Solid State Chemistry

Course: B.Sc. Sem 2

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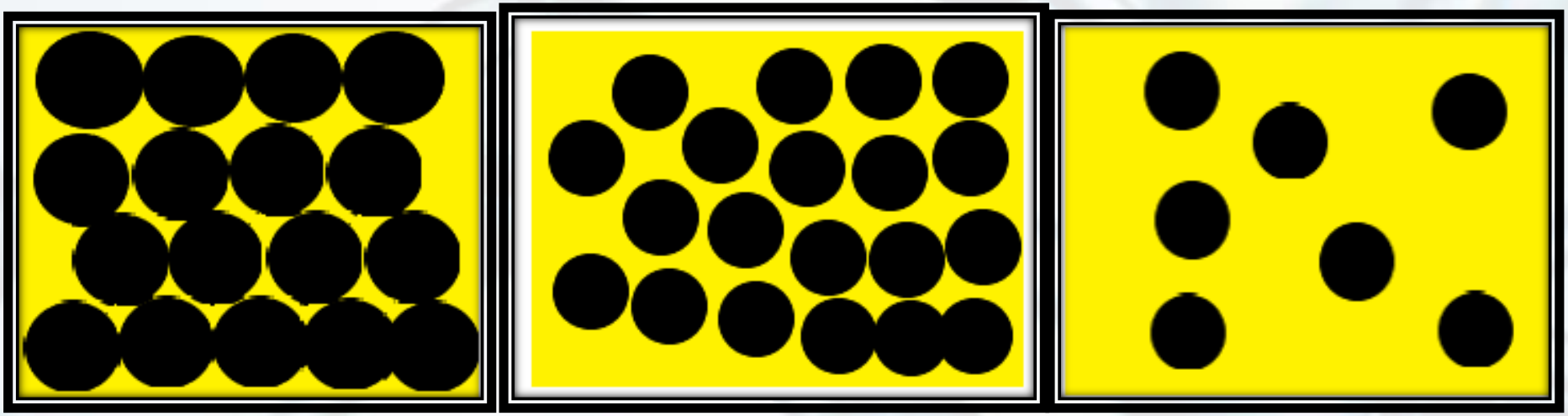
Matter

- Anything that occupies space and has some mass is called matter.
- Matter is mainly divided into three categories:

1. Solid: They are having fixed shape and volume
2. Liquid: Takes the shape of container and volume is fixed.
3. Gases: No fixed shape or volume.

Solids are further classified into crystalline and amorphous.

Intermolecular forces between solids, liquids and gases



The intermolecular forces between solid molecules are strongest, liquids have lesser and gases have least intermolecular forces to hold their molecules together

Crystalline solids

- Crystalline solids show high melting point.
- Observation by the naked eye (or by using a microscope for microcrystalline) shows crystals having well-developed faces and a characteristic shape.
- X-ray diffraction studies show a crystalline solid to have a regular, ordered structure composed of identical repeating units having the same orientation throughout the crystal.
- The repeating unit is a group of one or more atoms, molecules, or ions.

Amorphous solids

- They do not have a characteristic crystal shape.
- Mostly soften on heating and then melt over a temperature range.
- X-ray diffraction shows a disordered structure. Most of the polymers form amorphous solids. Some macromolecules or polymers also form crystalline solids. Others give solids that are partly crystalline and partly amorphous.

- **Glass is an amorphous solid obtained by cooling a liquid. Amorphous solids form on deposition of a vapor on a cold surface and on evaporation of solvent from a solution. The most common kind of glass is prepared from molten SiO_2 with various amounts of dissolved metal oxides. The chains and rings of Si-O-O bonds; their structure is disordered and irregular.**
- **Glycerol form glasses on cooling rapidly. The high viscosity of these liquids makes them hard for the molecules to become ordered into a crystalline solid. A glass phase is thermodynamically metastable; having a higher Gm (Glassy melting point) than does the crystalline form of the substance.**

Quasicrystal was discovered in 1984 and they are formed when certain molten alloys are very rapidly cooled. Unlike amorphous solids, quasicrystals have both short-range and long-range order. But beside despite their long-range order, the symmetry of the quasicrystal structure is incompatible with translational periodicity and so is of a type forbidden for ordinary crystals.

