

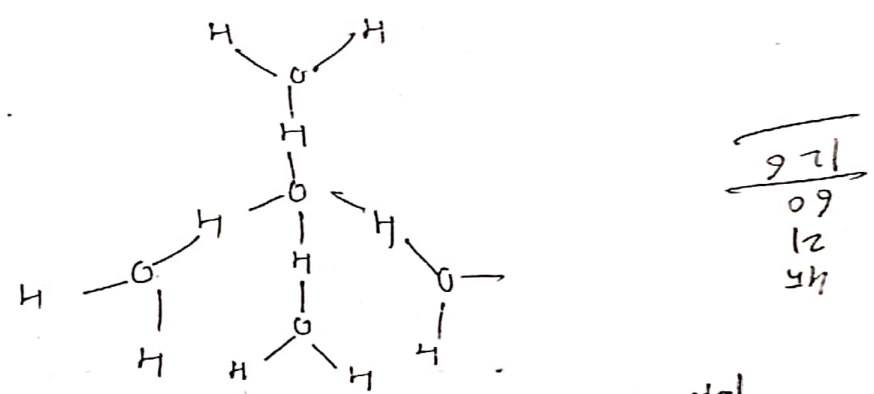
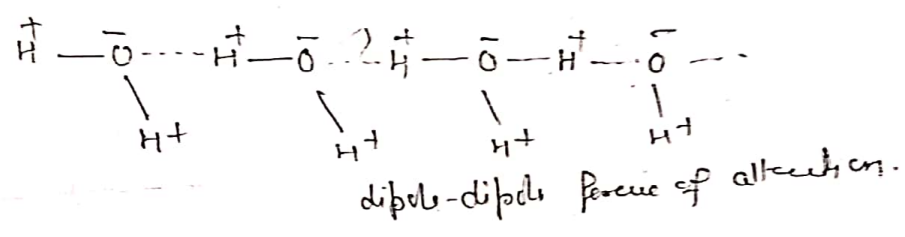
Solid State

(1)

Crystalline solid, the atom, or molecule, or ions are arranged in a definite pattern geometrically constantly repeated in a three-dimensional lattice. eg. NaCl, S, sugar, diamond etc. Amorphous solids do not have any definite geometrical form hence, long range order in their structure is absent. eg. glass, rubber, plastic etc.

Classification of Solid Types → The crystalline solids are classified broadly into four broad categories.

(1) Molecular Crystals → It is also known as Van der Waals crystals. In crystal bond by hydrogen bonds are usually classed with van der Waals crystals. Two forces are involved (i) dipole-dipole forces (ii) Van der Waals forces



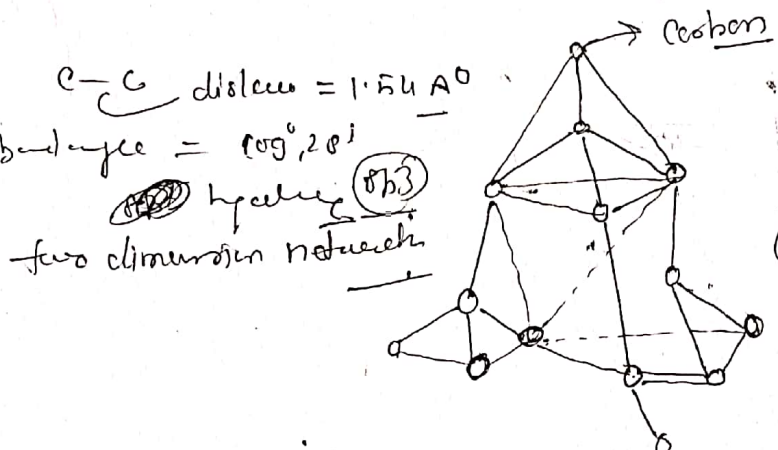
Tetrahedral structure of ice crystal

The negative end of one molecule attracts the positive end of the neighbouring molecule. (i) The molecular crystals are volatile, soft and possess low melting and bp. Because of the existence of weak intermolecular forces of attraction. The molecules retain their identity in solids because the intermolecular forces are weaker than the intramolecular forces. Since no charged particles are present, molecular crystals are insulators of electricity. Molecular crystals are easily compressible and can be easily distorted.

