~~Electrochemistry~~ Chapter ~~2~~ 1

Chemistry by Sumit Mishra

The Solid State

* Characteristic properties

i) The have definite mass, volume and shape.
ii) They have strong intermolecular forces and thus possesses very short intermolecular distances
iii) They are incompressible and rigid.
iv) The constituent particles have fixed positions and can oscillate only about their mean position.

* Classification of solids

1) Crystalline Solids

→ In crystalline solids, the constituent particles are arranged in a definite geometric pattern in all the three dimensions. In fact, a crystalline solid usually consists of a large no. of small crystals, each of them having a ~~small~~ same regular pattern.

→ It has a long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal.

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example: Sodium chloride, metals, gems, quartz etc.

⇒ Melting point of crystalline solids

→ Crystalline solids have sharp and characteristic melting points.

→ They have definite enthalpy of fusion i.e heat required to melt per unit mass of a crystal is always same for that crystal.

→ Due to these characteristics, crystals are called true solids.

⇒ Nature of Crystalline solids

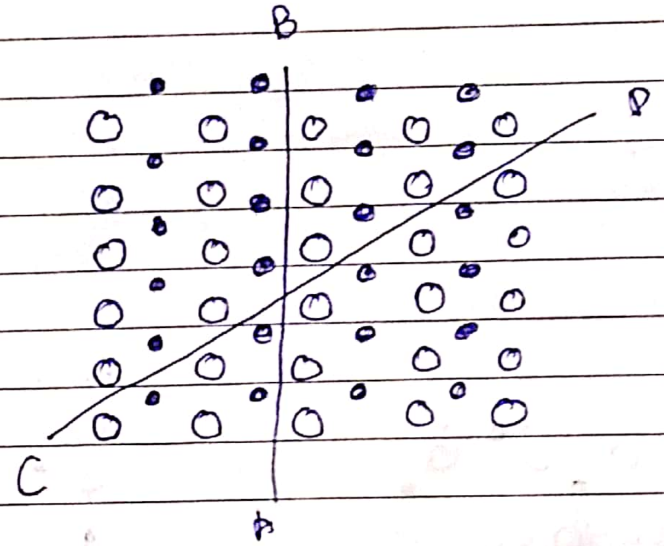
→ ~~Crystalline solids are anisotropic in nature~~

[Anisotropic: It is the property due to which crystals show different electrical and optical properties in different planes of the same crystals]

electrical property :- Electrical resistance
optical property :- Refractive index.

→ Crystalline solids are anisotropic in nature i.e some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arise from different arrangement of particles in different directions.

– Since, the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction.



on cutting with sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.

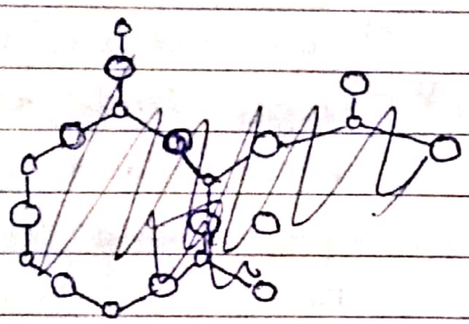
uses :- Calcite crystal is used in making optical instrument such as prism.

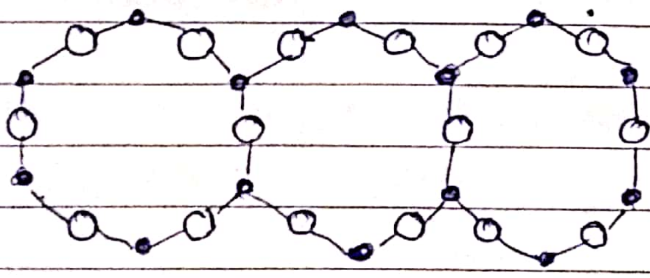
2) Amorphous Solids (Amorphous → No form)

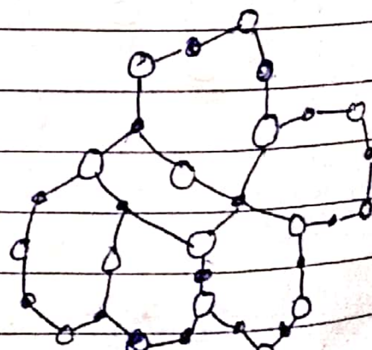
⇒ Arrangement of constituent particles

→ An amorphous solid consists of particles of irregular shape. The arrangement of constituent particles in such a solid has only short range order. This means a regular and periodically repeating pattern is observed over short distances only.

ex:- Quartz glass, rubber and plastics.