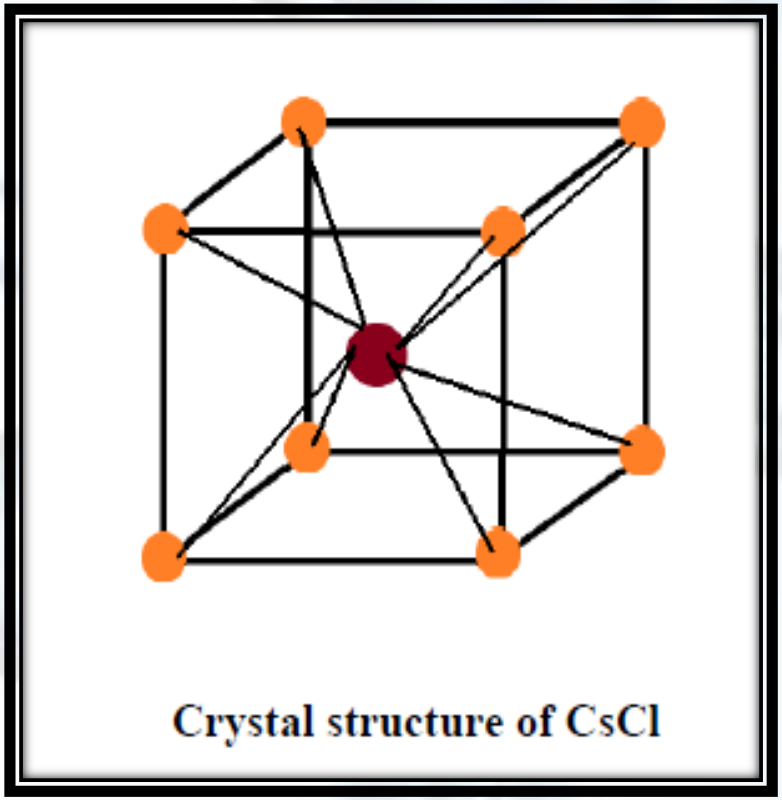
Chemical Bonding in solids

- There are four types of bonding that forms a crystalline solid:

1. Ionic
2. Molecular
3. Metallic
4. Covalent

Ionic

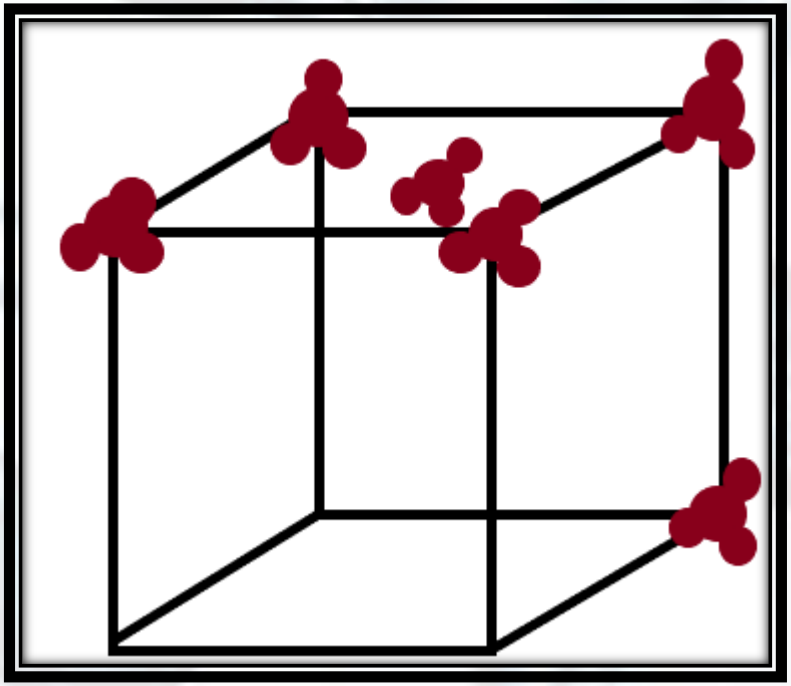
These are made up of an array of positive and negative ions which are held together by the electrostatic attraction between oppositely charged ions. Examples are NaCl, CsCl, MgO, $BaCl_2$, ZnS and KNO_3.