Ionic Crystals - The structural units are ions, both positive and negative and are held together by strong electrostatic force of attraction. (P.A. below)

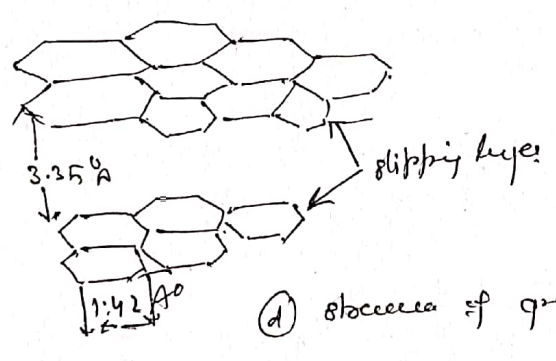
- (1) Due to the presence of strong electrostatic force of attraction between oppositely charged ions, the ionic crystals possess high lattice energy, high melting and boiling points, hardness and brittleness.
- (2) Since the ions are entrapped in fixed places in the crystal lattice and can not move, hence are insulators in the solid state. But at molten state it is a good conductor of electricity.
- (3) I.C. are soluble in polar solvents, and insoluble in non-polar solvents.
- (4) Possess very low vapour pressure.

(3) Covalent Solids:- In this, the bonds are formed only in special directions because of the direction character of the covalent bond. The structural units in covalent solids are either atoms of the same element or atoms of different elements with comparable electronegativities. ex. diamond, graphite, silicon etc. etc.

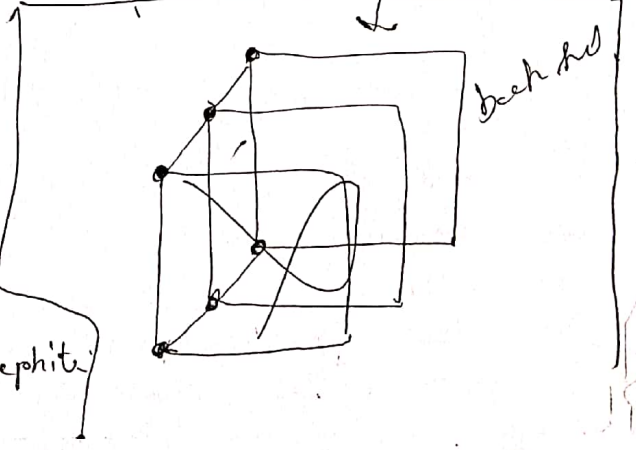


(a) Structure of diamond

The structure of the graphite is a planar network (sp^2 hybrid) and every carbon atom is bonded to three other carbon atoms covalently in a two dimensional network. Thus, all atoms in a single plane are linked to give flat hexagone, which is



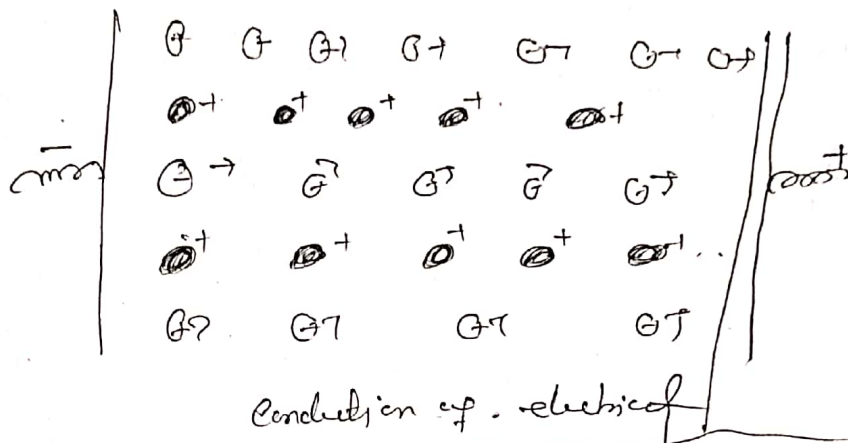
(d) Structure of graphite



- Covalent bonds are strong and directional, so covalent solids possess:
 - fairly high melting points and are hard solids. eg. diamond.
 - They are electrically insulators except graphite.
 - Depending upon the arrangement of atoms the solids can be isotropic if all the bonds are equivalent. If the bonds varies or not equivalent then these solids are anisotropic.