~~quartz/ Quartz (SiO2)~~
~~Crystalline~~

~~Silica glass~~
~~Quartz glass~~
~~fused silica~~
~~Amorphous.~~

Quartz (SiO_2)

Crystalline

Quartz glass

(fused silica)

Amorphous

⇒ Effect of Temperature

→ Amorphous solids soften over a range of temperature and can be moulded and blown into various shapes.

→ On heating they become crystalline at some temperature. That's why a few glass objects from ancient civilisations are found to become milky in appearance as they become crystalline due to regular heating and cooling over a long period of time.

→ Like liquids, amorphous solids have a tendency to flow but very slow. Therefore they are also called pseudo solids or supercooled liquids.

example: Glass panes fixed to windows or doors of old-buildings are found slightly thicker at the bottom than at top.

⇒ Nature of Amorphous solid

Amorphous solids are isotropic in nature. It is because there is no long range order of arrangement in them and short range arrangement is irregular along all the directions. Thus, the value of any physical property would be same along any direction.

uses: Amorphous solids (silica) is used as photovoltaic material for the conversion of sunlight into electricity.

* Classification of crystalline Solids

Crystalline solids are classified on the basis of nature of constituent particles and the intermolecular forces operating b/w them, into four categories.

1) Molecular Solids (Constituent particles are molecules)

a) Polar Molecular Solids

→ They Consist of molecules like HCl, SO_2 having polar covalent bonds.

→ In these solids, molecules are held together by relatively stronger dipole-dipole interactions.

→ These solids are soft, non-conductors of electricity and high melting points than that of non-polar. ~~[conduct electricity in molten state and aqueous solution]~~.

→ They exist in gaseous or liquid state at room temperature and pressure.

eg:- Solid SO_2 and Solid NH_3.

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b) Non-polar Molecular Solids

→ Constituent particles are either atoms or the molecules formed by non-polar covalent bonds (H_2, Cl_2, and I_2)

→ In these solids, atoms or molecules are held together by weak dispersion forces or London Forces (a type of van der ~~wall~~ waals forces) Therefore these solids are soft, non-conductor of electricity and have low melting point and in gaseous or liquid state at room temperature and pressure.

c) Hydrogen bonded Molecular solids: H_2O - ice.

These are volatile liquids or soft solids at room temp and pressure

(2) Ionic Solids

→ In these solids, constituent particles are cations and anions. Cations and anions are arranged in 3-D space.

→ These ions are held together by strong coulombic (Electrostatic) forces.

→ These solids are hard, brittle and have high melting and boiling points.

→ In solid state, ionic solids are electrical insulators because ions are not ~~fre~~ free to move. But in molten state or in aqueous solution they conduct electricity because ions become free to move.

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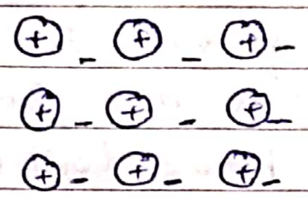
3. Metallic Solids

→ In these solids, constituent particles are positively charged metal ions called Kernels and free electrons.



→ These electrons can easily flow throughout the metal crystal like water in the sea. Hence, we call it a sea of free electrons.

→ Each metal atom contributes one or more electrons towards this sea of mobile electrons.

→ These free and mobile electrons are responsible for high electrical and thermal conductivity of metals.

→ The force that holds the metal ions together in the crystal is called mettalic bond.

→ Metals possess high melting point due to the strong metallic bonds.

