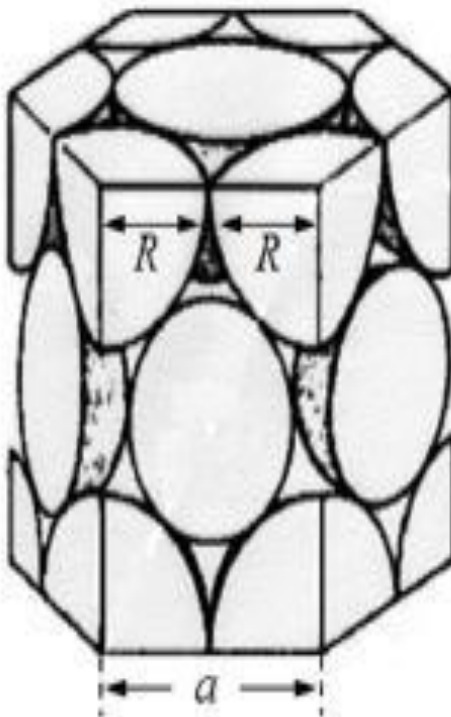
$$APF(BCC) = \frac{2 \times \frac{4}{3} \pi R^3}{a^3} = \frac{8 \times 3\sqrt{3}\pi a^3}{3 \times 64a^3} = 0.68$$

Hexagonal lattice

In the Hexagonal unit cell, number of atoms = 12 corner atoms $\times \frac{1}{6}$ (shared by six unit cells) + Two face atoms $\times \frac{1}{2}$ + 3 interior = 6.

$$2R = a$$

$$\text{Unit cell volume} = (6 \times \frac{1}{2} \times a \times h) \times c = (3 \times a \times a \sin 60^\circ) \times c = 3a^2 c \sin 60^\circ$$



Atomic Bonding:

It is useful to classify the bonds that hold atoms to one another in chemical compounds and crystals into three types.

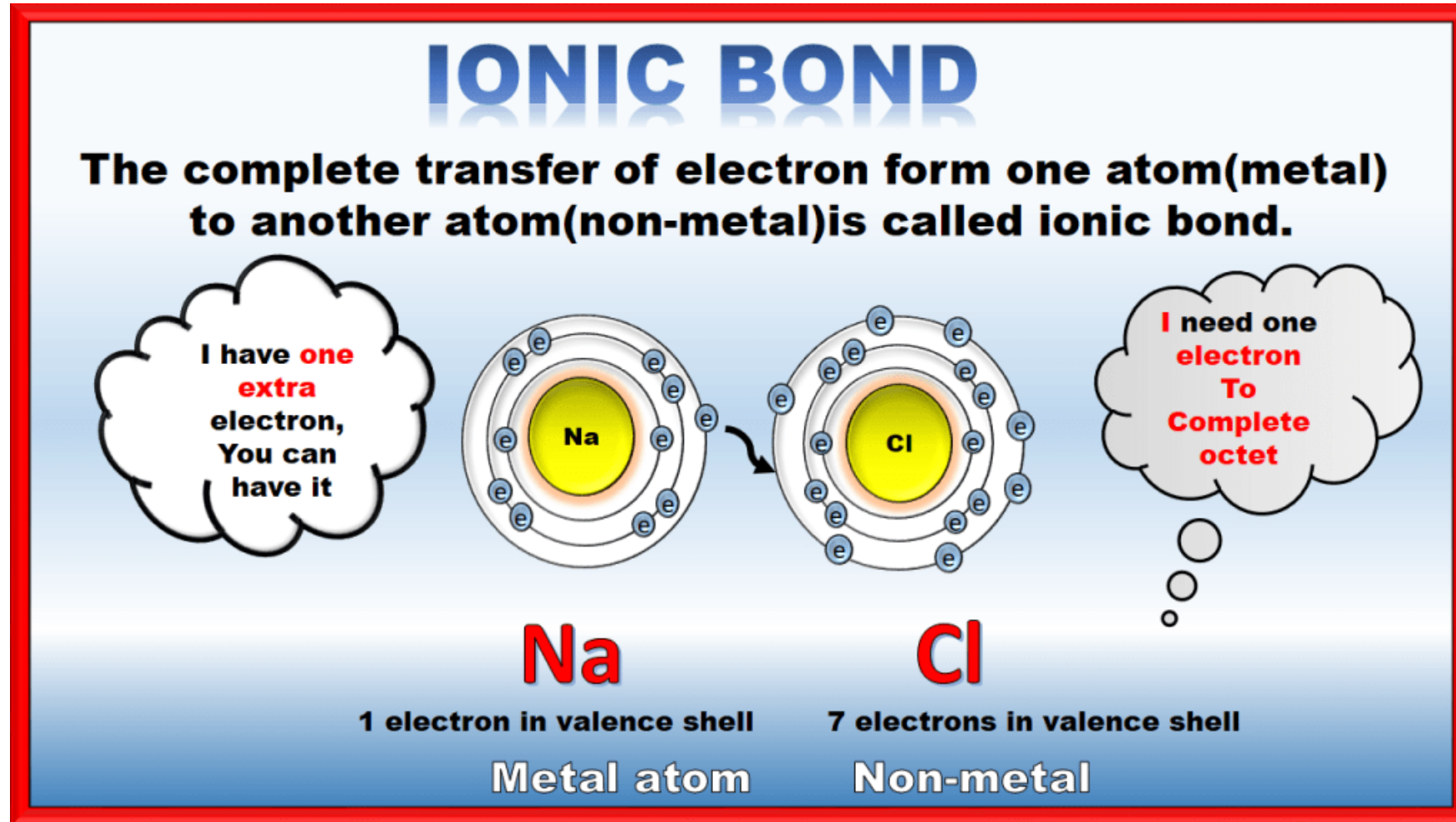
There are three primary types of bonding:

- Ionic bonding,
- Covalent bonding and
- Metallic bonding.

As the name implies, ionic bonding is due to the attractions between positively and negatively charged ions.

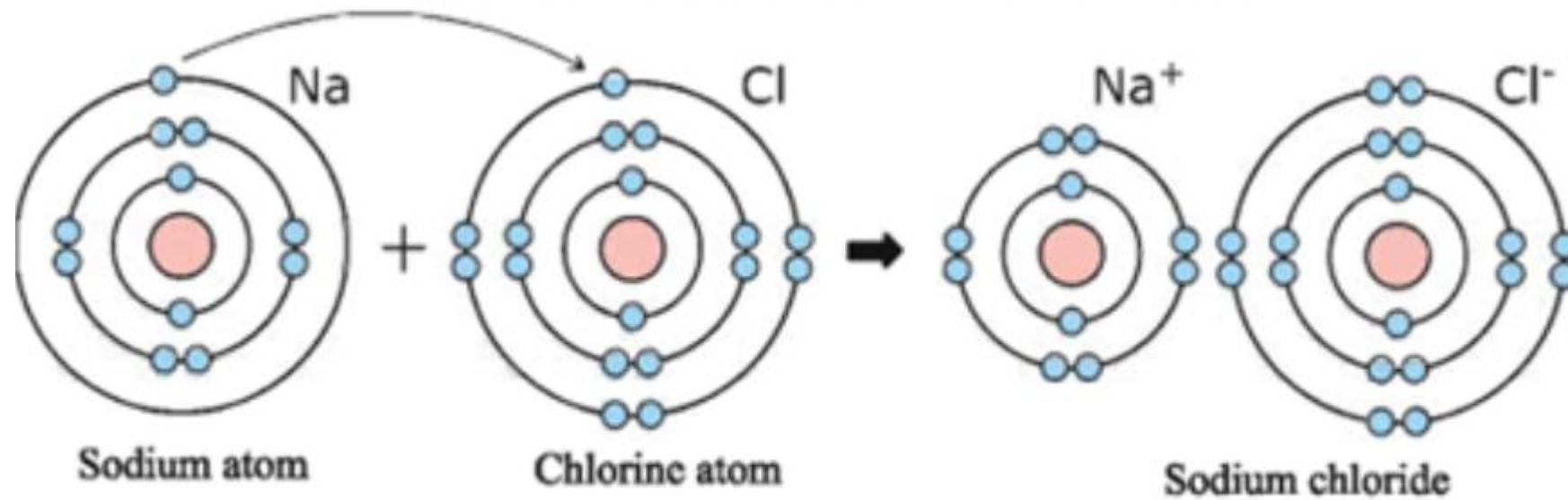
- Under these conditions they lose a few electrons forming cations, ions with a positive charge; the electron greedy atoms gain electrons to become anions, ions with a negative charge.
- Oppositely charged ions attract one another forming ionic bonds. The optimum arrangement is one which surrounds each charged ion with several charged ions with the opposite charge.