(14) Metallic Solids: — A metallic crystal consists of an assemblage of (+ve) ions (cores) immersed in a "pool" of mobile electrons. The binding forces that binds the (+ve) ions of the metal and the electrons cloud within its sphere of influence is called metallic bonds.

- They usually possess high melting and boiling points.
- They are very good conductors of both heat and electricity.
- They are non-directional one.
- ~~They are hard and possess high~~
- Metals possess elasticity and have high tensile strength. eg. Iron, Cu, Ag, Na etc.



BAND Theory of Solids: → MO Theory is known as band theory.

A metallic conductor is a substance with a conductivity that decreases as the temp. increases. Semiconductor is a substance with a conductivity increases with temp.

Metallic Conductors: — A large number of electrons are available for electric conduction. In terms of energy bands the conduction band (where electrons can move) of a conductor is partly filled and contains a large number of electrons. By the external electric or thermal energy, these electrons can be promoted to the nearby vacant levels.

Formation of Bands → orbital to cellulas band

(4)

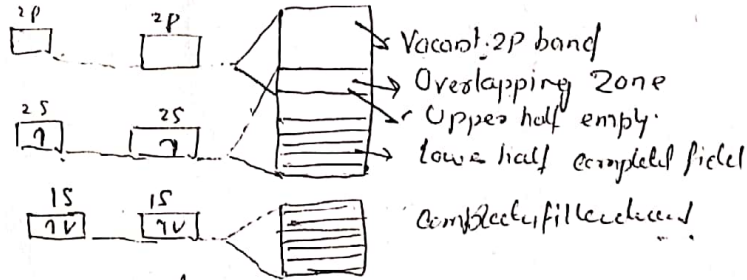
- 1s - 1s band
- 2s - 2s band
- 2p - 2p band

there is an energy gap between s band and p band is called band gap

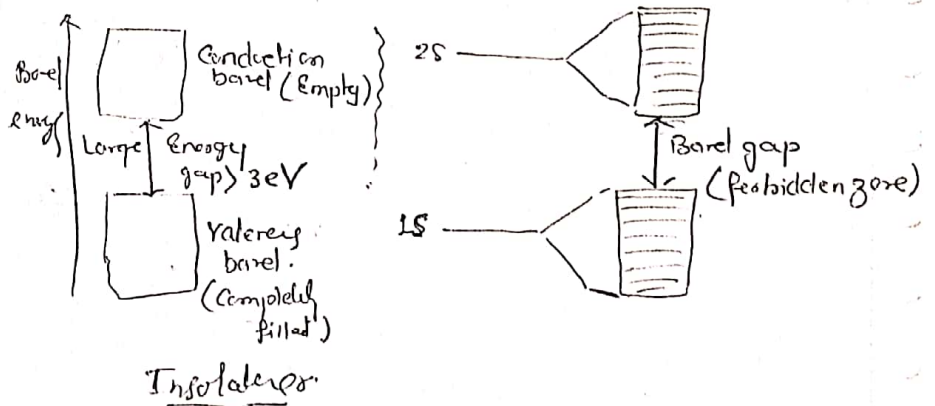
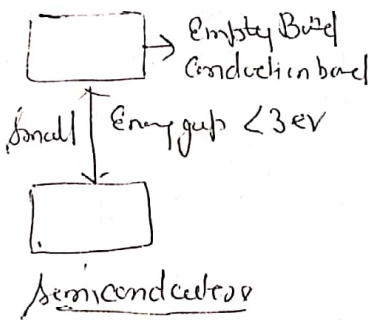
eg - $Li \rightarrow 1s^2, 2s^1, 2p^0$

1s → Filled

2s - half filled, upper half of this band is empty while the lower half is completely filled. the energy difference between these two halves is very small, the electron from the lower half can promote to the upper half by giving external energy.