4. Covalent or Network Solids

→ A wide variety of crystalline solids of non-metals result from the formation of covalent bonds b/w adjacent atoms throughout the crystal.

→ They are also called Giant molecules.

→ Covalent bonds in network like structure are strong and directional in nature. therefore atoms are held very strongly at their positions.

→ These solids are very hard, brittle and have extremely high melting points and may even decompose before melting.

→ They are insulators and do not conduct electricity. e.g. diamond.

Structure of Solids

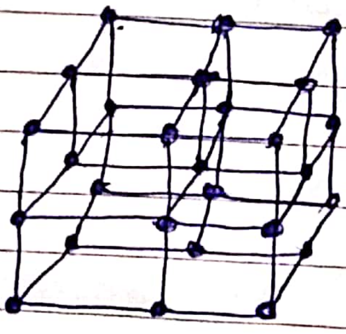
Crystal Lattice

→ The main characteristics of crystalline solids is a regular and repeating pattern of constituent particles.

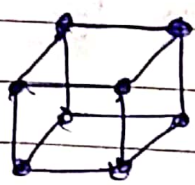
→ If the three-dimensional arrangement of constituent particles in a crystal is represented diagramatically in which each particle is depicted as a point, then the arrangement is called crystal lattice.

→ Thus a regular arrangement of the constituent particles of a crystal in 3-D space is known as crystal lattice.

→ There are only 14 possible 3-D Lattices known as Bravais lattices.



crystal Lattice



unit cell

Characteristics of Crystal lattice

i) Each point in a crystal lattice is called Lattice point or lattice site.

ii) Each point in a crystal lattice represents one constituent particles which may be an atom, a molecule or an ion.

iii) Lattice points are basically joined by straight lines to bring out the geometry of the lattice.

Unit Cell

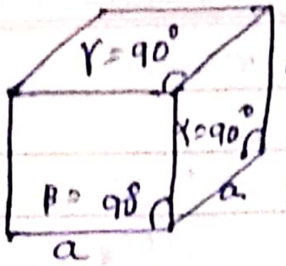
The smalles portion of the crystal Lattice which when repeated in different directions, generates the entire lattice.

Types of Unit Cell

① ~~Cubic~~ Primitive Unit Cell

when constituent particles are present only on the the corner positions of the unit cell, then unit cell is called primitive unit cell. Primitive unit cells are of seven types.

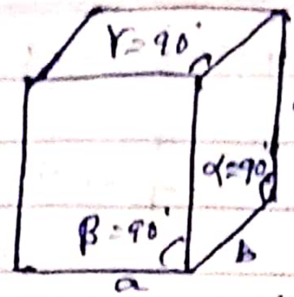
$NaCl$, ZnS and Cu



Cubic

($\alpha = \beta = \gamma = 90°$)

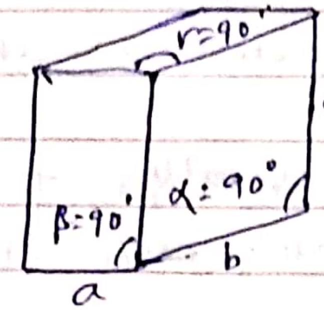
White tin, SnO_2, TiO_4, $CaSO_4$



Tetragonal

($\alpha = \beta = \gamma = 90°$)

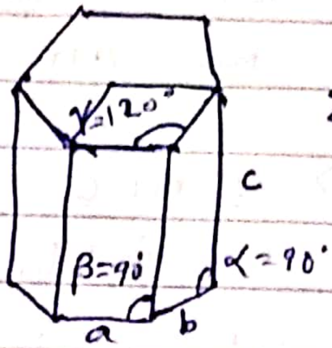
KNO_3, $BaSO_4$



Orthorhombic

($\alpha = \beta = \gamma = 90°$)