Ionic bonding: Definition: An ionic bond is formed when valence electrons are transferred from one atom to the other to complete the outer electron shell. *Example: A typical ionically bonded material is NaCl (Salt):*



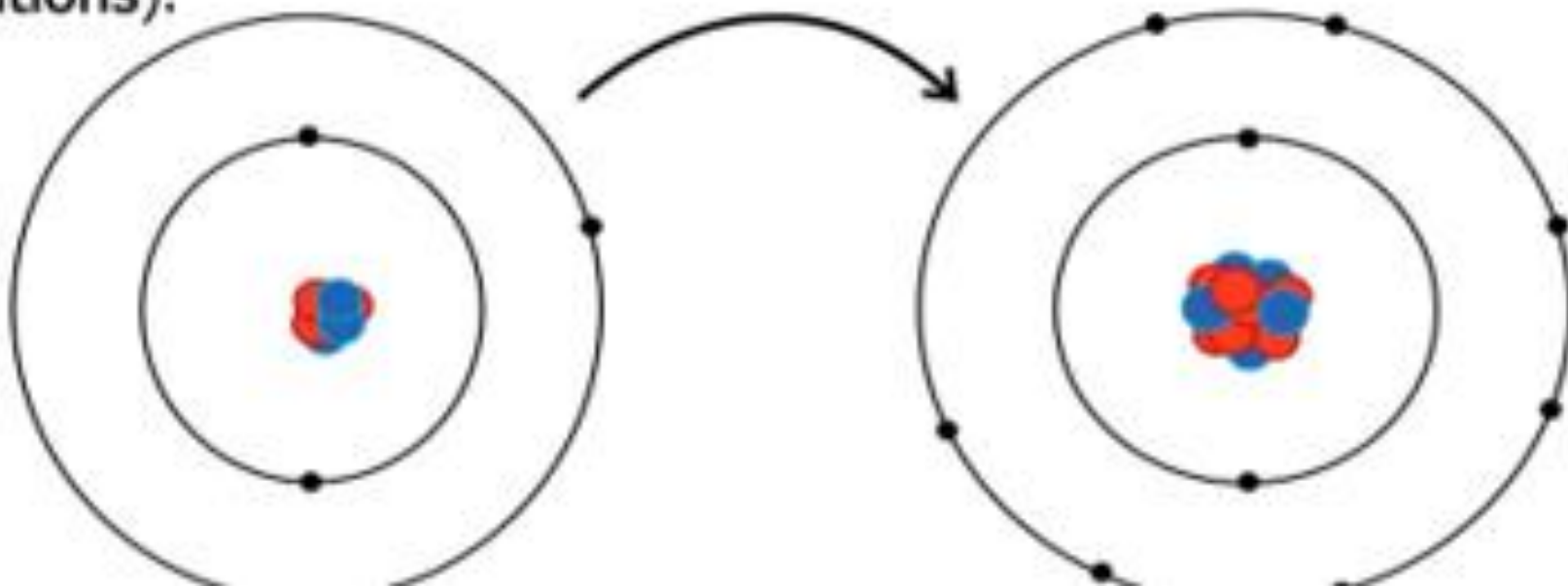
Ionic bond

Formation, Definition & Properties



What is an ionic bond?

Ionic bonds occur between a metal and a non-metal. An ionic bond results from the transfer of **electrons** from a **metal** to a **non-metal** in order to obtain a full valence shell for both atoms. Atoms that gain electrons make negatively charged ions (called **anions**). Atoms that lose electrons make positively charged ions (called **cations**).



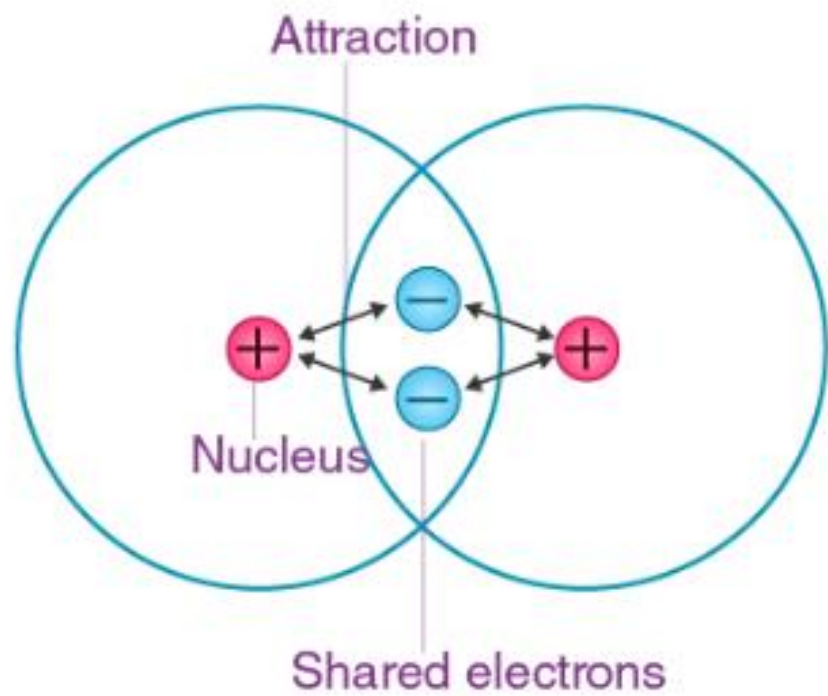
Covalent bonding :