Crystal structure of CsCl

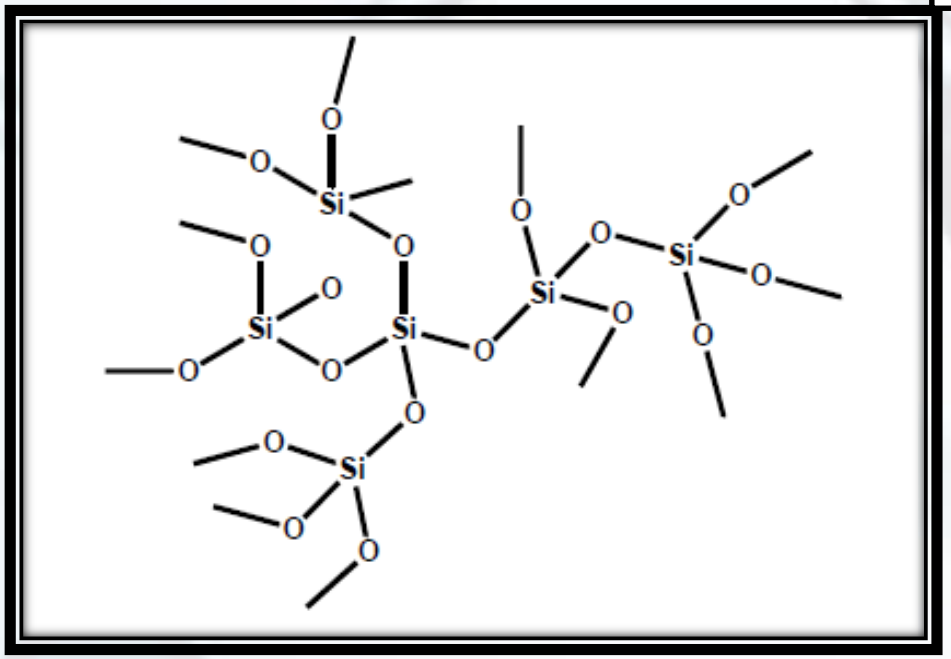
Covalent

Covalent (or non-metallic network) crystals consist of an "infinite" network of atoms that are held together by polar or nonpolar covalent bonds with no individual molecules being present such as carbon in the forms of diamond, graphite, and carbon nanotubes, Si, SiO_2, and SiC.

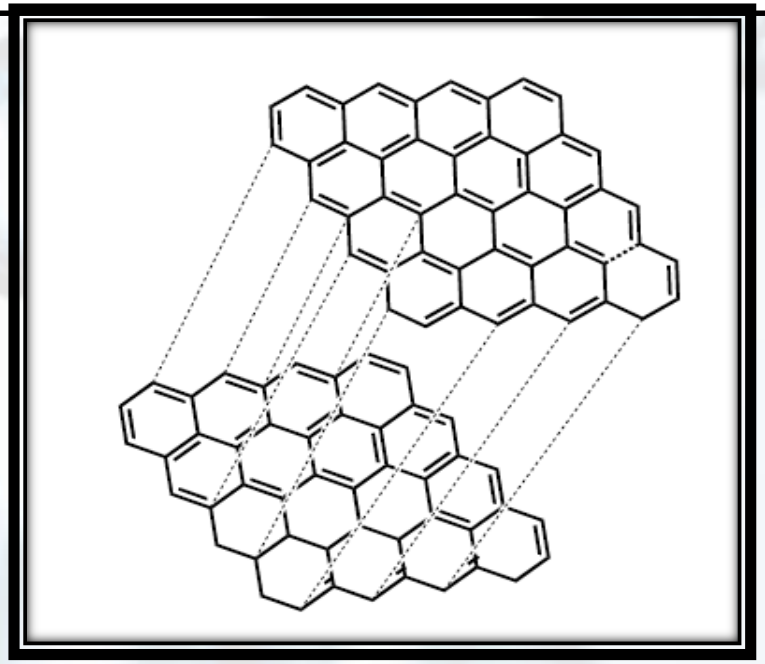


In diamond each carbon atom is bonded to four other carbon atoms that surround it tetrahedrally, and hence gives them a three-dimensional network that extends throughout the crystal.

Silicon has the same structure. SiO_2 has a three-dimensional network in which each Si is bonded to four O's at tetrahedral angles, and each O is bonded to two Si atoms



Graphite consists of layers of fused hexagonal rings of bonded carbons; the bonds are intermediate between single and double bonds just like the benzene. The layers have been held together by weak van der Waals forces



Metallic

They are mostly composed of bonded metal atoms; some of the valence electrons are delocalized over the entire metal and hold the crystal together. For example metals such as Na, Cu, Fe, and various alloys.

Molecular

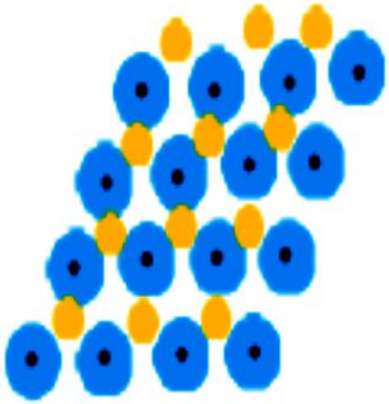
Mostly composed of individual molecules. The atoms within each molecule are held together by covalent bonds and relatively weak intermolecular forces (such as dipole-dipole or Hydrogen bonding) hold these molecules together in the crystal. Subdivided into van der Waals crystals (intermolecular attractions are dipole– dipole, dipole–induced-dipole, dispersion forces) such as Ar, CO_2, CO, O_2, HI, HgCl2 and hydrogen-bonded crystals (H2O, HF, NH_3 and amino acid).