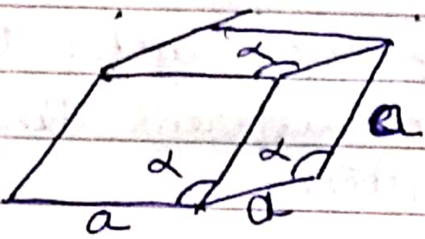
ZnO, CdS



Hexagonal

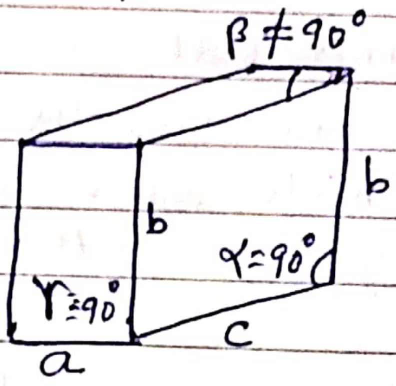
$\alpha = \beta = 90°$ $\gamma \neq 90°$

(Calcite) $CaCO_3$, HgS (Cinnebar)



Rhombohedral / Trigonal

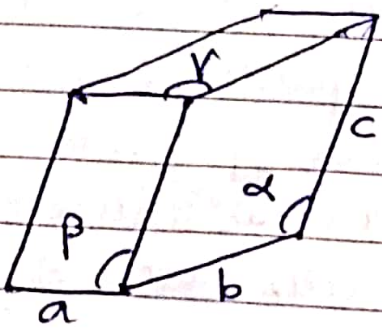
$\alpha = \beta = \gamma \neq 90°$



$Na_2SO_4 \cdot 10H_2O$

Monoclinic

$\alpha = \gamma = 90°$ $\beta \neq 90°$

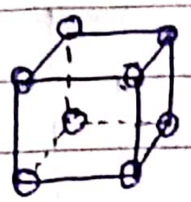


$CuSO_4 \cdot 5H_2O$, H_3BO_3, $K_2Cr_2O_7$

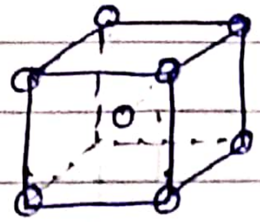
Triclinic

$\alpha \neq \beta \neq \gamma \neq 90°$

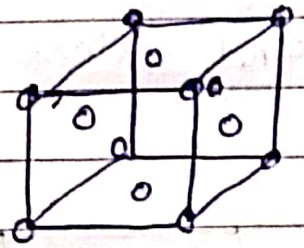
Unit cells of 14 Types of Lattices (Bravais Lattice)



Primitive
(Simple)