When the different atoms are almost equal competitors for electrons, neither can take an extra away from the other, and so such atoms bond together by sharing electrons.

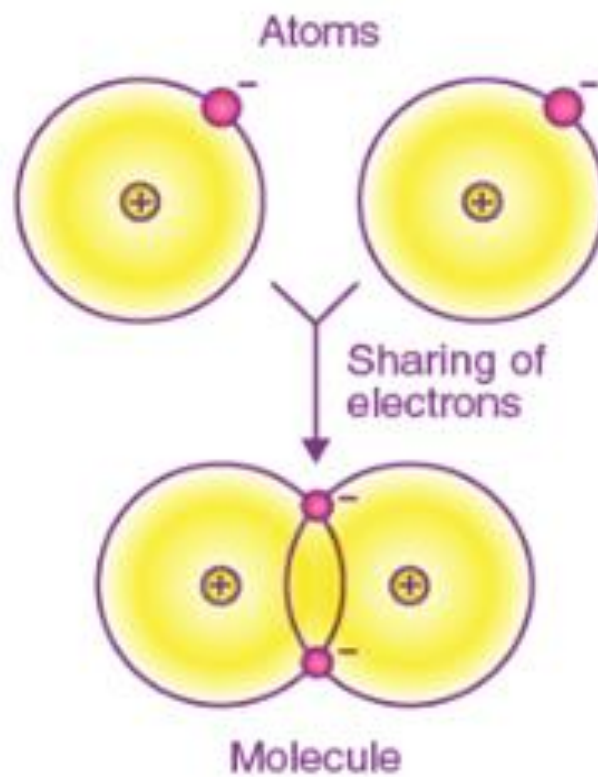
This kind of bonding is called *covalent bonding*. It holds two partners together in a very precise geometrical arrangement. The two bonded atoms can be thought of as an ellipsoid with nuclei at the two foci.

- ❖ A covalent bond is formed by equal sharing of electrons from both the participating atoms. The pair of electrons participating in this type of bonding is called shared pair or bonding pair.
- ❖ The covalent bonds are also termed as molecular bonds. Sharing of bonding pairs will ensure that the atoms achieve stability in their outer shell.

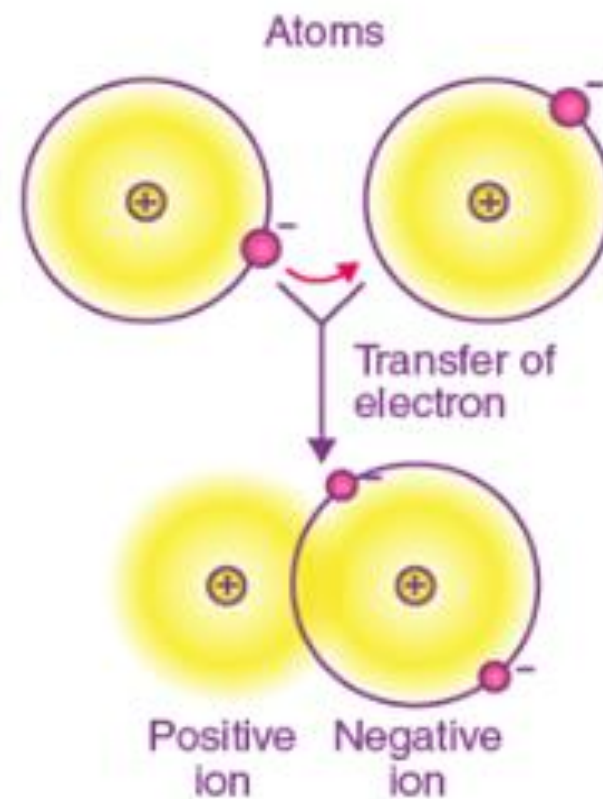
- Elements having very high ionisation energies are incapable of transferring electrons and elements having very low electron affinity cannot take up electrons.
- The atoms of such elements tend to share their electrons with the atoms of other elements or with other atoms of the same element in a way that both the atoms obtain octet configuration in their respective valence shell and thus achieve stability.
- Such association through sharing of electron pairs among different or same kinds is known as Covalent Bond.



