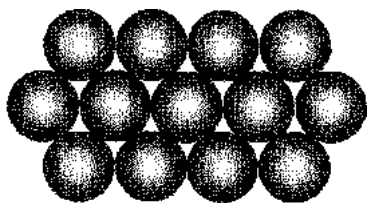


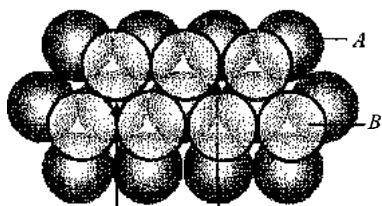
Place a sphere on a flat surface. Surround it with six equal spheres as close as possible in the same plane. Looking down on the plane, the projection is as shown in figure.



'A' layer of spheres

Let us call this layer as the *A* layer.

Now form a second layer over the first layer of equally bunched spheres, so as to nestle into the voids (empty spaces). It will be clearly seen that once a sphere is placed over a void, it blocks the void which are adjacent to that void. Let us call this layer as the *B* layer.



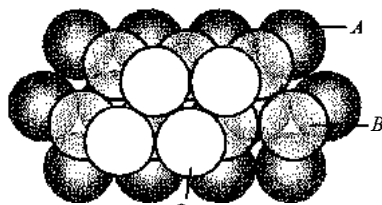
'x' type void 'y' type void
'A' and 'B' layer of spheres

Hexagonal Close Packing

- If a sphere is placed on the *x* - type of voids, it would resemble the *A* layer of spheres in the sense that it eclipses the spheres of the *A* layer. This arrangement (*i.e.*, *ABAB...*) is called the hexagonal close packing (*hcp*) or hexagonal primitive.

Cubic Close Packing

- On the other hand, if the spheres were to be placed on the *y* - type of voids, it would neither eclipse the *A* layer nor the *B* layer of spheres. This would clearly be a unique layer. Let us call this layer as the *C* layer. This arrangement (*i.e.*, *ABCABC...*) is called the cubic close packing.

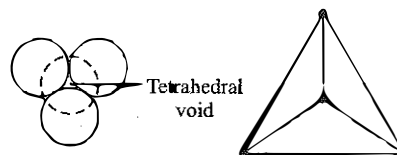


'A', 'B' and 'C' layer of spheres

Void Space or Holes

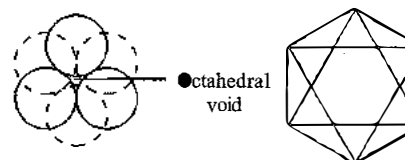
- In a unit cell some empty space exists between spheres, this is called **void space** or **hole**, also called **interstitial void**, or **interstices**.
- Two types of interstitial voids are present in three dimensional close packing systems:
 - **Tetrahedral Voids** are holes or interstices surrounded by four spheres present at the corners of a tetrahedron.

Number of tetrahedral voids is double the number of spheres.



- **Octahedral Voids** are holes surrounded by six spheres located on a regular octahedron.

Number of octahedral voids is equal to the number of spheres.



Packing Efficiency

- The percentage of total space occupied by the particles is known as packing efficiency.

Packing efficiency

$$= \frac{\text{Volume occupied by spheres in unit cell}}{\text{Total volume of unit cell}} \times 100$$

Type of Packing	Packing efficiency
<i>hcp</i>	74%
<i>ccp</i>	74%
<i>bcc</i>	68%
simple cubic	52.4%

Radius Ratio

- Radius ratio is the ratio of the radii of positive and negative ions in a crystal:

$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}} = \frac{r_+}{r_-}$$

The coordination number and structure of ionic solid depends upon the relative size of ions, *i.e.*, on their radius ratio.

Radius Ratio	C.N.	Structural Arrangement	Example
0.155–0.225	3	Planar triangular	Boron oxide
0.225–0.414	4	Tetrahedral	ZnS
0.414–0.732	6	Octahedral	NaCl
0.732–1	8	Body-centred cubic	CsCl

Structure of Ionic Solids

- In simple ionic compounds, generally two arrangements are possible *hcp* and *ccp*. The larger ions *i.e.* anions adopt these arrangement and cations occupy different voids.