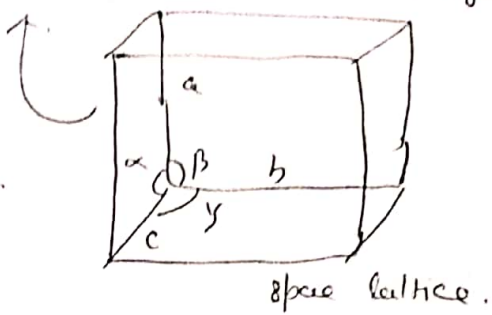


Since 2s and 2p energy levels are close to each other, hence these two orbitals can overlap so that the electrons from 2s orbitals can move to 2p orbitals.



Crystal lattices and Unit Cells:-

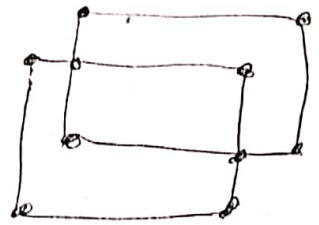
Space lattice - There is the smallest or asymmetric unit, the atoms, ions, molecules from which the crystal is formed. The positions of these asymmetric unit in a crystal relative to one another in space, are designated usually by points. The pattern formed by points representing the locations of structural units is called space lattice. The space lattice is a three dimensional infinite set of points repeated regularly through space and which defines the basic structure of the crystal. A space lattice can be described by the distance between each point along three axes (a, b, c) and three angles (α, β, γ).



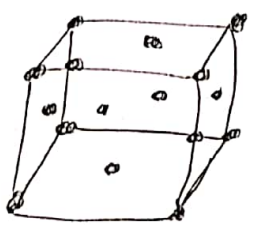
Bouvaix Lattices:-

There are only 14 different ways in which similar points can be arranged in a 3D space. These (exp) for exp, the crystals belong to cubic system have these kinds of Bouvaix lattices.

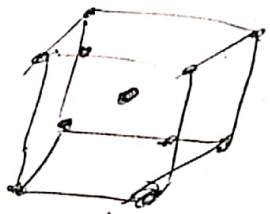
- (i) Simple cubic lattice - points arranged only at the corners of each unit.
- (ii) Face centered cubic lattice ... points at the each corner as well as at the center of each of the six faces of the cube.
- (iii) Body centered cubic lattice in which there are points of each corner and at the center of the cube.



Simple cubic



Face centered



Body centered cubic lattice.

UNIT cells:- A unit cell is formed by joining neighboring lattice points by straight lines, so that each unit cell has one lattice point as its origin. The length of the sides of the unit cell along three axes are denoted as a, b, c and the angles between as α, β, γ . The effective number of particles present in a unit cell is known as unit-cell content and this effective number of particles can be calculated.

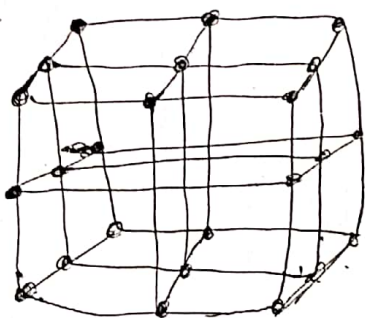
(1)

- (i) A corner is shared by eight cells, so any particles at a corner gives $\frac{1}{8}$ th of its share to each unit cell.
- (ii) A side is shared by four unit cells, only $\frac{1}{4}$ th of the particle effectively belongs to a unit cubic cell.
- (iii) A face is shared by two unit cells thereby it shares only $\frac{1}{2}$ of the particle to a unit cell.
- (iv) Any particle inside the unit cell gives its share to that unit cell completely. For ex:

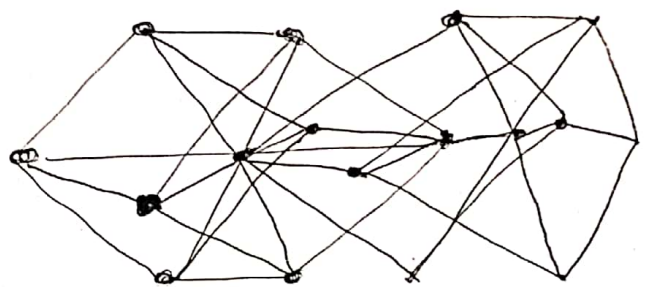
Simple cubic lattice = $\frac{1}{8} \times 8 = 1$ effective no. of particles
 Face centered = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$ " " "
 Body centered cubic = $\frac{1}{8} \times 8 + 1 = 2$ " " "