Crystal structures

- A crystal consists of structural unit which called the basis or the motif which repeat themselves in three dimensions to generate the crystal structure.
- The environment of each repeated unit is same throughout the crystal except some of the surface deformities. These may be atom or molecules or ions or group of them. The entire repeated basis groups possess the same structure, same spatial orientation and same stoichiometric composition as every other basis group in the crystal.
- For example in NaCl, the basis consists of one Na^+ ion and one Cl^- ion (ionic crystal), in Cu the basis is a single Cu atom (metallic crystal), in diamond the basis is two C atoms which are surrounded tetrahedrally by four carbons, but the four bonds at one basis atom differ in orientation from those at the other atom (covalent crystal) and in CO_2, the basis is four CO_2 molecules (molecular crystals).

The Space Lattice

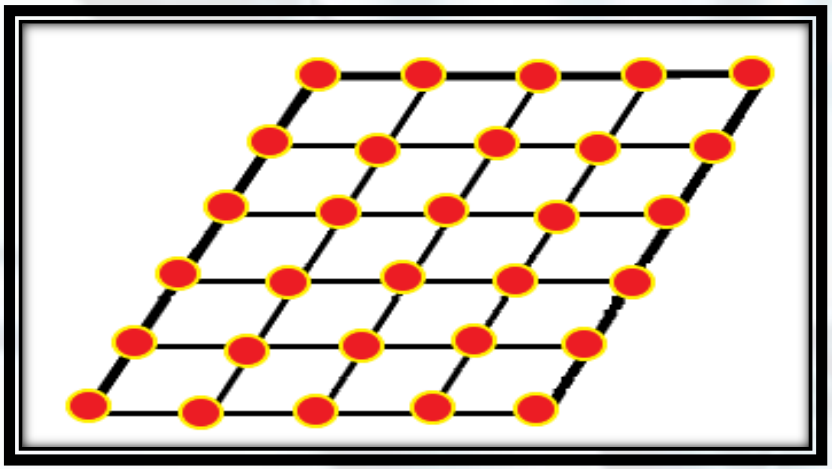
On placing the single point at the same location in each repeated basis group, a set of points are obtained that forms the (space) lattice of the crystal. Each point of the space lattice has the same environment and it is not same as crystal structure. However, the crystal structures are generated by placing an identical structural group (the basis) at each lattice point. The space lattice is primarily a geometrical abstraction and it shows a two-dimensional lattice (which is mainly a hypothetical two-dimensional crystal structure that is formed by joining each lattice point a basis as shown in the image below in which the crystal structure is generated by associating a basis group with each lattice point.



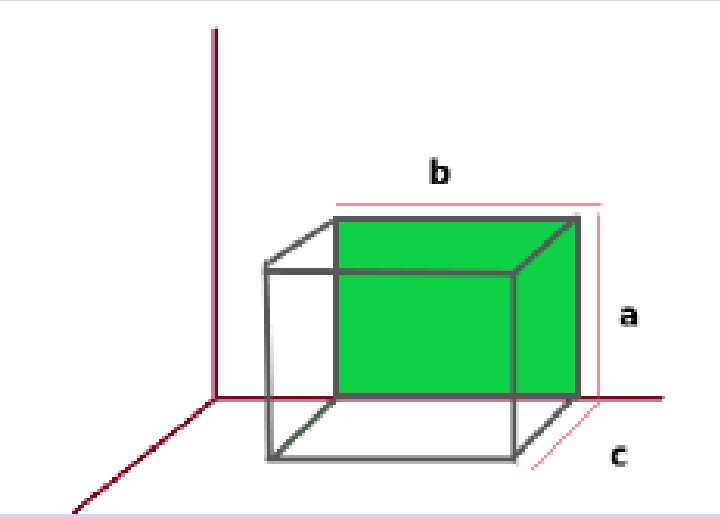
The blue and yellow circle represents two atoms and the black dots represent the lattice points

The Unit Cell

- The space lattices of any crystal are mainly divided into similar or identical parallelepipeds by joining the lattice points with straight lines.
- *Parallelepipeds* are six-sided geometrical solid whose faces are all parallelograms.
- A unit cell is a kind of parallelepipeds and a lattice is broken up into unit cells is not unique.