Formation of Covalent Bond



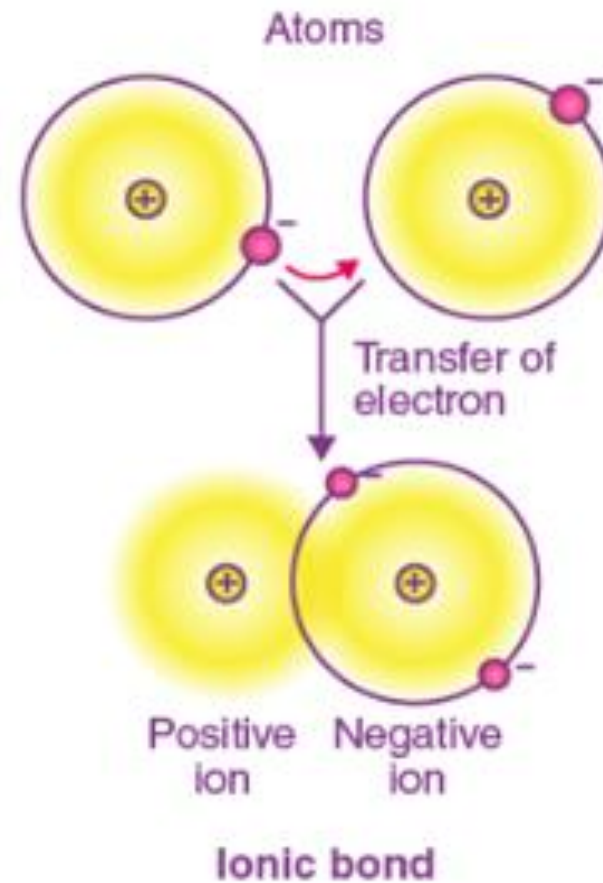
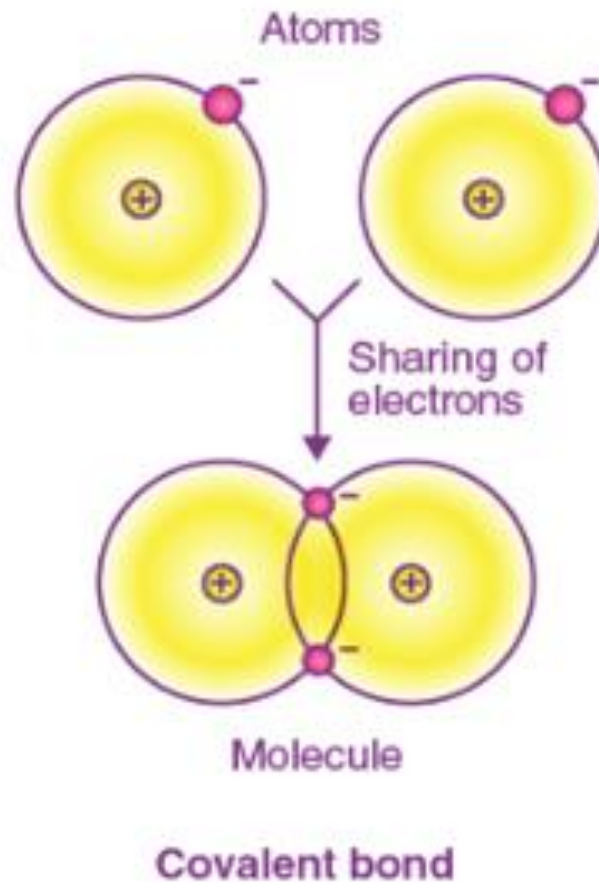
Covalent bond



Ionic bond

Difference Between Covalent and Ionic Bonds

Covalent bonds and ionic bonds are types of atomic bonds. These bonds are different in their properties and structure. The covalent bonds include pairs of electrons by two atoms binding them in a fixed orientation. While a bond between two ions is called ionic bonds.