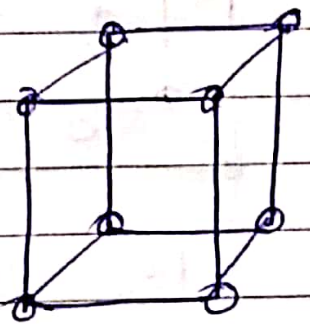


Body Centered

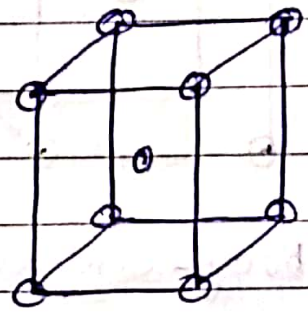


face centered

3 Cubic Lattice



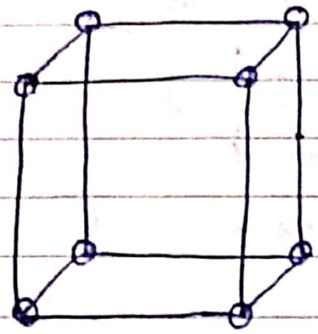
Primitive



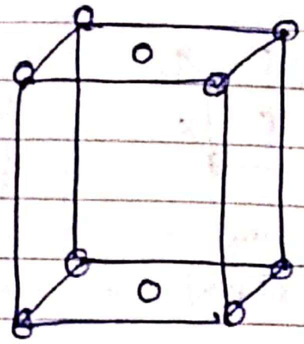
Body Centered

2 Tetragonal Lattice

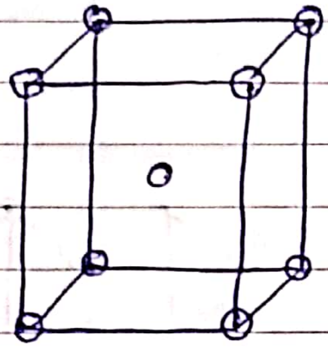
4 orthorhombic lattice



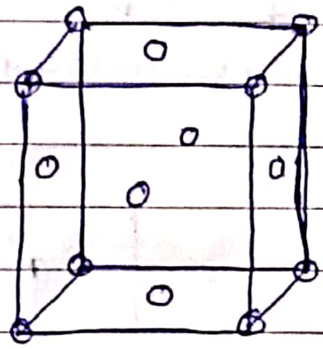
Primitive



End centered

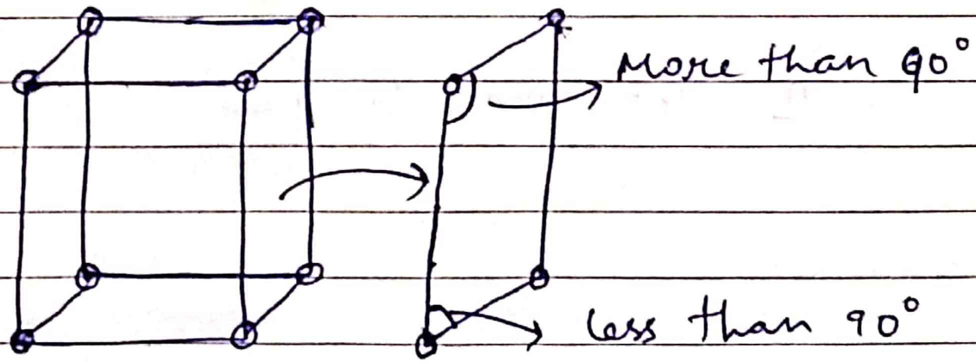


Body-centred

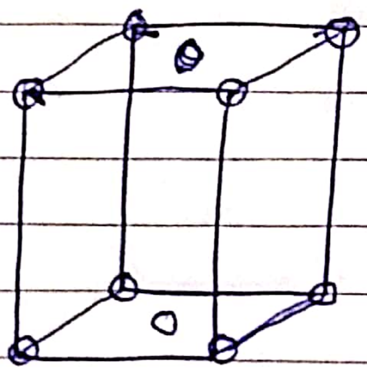


Face centered

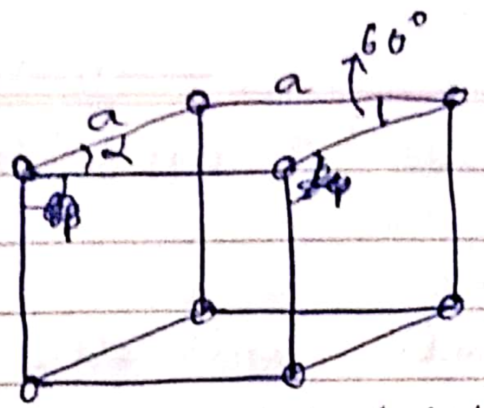
Primitive



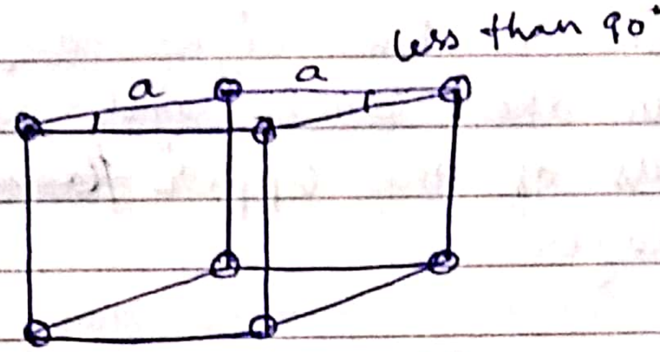
End-centered



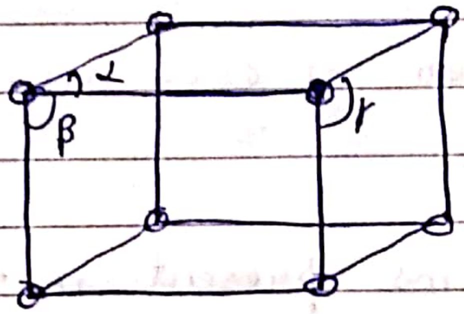
Two monoclinic lattices



Hexagonal Lattice



Rhombohedral Lattice



Triclinic Lattice.