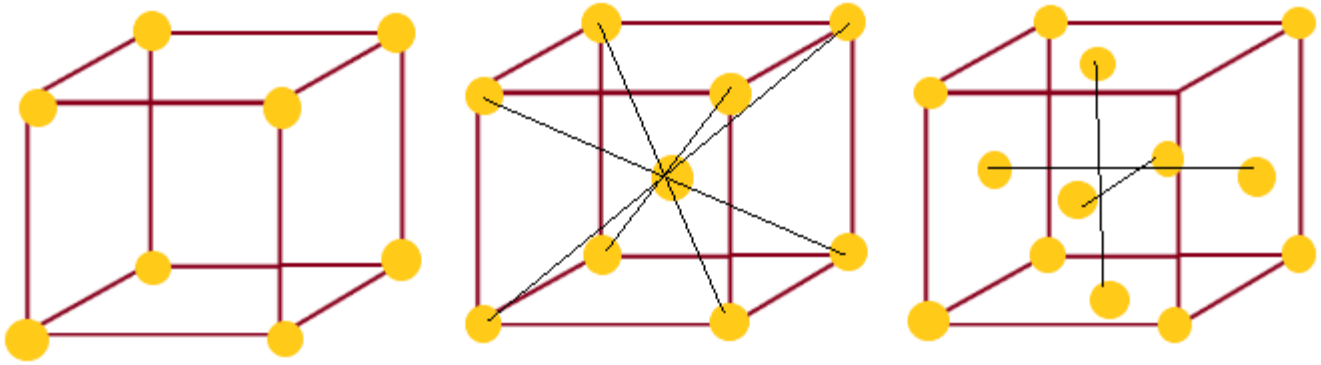
The above arrangement shows a unit cell in a two dimensional lattice. Similar arrangements are found for a three dimensional structure. The unit cell with maximum symmetry and smallest volume is always preferred in crystallography. Here, maximum-symmetry refers to the maximum number of perpendicular unit-cell edges. In two dimensions, a unit cell is a parallelogram with sides having length a, b.



The angles between the edges a, b and c represented by α, β and γ, some of the arrangements are been shown. Bravais (1848) showed that there are 14 kinds of lattices that are arranged in three dimensions. These unit cells of the 14 Bravais lattices are tabulated as below and they are classified into seven crystal systems on the basis of their unit-cell symmetry.

- **There are 14 types of crystal systems divided into seven Bravias lattices.**
- **Unit cells that have lattice points only at their corners are called primitive (or simple) unit cells.**
- **A body-centered lattice (I which is derived from the German *innenzentrierte*) consists of lattice point within the unit cell as well as at each corner of the unit cell.**
- **A face-centered (F) lattice has a lattice point on each of the six unit-cell faces as well as at the corners.**
- **End-centered lattice (C) with a lattice point on each of the two faces bounded by edges of lengths a and b.**

1. Cubic Systems



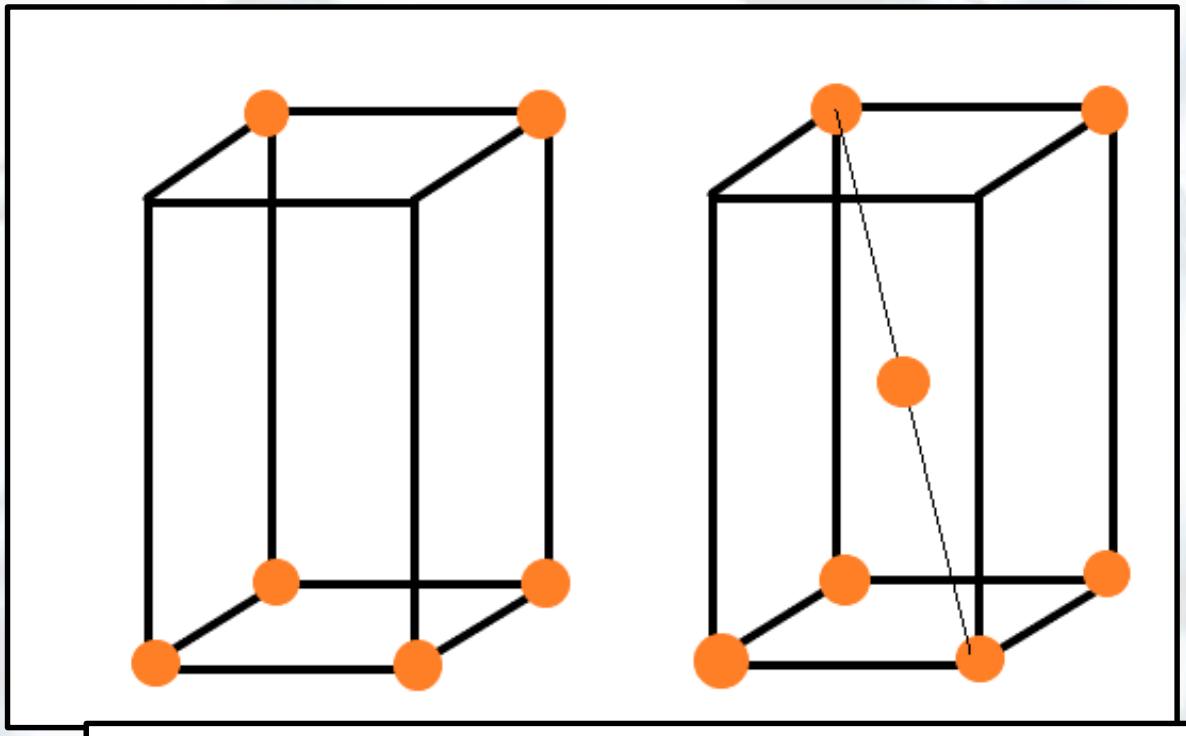
A	B	C
Primitive	Body-centred	Face centred

$$a = b = c$$

and $\alpha = \beta = \gamma = 90^o$

The parameters of length of the unit cell and its angles are equivalent. Eg. NaCl, KCl, ZnS