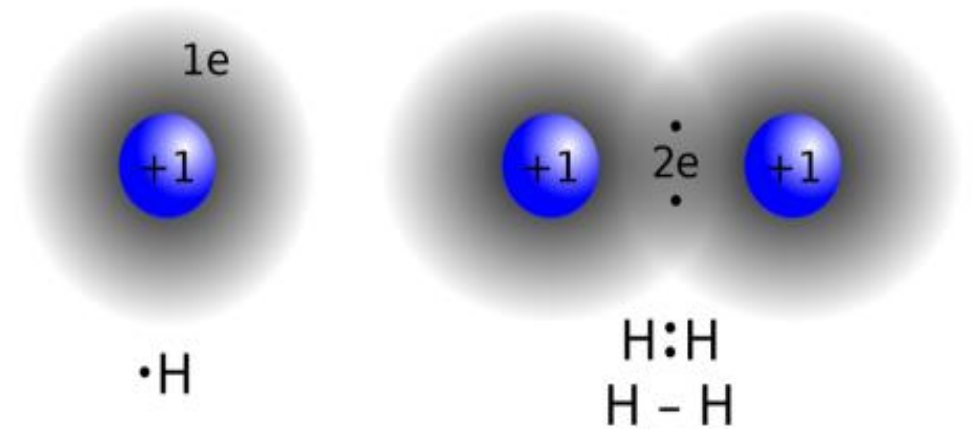
Covalent vs Ionic Bonds

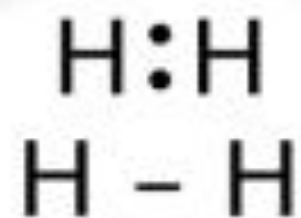
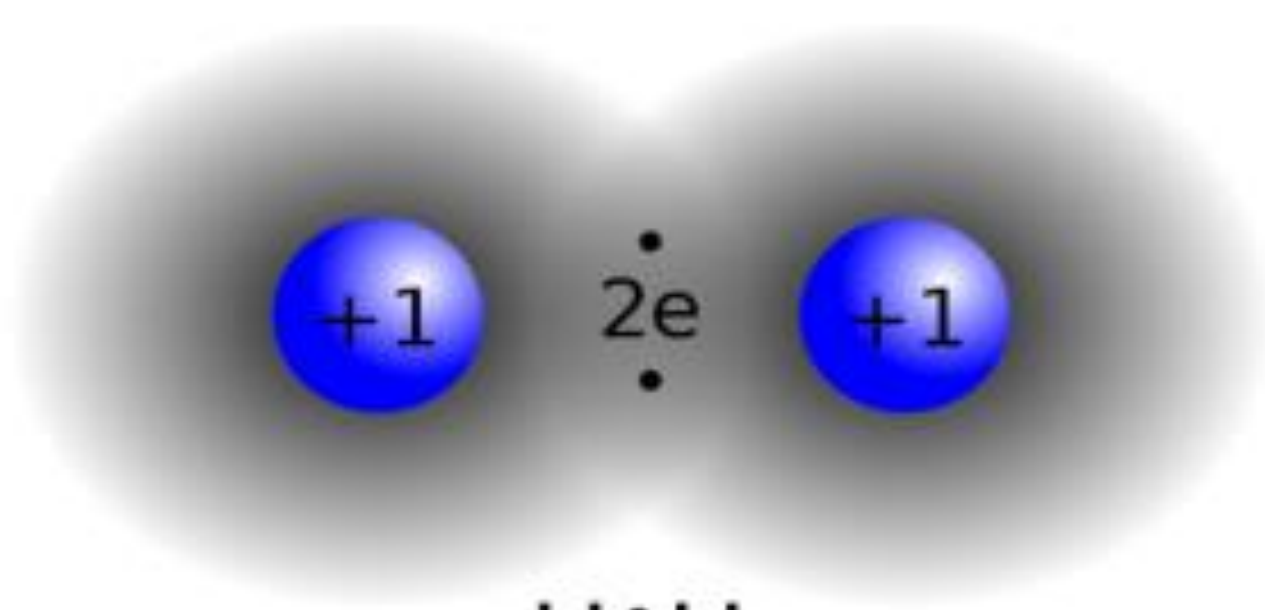
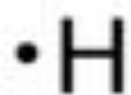
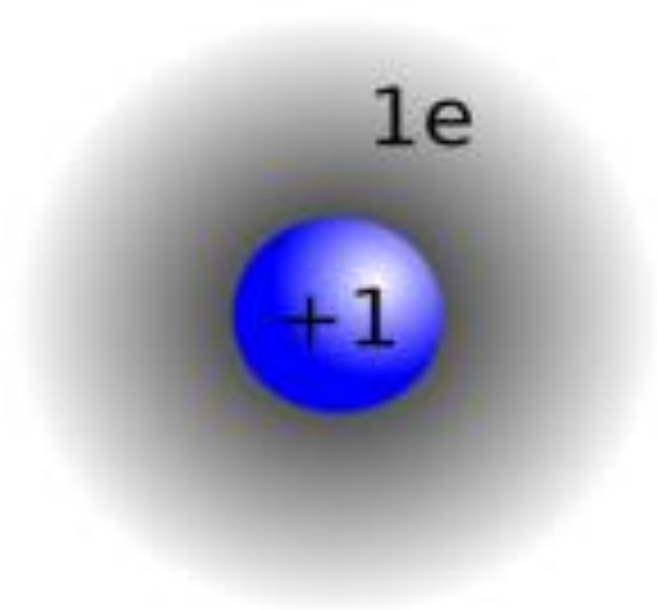
- ❖ Covalent bonding occurs between two non-metallic atoms characterized by the sharing of electron pairs between the atoms and other covalent bonds with electronegativity difference is greater than 2.0 (<2.0).
- ❖ In the case of covalent bond formation, polyatomic ions are formed. Whereas, the ionic bond is formed as a result of electrostatic attraction between the oppositely charged ions.