Number of Atoms in a unit cell

* Simple or Primitive Cubic unit cell.

→ Primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared b/w eight adjacent unit cells in the same layer and four unit cells of the upper ~~(lower)~~ or lower layer.

∴ only $\frac{1}{8}$th of an atom actually belongs to a particular unit cell.

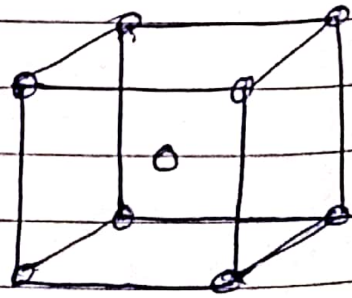
. Thus contribution of each atom present at the corner $= \frac{1}{8}$

∴ No. of atoms present in the unit cell $= \frac{1}{8} \times 8 = 1$.

* Body Centered cubic (BCC) unit cell

No. of atoms $= \frac{1}{8} \times 8 + 1$

$= 2$.



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* Face - Centred Cubic (FCC) unit cell.

~~note~~ A face centred unit cell contains atoms at all the corners and at the centre of all the faces of the cube.
Each atom located at face-centre is shared between two adjacent unit cells and only $\frac{1}{2}$ of each atom belongs to a unit cell.

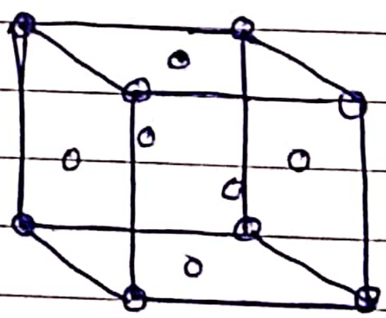
Thus, contribution of each atom on the face $= \frac{1}{2}$

As this lattice has 8 atoms on the corners and 6 atoms on the faces

$\therefore$ Contribution by atoms on the corner
$$= \frac{1}{8} \times 8 = 1$$

Contribution by atoms on the face-centred
$$= \frac{1}{2} \times 6 = 3$$

$\therefore$ Total no. of atoms present in per unit cell $= 1 + 3$
$= 4$.

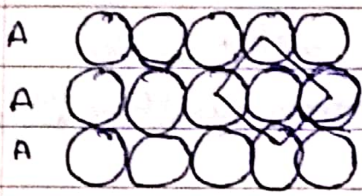


close packing: Packing of spheres in such a way that they occupy the max available space and min. empty space. and hence the crystal has max density.

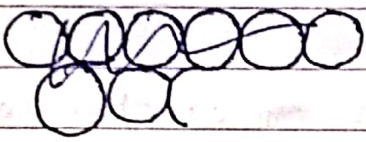
Close Packing in Crystals

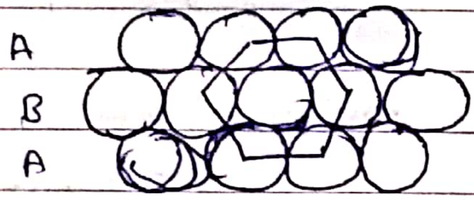
a. Close packing in one-Dimension

b. Close packing in 2 dimension.