2. Tetragonal



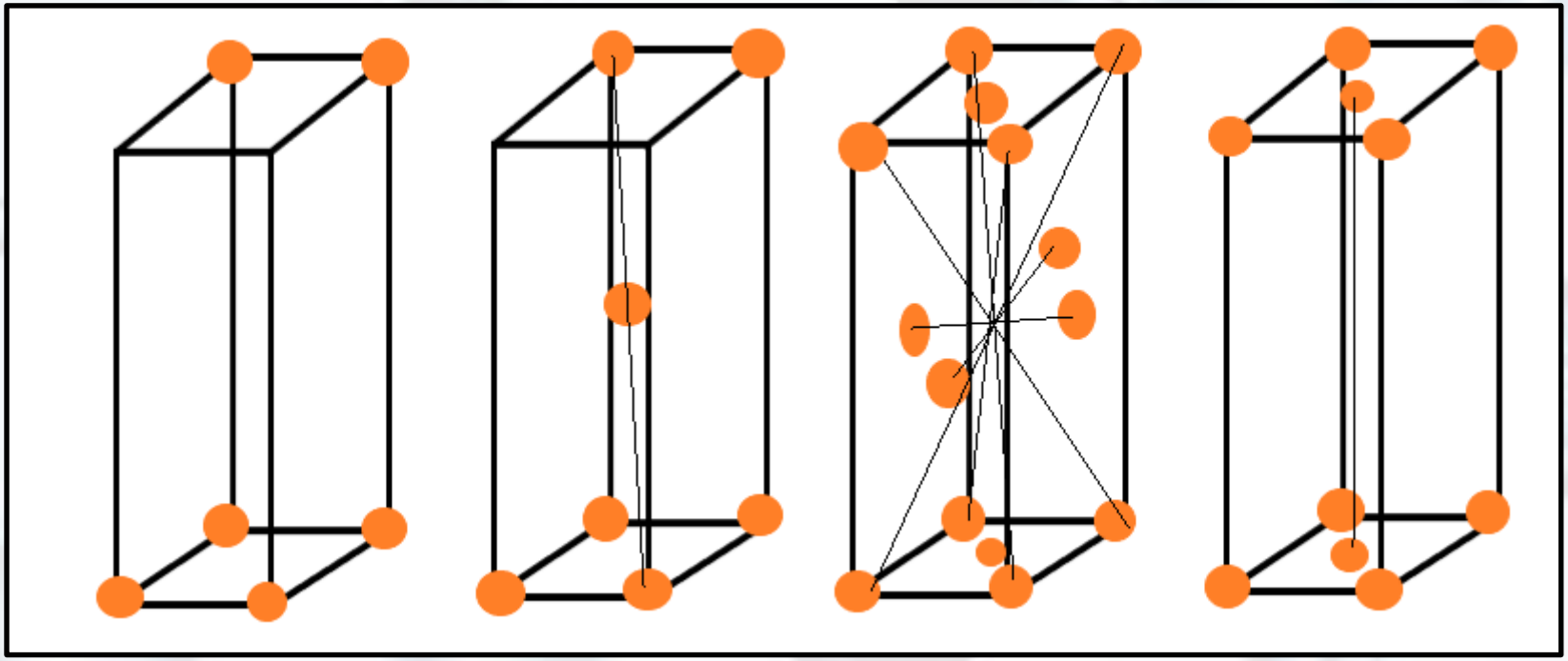
Primitive Body centred

$$a = b \neq c$$

and $\alpha = \beta = \gamma = 90^o$

Eg. SnO_2, TiO_2

3. Orthorhombic



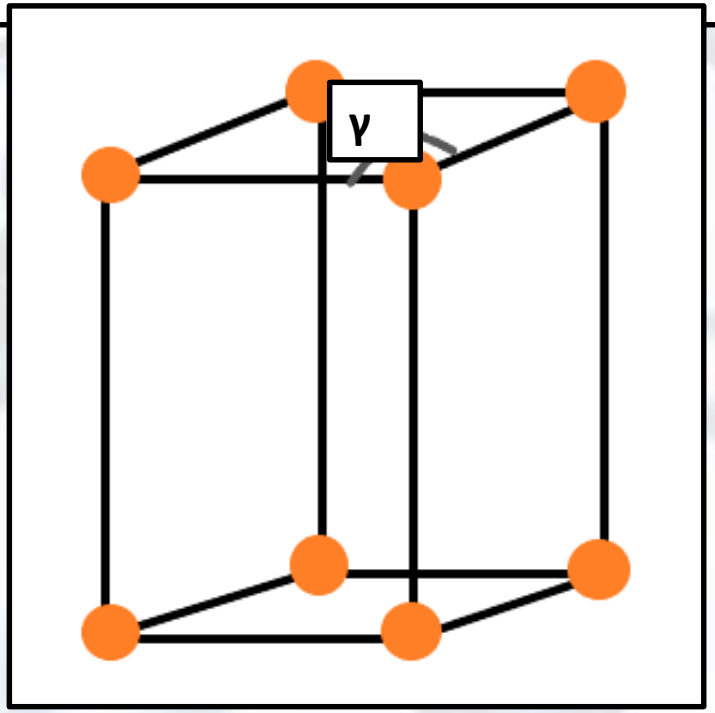
A	B	C	D
Primitive	Body Centred	Face Centred	End Centred