COORDINATION NUMBER (C.N.) of a cubic lattice → The total number of nearest neighbour unit which surround a given unit in the crystal lattice is called co-ordination number. The C.N. depends upon the size of the ions. The larger the size of the cation, the greater will be its C.N. as large no. of anions will be available to surround the cation. Similarly, the smaller the size of the anion, the greater will be the coordination number of the cation.

(i) Simple Cubic Cell → The C.N. in face crystals is six and it crystallizes in simple cubic (SC) lattice. In such a cell, there are six atoms which are the nearest neighbours for every corner atom. There are two nearest atoms in each axis of a three dimensional network. Thus, every ion is surrounded by six nearest oppositely charged ions.



Simple cubic 6:6 coordination



Body centered cubic lattice 8:8 co-ordination, cscp type.

1) Schottky Defect: \rightarrow This defect arises due to interaction of cations and anions. When a pair of one cation and one anion are missing from an ionic crystal lattice a large void is created so that the mass of the crystal will decrease w.r.t. the volume. Hence, the density of the crystalline ionic substance decreases considerably. This type of defect arises when the cation and anions are of similar size.

LIQUID CRYSTAL \rightarrow When the solid crystal is liquified, the molecular arrangement is not completely destroyed, since on melting a crystal expands only about 10% in volume or about 3% in intermolecular spacing. The thermal motion introduces a disorder into a crystal which would cause disturbance in the long range and destroy the crystalline arrangement. In liquid crystal, molecules have sharply anisotropic interactions. An important type of liquid crystal

Properties - ① L.C. (Liquid crystals) are used in gas liquid chromatography because their mechanical and electrical properties lie between crystalline solids and isotropic liquids.

② L.C. are employed in digital displays like digital watches, pocket calculators etc.

③ L.C. are used as solvent during the spectroscopic study of structure of anisotropic molecules.

④ Cholesteric liquid crystals are used in thermography.

CRYSTAL IMPERFECTIONS (C.I)

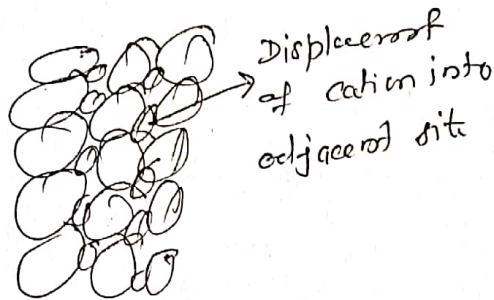
At absolute zero temp. (0K) the crystals are in the state regular geometry of their structural units. As the temp. increases, there is a deviation from their regular geometry in space lattice is known as crystal defect or crystal imperfection. C.I. occur due to (a) improper or unequal growth of crystals during crystallization (b) presence of impurities.

\rightarrow The C.I. lead to change the physical properties of the crystals like

① lower the tensile strength, ② increase brittleness and other physical

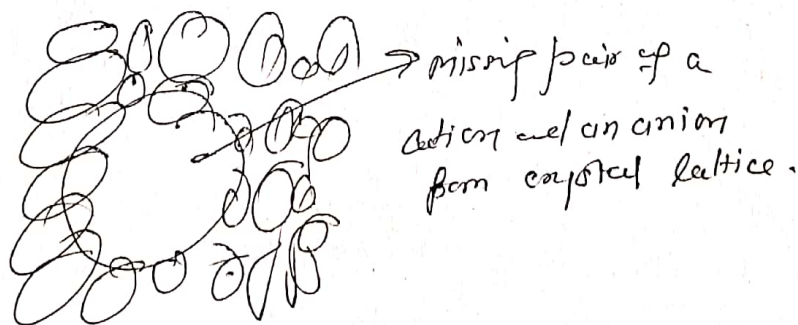
The conductivity, mechanical strength etc. can be explained by two important theories based on the size of the cation and the interaction of cation and anion.