	Compound	Description	Co-ordination Number	Other examples
1.	NaCl (Rock salt str.)	ccp arrangement of Cl ⁻ and Na ⁺ occupy all octahedral voids	Na ⁺ = 6 Cl ⁻ = 6	LiCl, KCl, AgCl AgBr, CaO, MgO
2.	CsCl	Simple cubic arrangement of Cl ⁻ and Cs ⁺ in cubic sites	Cs ⁺ = 8 Cl ⁻ = 8	CsBr, CsI
3.	ZnS (Zinc Blende str.)	ccp arrangement of S ²⁻ and Zn ²⁺ in alternate tetrahedral voids	Zn ²⁺ = 4 S ²⁻ = 4	CuCl, CuI, BeO, AgI
4.	ZnS (Wurtzite)	hcp arrangement of S ²⁻ and Zn ²⁺ in alternate tetrahedral voids	Zn ²⁺ = 4 S ²⁻ = 4	
5.	CaF ₂ (Fluorite str.)	ccp arrangement of Ca ²⁺ and F ⁻ in all tetrahedral voids	Ca ²⁺ = 8 F ⁻ = 4	BaF ₂ , SrF ₂
6.	TiO ₂ (Rutile str.)	Distorted bcc of Ti ⁴⁺ and O ²⁻ in octahedral voids	Ti ⁴⁺ = 6 O ²⁻ = 3	MgF ₂ , ZnF ₂ SnO ₂ , PbO ₂
7.	Na ₂ O (Anti-fluorite)	ccp arrangement of O ²⁻ and Na ⁺ in all tetrahedral voids	Na ⁺ = 4 O ²⁻ = 8	Li ₂ O, K ₂ S

IMPERFECTION IN SOLIDS

- An ideal crystal is the one which has the same unit cell and contains the same lattice points throughout the crystal. At absolute zero all ionic crystals show well ordered arrangements of ions and there are no defects, but as temperature is increased there is a chance that one or more of the lattice sites may remain unoccupied by the ions. This constitutes a defect. The number of n such defects per cm³ at a given temperature T on the absolute scale, is given by the equation

$$N_V = N \exp. (-Q_V/KT)$$

N_V = Equilibrium no. of vacancies

N = Total no. of atomic sites

Q_V = Energy required for vacancy formation (in eV)

K = Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$ or $8.62 \times 10^{-5} \text{ eV K}^{-1}$)

T = Temperature (in K)

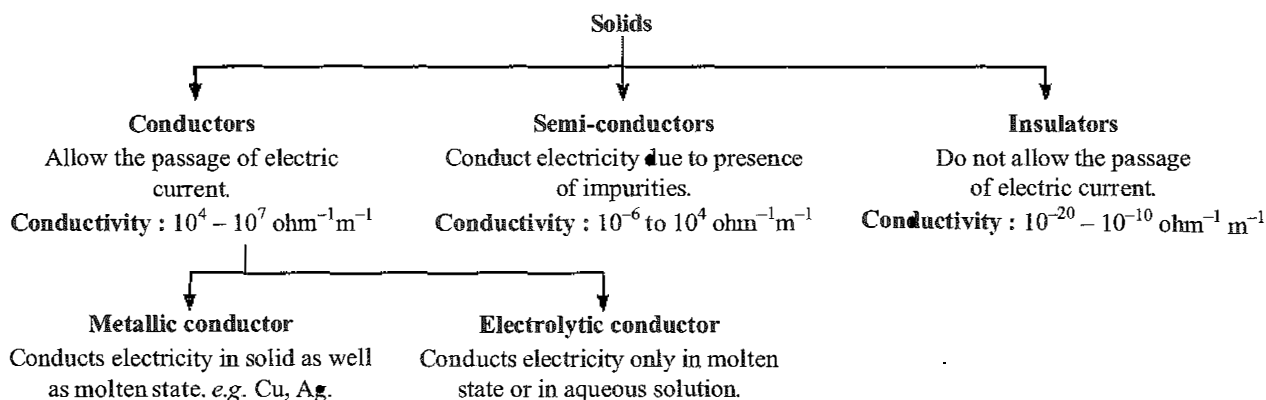
- Two types of defects are generally observed in crystals. These are
 - **Stoichiometric point defects** : Stoichiometric defects do not disturb the ratio of positive and negative ions, only their position changes. These are of following types.
 - Schottky defects are common in ionic compounds of high C.N., where one positive and one negative ion

go missing from their respective sites. e.g. NaCl.