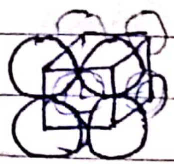
Square close packing

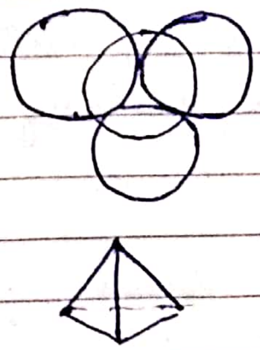




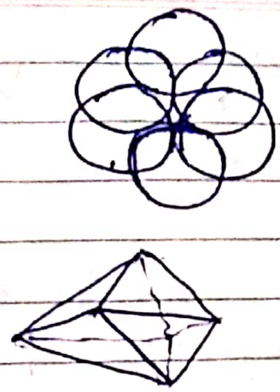
Hexagonal close packing.

c. Close-packing in 3-D.





tetrahedral void



Octahedral void.

The voids or holes in crystals are also called interstices

Co-ordination number:

The number of closest neighbours of any constituent particle in the crystal lattice is called its coordination no.

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Calculation of the Space occupied i.e Packing Efficiency or Packing fractions,

→ The % of the total space filled by the particles is called packing efficiency or the fraction of the total space filled is called packing fraction.

(1) In a Simple cubic unit cell.

Location of octahedral voids and tetrahedral void.

Summary

If there are N - atoms in a packing

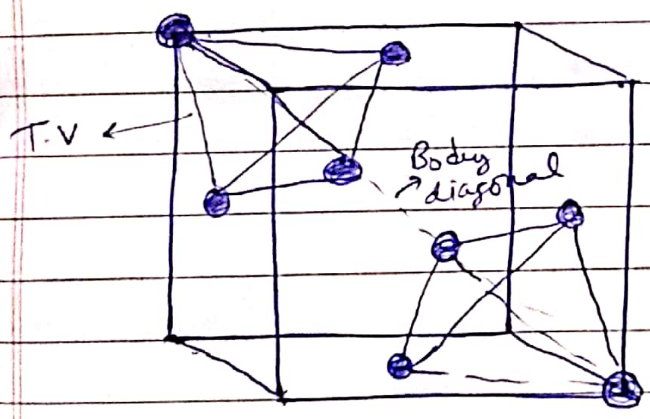
no. of Tetrahedral void = 2N

no. of Octahedral void = N

$\frac{r_{c^+}}{r_{a^-}} = 0.225$ [In tetrahedral void]

$\frac{r_{c^+}}{r_{a^-}} = 0.414$ [In octahedral void]

⇒ Location of T.V in FCC.



There are 2 T.V at each body diagonal.

no. of body diagonal = 4

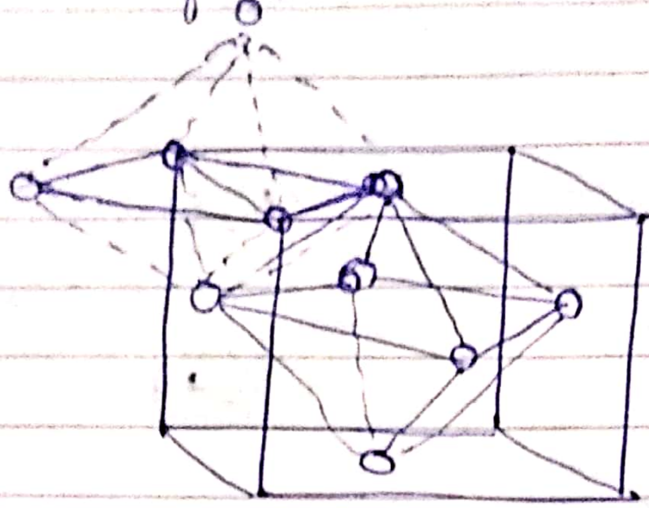
∴ no. of T.V = 2×4
= 8.

In fcc no. of atom = 4

∴ no. of tetrahedral void = 2×4
= 8.

∴ no. of T.V = 2N.

location of O.V in FCC



one O.V at the centre of the each edge and one at the centre of Cube

no. of actahedral void $= 12 \times \frac{1}{4} + 1 \times 1$

$= 3 + 1$

$= 4$

and no. of atoms in FCC $= \frac{1}{8} \times 8 + \frac{1}{2} \times 6$

$= 4.$

$\therefore$ If N no. of atom in a lattice then no. of actahedral void $= N$