Covalent bonds

- The outer electron levels of atoms, which are close to each other, can interact. The interaction leads to a sharing of electrons between the atoms.
- One pair of electrons shared => single covalent bond
- Two pairs of electrons shared => double covalent bond and so on
- The shared electrons are said to be delocalized i.e. they do not belong to any particular atom
- Generally, between non-metallic atoms
- Examples:

H_2 , CO_2 , $\text{C}_6\text{H}_{12}\text{O}_6$ (Glucose) and other molecules





Single hydrogen atom (left) and two hydrogen atoms forming a covalent bond with a shared electron pair (right)

Covalent Bonding can be Achieved in two Ways:

- **Sharing of electrons between atoms of the same kind E.g. Formation of H_2 , Cl_2 , O_2 , etc.**
- **Sharing of electrons between atoms of different kind E.g. Formation of CH_4 , H_2O , NH_3 , etc.**

Difference Between Ionic and Covalent Bond

Covalent Bonds	Ionic Bonds
A covalent bond is formed between two similar electronegative non-metals	This type of bond is formed between a metal and non-metal
Bonds formed from covalent bonding have a Definite shape	Ionic Bonds have No definite shape
Low Melting Point and Boiling Point	High Melting Point and Boiling Point
Low Polarity and more Flammable	High Polarity and less Flammable
Covalent Bonds are in Liquid or gaseous State at room temperature	At room temperature, Ionic Bonds have Solid-state.
Examples: Methane, Hydrochloric acid	Example: Sodium chloride, Sulfuric Acid