e.g. $BaSO_4$, AgBr

$$a \neq b \neq c$$

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

4. Hexagonal



e.g. ZnO, CdS, HgS

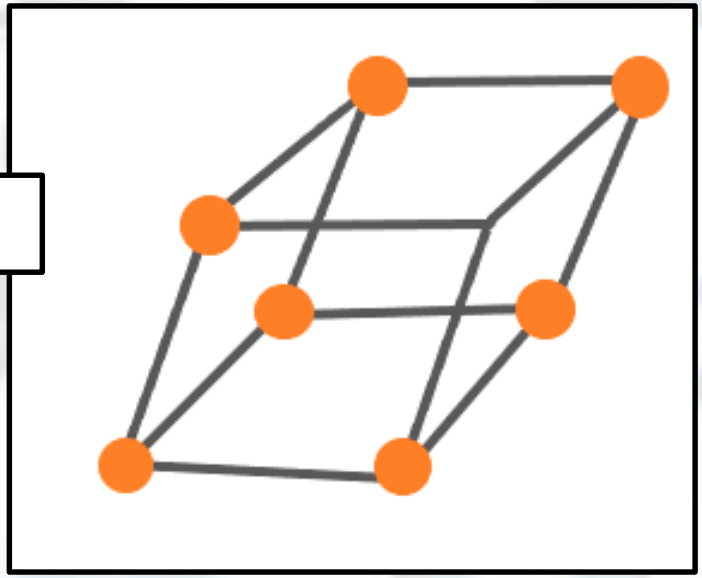
$$\boldsymbol{Primitive}$$

$$\boldsymbol{a = b \neq c}$$

$$\boldsymbol{\gamma = 120^o \quad \alpha = \beta = 90^o}$$

5. Trigonal (rhombohedral)

e.g. Graphite, As, Sb

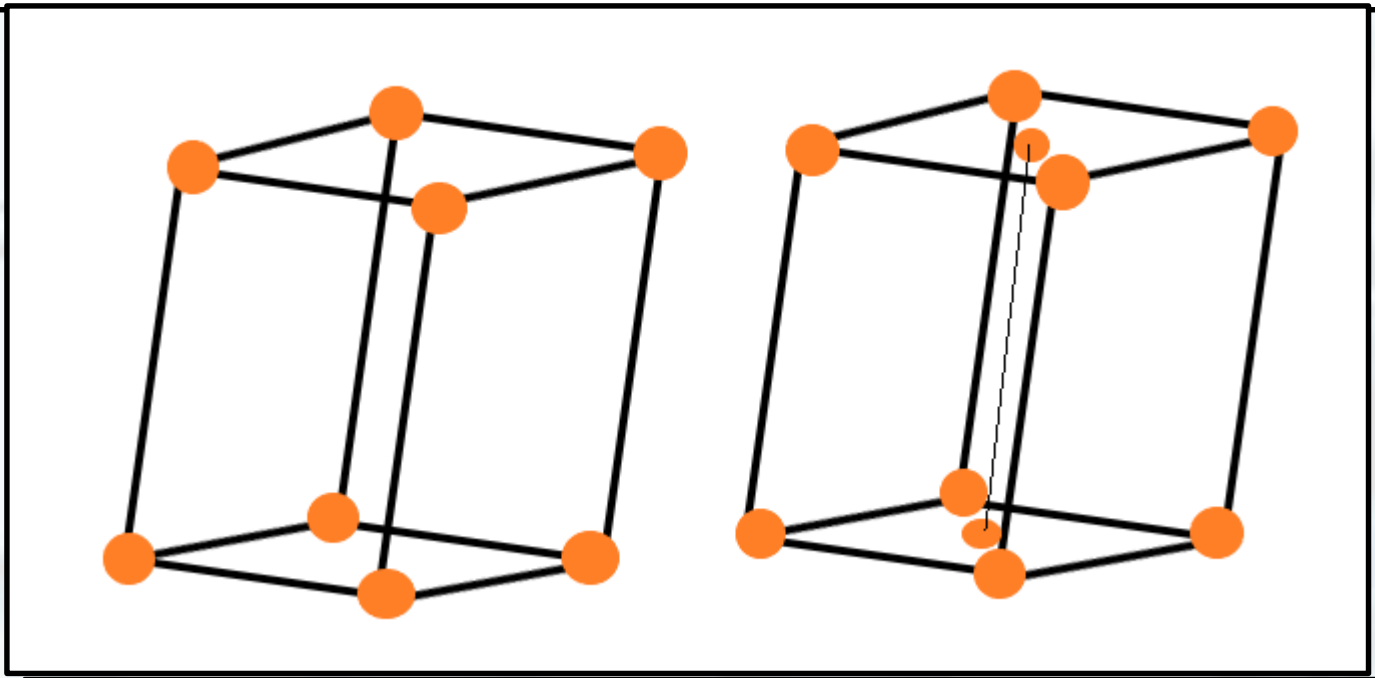


Primitive

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90° < 120^{o}$$

6. Monoclinic

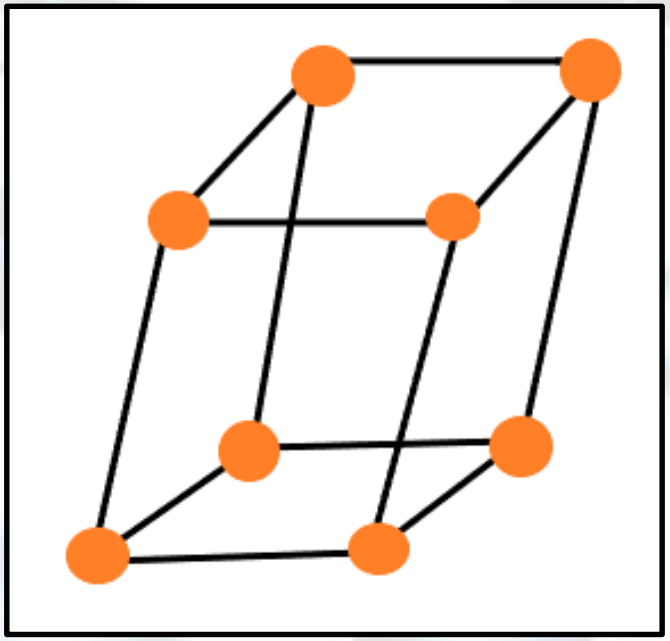


Primitive	End Centred

Calcium sulphate Monoclinic sulfur	$a \neq b \neq c$ $\alpha = \gamma = 90° \; \beta > 90°$