1) Frenkel Defect: - Cations are much smaller than anions then it is possible that the cation leaves its lattice site and enters an interstitial site in an ionic crystal lattice. For e.g. the ionic crystal silver halide ($AgBr$) where the size of Br^- is much larger than the size of Ag^+ ion.



Ex: Frenkel defect in ionic crystals.

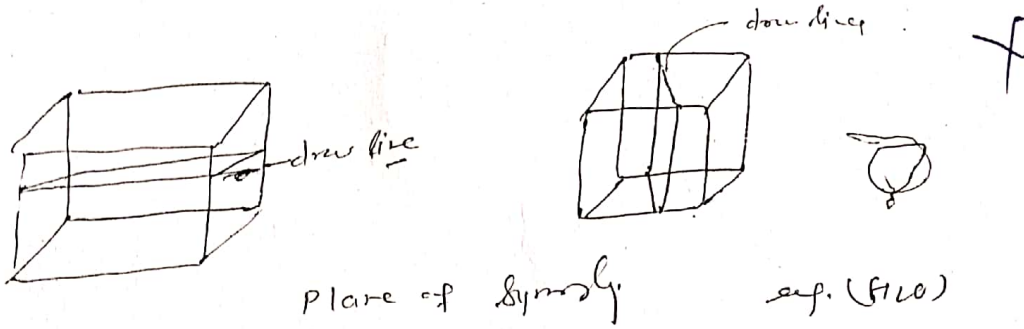
2) Schottky Defect: - This defect arises due to interaction of cations and anions. When a pair of one cation and one anion are missing from an ionic crystal lattice a large void is created so that the mass of the crystal will decrease without the volume. Hence, the density of the crystalline ionic substance decreases reasonably. This type of defect arises where the cation and anion are of similar size.



Ex: Schottky defect.

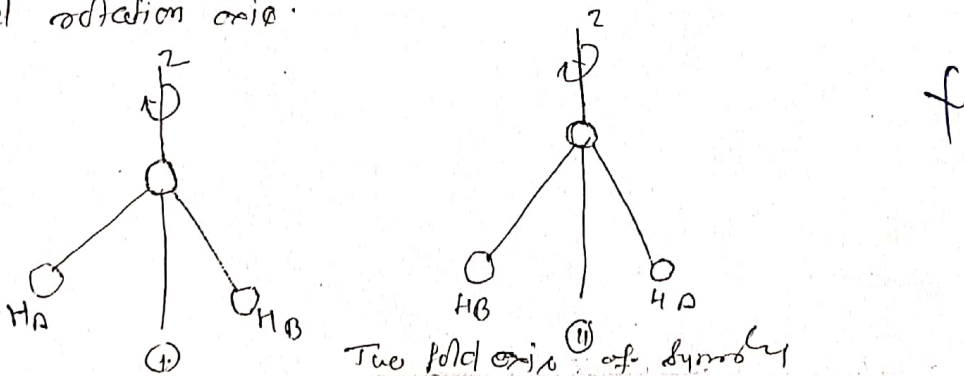
Crystal Symmetry :- Symmetry in crystals may be due to a plane, a line or a point. Three types of symmetry -

(1) Plane of Symmetry :- It can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other. eg, in case of water molecule, two planes of symmetry can be drawn along z-axis.



(2) Axial of Symmetry :- An axis of symmetry is an imaginary line drawn through the crystal such that during rotation of the crystal through 360° , the crystal presents exactly the same appearance more than once. If similar view appears twice, it is called an axis of two fold symmetry or diad axis. If it appears thrice, it is an axis of three fold symmetry or triad axis, and so on.

(i) Consider the water molecule, an axis passing through the centre perpendicular to the plane in such that when molecule is rotated through 180° , it reappears exactly the same appearance two times in one revolution (rotation through an angle of 360°). Thus, the axis shown for H_2O is $\frac{360}{180} = 2$ fold rotation axis.