Metallic bonds

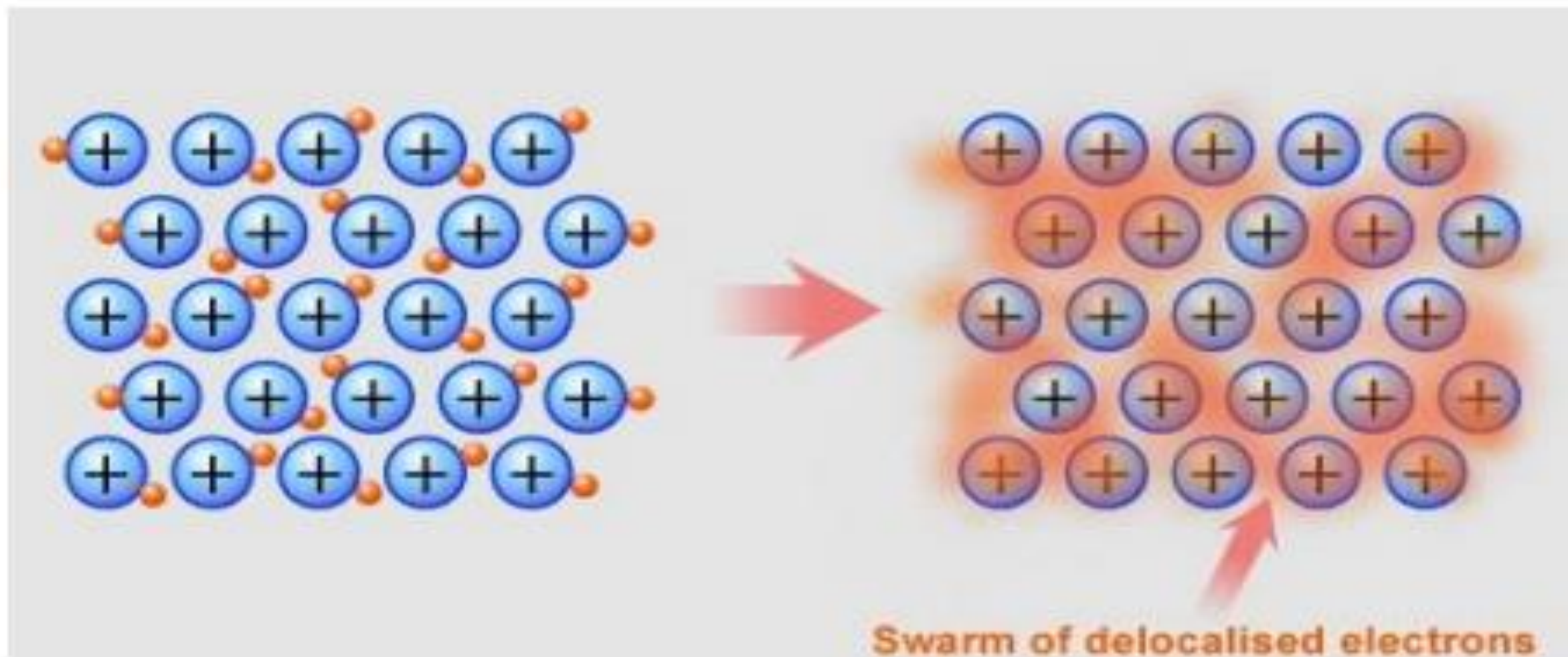
A metal is defined as any element that tends to lose electrons from the outer shells of its atoms. The resulting positive ions are held together in a crystalline structure by the cloud of these free electrons in what is known as the metallic bond.

The metallic bond yields three physical characteristics typical of solid metals:

- Metals are good conductors of electricity,
- Metals are good conductors of heat, and
- Metals have a lustrous (shiny) appearance.

Metallic bonds

- Atoms come together, electrons from outer shell of atoms share space with neighboring atoms.
- The electrons can move freely within the atom orbitals.
- Sharing of 'free' electrons among a lattice of positively charged ions (An array of positive ions in a sea of electrons)
- Electrostatic attractive forces between delocalized electrons and positively charged metal ions.
- The chemical bonding that results from the attraction between metal cations and the surrounding sea of electrons, Valence electrons do not belong to any one atom.
- Between metallic atoms
- Examples: Ni, Fe and other metals



The outer electrons are so weakly bound to metal atoms that they are free to roam across the entire metal. This results in a lattice of positively ions in a sea of communal electrons

The electron swarm is **all those loose outer electrons**. In technical terms, they've been delocalized because their 'parent' atoms can't hold onto them. So instead of hanging around the outskirts of one atom, the outer electrons are shared across the entire metal.

What are delocalised electrons

Delocalized electrons are spread across more than one atom. Usually electrons in materials are bound to one atom, and atoms are held together by the interactions of the charges on different atoms.

In some cases, electrons can be shared between atoms, and are then called delocalized. In the case of hydrocarbons, delocalization occurs in Benzene rings, where a hexagon of six carbon atoms has delocalised electrons spread over the whole ring.

In metals, electrons are delocalized over the whole crystal structure, and carry currents - the outer electrons of the metal atoms are shared in an electron sea, and are not confined to particular atoms.

- In metallic bonding, each atom in the metal contributes its valence electrons to the formation of an electron cloud that surrounds the positively charged metal ions, as illustrated in the diagram. Hence, the valence electrons are shared by all of the atoms.
- The positively charged ions repel each other uniformly, so they arrange themselves into a regular pattern that is held together by the negatively charged electron cloud.
- Since the negative electron cloud surrounds each of the positive ions that make up the orderly three dimensional crystal structure, strong electronic attraction holds the metal together.

Geometrical Crystallography

Crystal Symmetry

Geometrical Crystallography

Crystal Symmetry

The concept of symmetry describes the repetition of structural features. Crystals therefore possess symmetry, and much of the discipline of crystallography is concerned with describing and cataloging different types of symmetry.

Two general types of symmetry exist:

Internal or Translational symmetry : describes the periodic repetition of a structural feature across a length or through an area or volume.

External or Point symmetry : describes the periodic repetition of a structural feature around a point. Reflection, rotation, and inversion are all point symmetries.

Symmetries are most frequently used to classify the different crystal structures.

Thank you