7. Triclinic

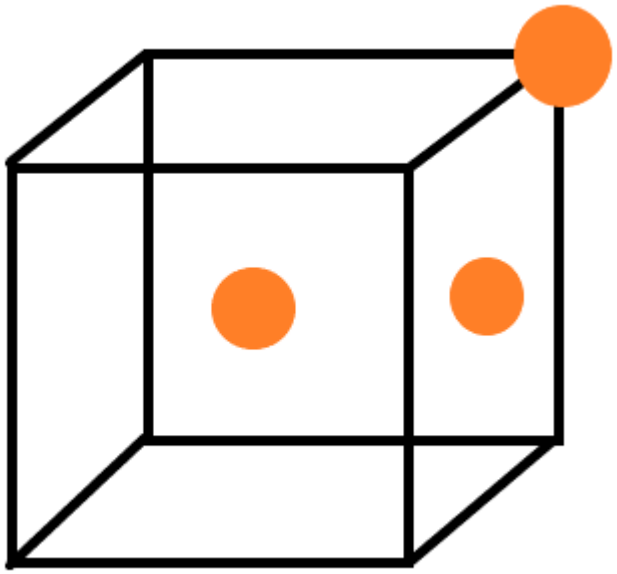
Copper Sulphate



$$a \neq b \neq c$$

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

Sharing of atoms



The atom at the corner of unit cell is shared by 8 adjacent unit cells, the atoms at the face are shared by two adjacent unit cells and body centre is shared by one Therefore their total contribution in unit cell can be given as:

8 X 1/8 = 1 for the corners, 6 X ½= 3 and Thus a Face centred lattice has total four atoms.

For body centred it is 8 X 1/8= 1 and 1 at the centre i.e. 2

For primitive it 1

And for end centred it is 2

Thank You

Stay At home

Keep Studying

Stay safe