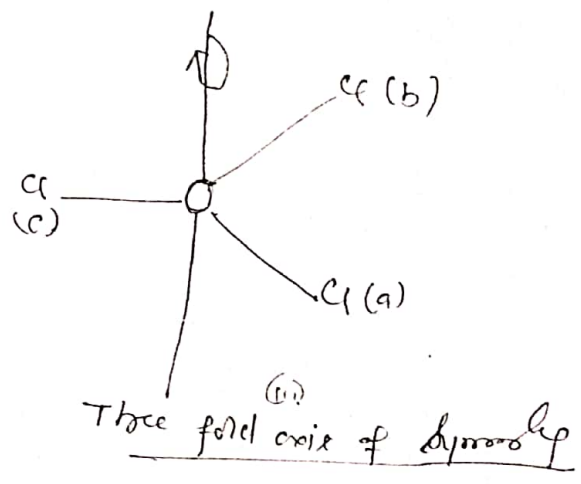


consider the molecule of BF_3 , i.e. triangular plane. if we choose ⁽ⁱⁱ⁾ an axis normal to the plane of molecule and passing through the boron atom will generate an equivalent appearance after every rotation of 120° . thus this axis is $360^\circ/120^\circ = 3$ fold axis and there are three such C_3 fold axis.

(iii) PF_6^{2-} - four fold axis.

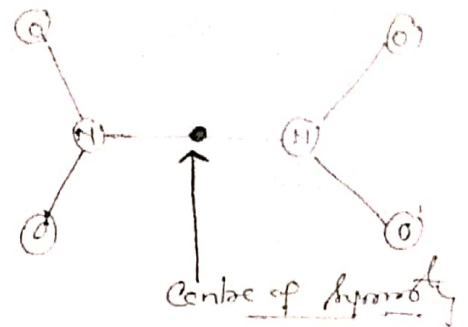
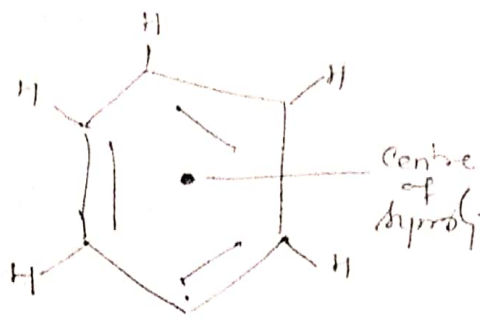
(iv.) In case of benzene, there is six fold axis of rotation, passing through centre of symmetry, six fold axis means the original appearance is repeated after an angle of 60° . A hexagonal crystal has six fold axis of symmetry.

In general, if the same appearance of a crystal is repeated on rotating through an angle of $360^\circ/n$, around an imaginary axis, the axis is called an n-fold axis. The axis of symmetry can be represented by rotation C_n , where n is the order of axis.



Order of Axis (n)	Type of Axis	Degree of rotation	Symbol.
1	Identity	360°	I or E
2	Two fold	180°	C_2
3	Three fold	120°	C_3
4	Four fold	90°	C_4
6	Six fold	60°	C_6

(ii) Centre of Symmetry - It is point at the centre of the crystal. so that any line drawn through it will meet the surface of the crystal at equal distances on either side. It is noteworthy that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.



Centre of Symmetry
"Seven Crystal System"

Crystal System	Bravais Lattices	Minimum Symmetry Elements	Parameters of Unit Cell Intercepts	Crystal Angles	Examples
1. Cubic	Primitive, Face-centred, Body-centred	3-fold, 4-fold	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, Diamond, Zircon blende.
Orthorhombic	Primitive, face-centred, Body-centred, End-centred	Three mutually perpendicular 2-fold	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_3 , K_2SO_4 , $BaSO_4$, $PbCO_3$, Rhombic Sulphur.
Tetragonal	Primitive, Body-centred,		$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	ZnO_2 , SnO_2 , TiO_2 .
Monoclinic	Primitive		$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Na_2SO_4 , $10H_2O$
Triclinic	Primitive		$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$.
Hexagonal	Primitive		$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	HgS , I_2 , Graphite, Zn , Zd .
Rhombohedral	Primitive		$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$, $\beta \neq 90^\circ$	NaN_3 , As , Sb , Bi , Calcite ($CaCO_3$).