- Interstitial defects are caused due to ions occupying some of the vacant interstitial sites.
- Frenkel defects are common in ionic compounds of low C.N., where an ion leaves its correct site and occupies an interstitial site. e.g. AgBr
- **Non-Stoichiometric point defects** : Compounds in which the ratio of ions is not exactly the same as shown by its chemical formula are non-stoichiometric. These are of following types :
 - Metal excess defects or anionic vacancies defect, arises when a negative ion is absent from its site, resulting in excess of metal ion.
 - Metal excess defects due to interstitial cations arise due to presence of an extra cation in an interstitial site.
 - Metal deficiency due to cation vacancies arises when a metal ion is absent from its lattice site. To balance the charge, an adjacent ion has a higher positive charge.

PROPERTIES OF SOLIDS

- **Electric properties** : The electrical conductivity of solids varies from 10^{-20} to $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$. So on the basis of electric conductivity solids are classified as:



BAND THEORY

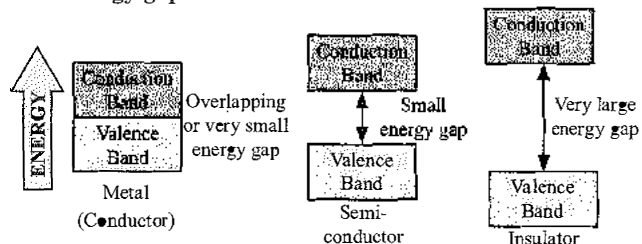
- In metals, conductivity strongly depends on the number of valence electrons available per atom. The difference in electrical conductance behaviour of conductors, insulators and semiconductors can be explained with the help of band theory.

The atomic orbitals of metal atoms form a large number of molecular orbitals which are so close in energy to each other that they form a band. If the band is partially filled or it overlaps with a higher energy unoccupied band, then electrons can easily flow under an applied electric field and metal shows conductivity.

Therefore, when some electric field is applied electrons can easily move within partially filled band or empty overlapping band and this movement is responsible for electrical conductance of the substance. This type of behaviour is shown by metals.

In general, the electrical conductance of solids depends upon the energy gap between the filled valence band and next higher vacant energy band. The outermost filled energy band is called valence band and the next empty band in which electrons can move is called conduction band.

The spaces between valence band and conduction band represent energies forbidden to electrons and are called energy gaps or forbidden zone.



- In metals, the conduction band is close to valence band and, therefore, the electrons can easily go into the conduction band. Therefore, metals are good conductors.
- In insulators, the energy gap between valence band and conduction band is very large.
- Semi-conductors have only small difference in energy between the filled valence band and empty conduction band.
 - Electrical conductivity of semi-conductors increases with rise in temperature because more electrons can jump to the conduction band.
 - Conductivity of semi-conductors can also be increased by doping *i.e.*, a process of adding impurities to a crystalline substance to change its properties. Impurities are either electron rich or electron deficient. The semiconductors thus obtained are ;
 - n*-type semiconductors : When group-14 elements doped with group-15 elements (conductivity due to electrons) *e.g.*, Silicon doped with phosphorus.
 - p*-type semiconductors : When group-14 elements doped with group-13 elements. (conductivity due to holes). *e.g.*, Germanium doped with Boron.

Magnetic properties

- Magnetic moment arises due to orbital motion of the electron around the nucleus and spin of electron around its own axis. The magnetic properties of solids are related to the electronic structure. On the basis of response toward magnetic field solids are divided as follows:

