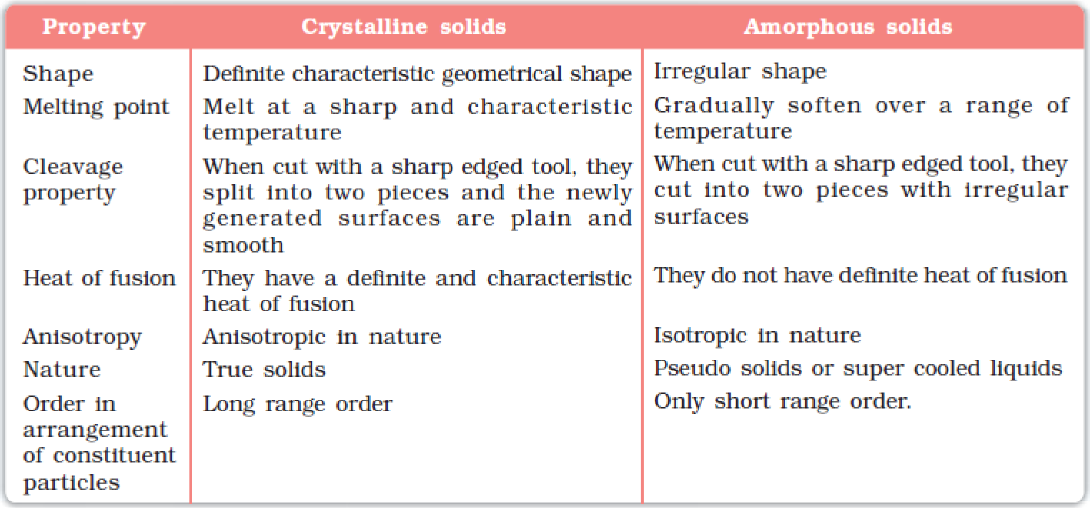
Chapter 1: The Solid State

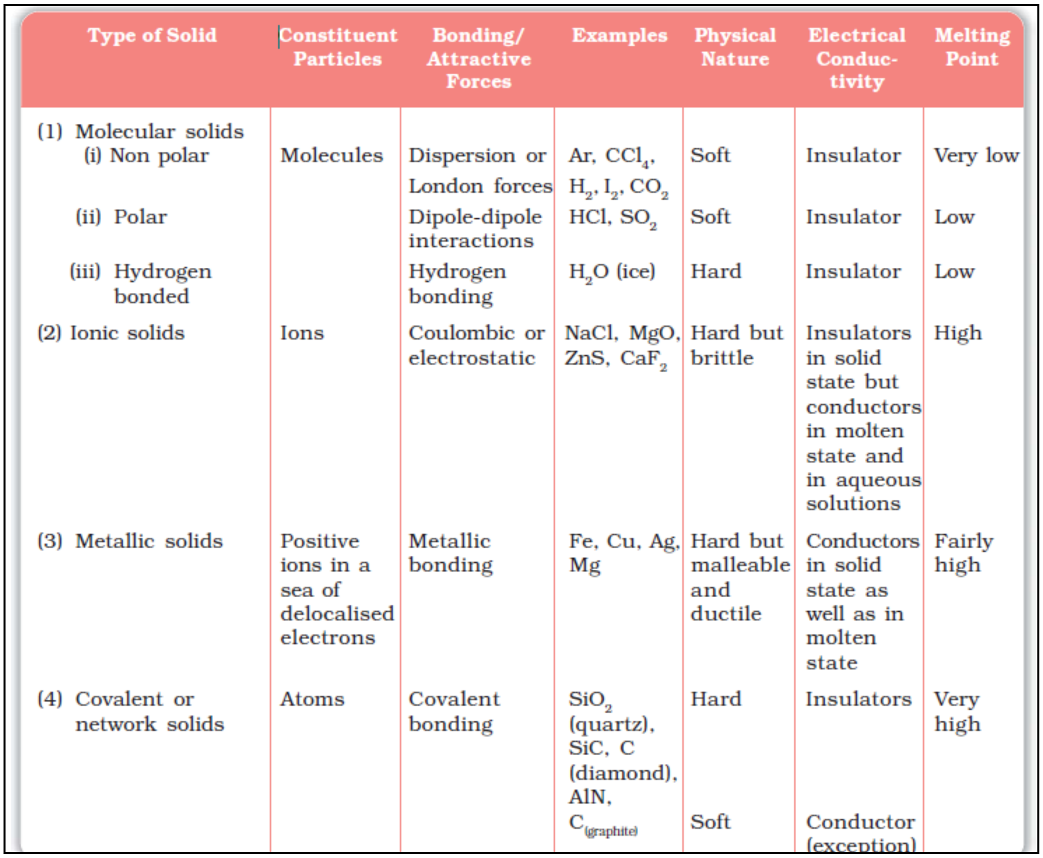
1. Solids: Solids are the chemical substances which are characterized by define shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces

2. Types of Solids: Solids are two types: Crystalline solids and amorphous solids. Distinction between Crystalline and Amorphous Solids as follows



Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

3. Classification of crystalline solids:



Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular solids						
(i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN,	Hard	Insulators	Very high
			$C_{(graphite)}$	Soft	Conductor (exception)	

4. Crystal Lattices: A regular ordered arrangement of constituent particles in three dimensions is called crystal lattice.

5. Unit Cell: The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

Part of Unit Cell: Allen: 4

(i) No. of Corner = 8 (ii) No. of Face = 6 (iii) No. of Edge = 12

(iv) No. of body center = 1 (v) No. of Face diagonal = 12 (vi) No. of body diagonal = 4

Types of Unit Cell:

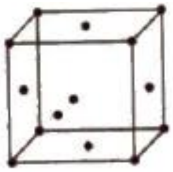
(i) **Simple or primitive cubic unit cell:** In which the particles are present at the corners only.

(ii) **Face centred cubic (FCC) unit cell:** In which the particles are present at the corners as well as at the centre of each of six faces.

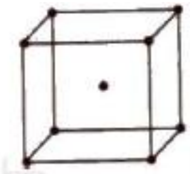
(iii) **Body centred cubic (BCC) unit cell:** In which the particles are present at the corners as well as at the centre of the unit cell.

(iv) **End centered cubic unit cell:** In which the particles are present at the corners and at the centre of two opposite faces.

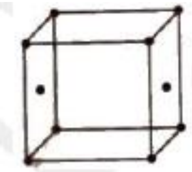
primitive



Face centred



Body centred



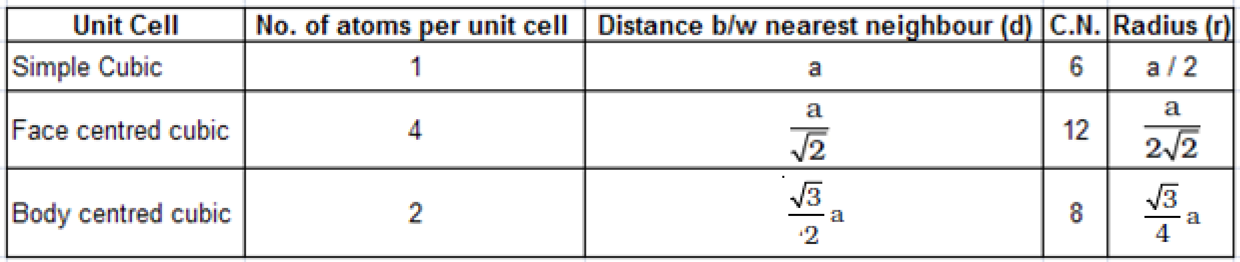
End centered

6. Number of Atoms (Particles) in a Unit Cell:

Unit Cell	No. of atoms / spheres			Total
	Corner	Face	Centre	
Simple Cubic	$8 \times \frac{1}{8}$	~	~	1
Face centred cubic	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	~	4
Body centred cubic	$8 \times \frac{1}{8}$	~	1	2
End centred cubic	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$	~	2

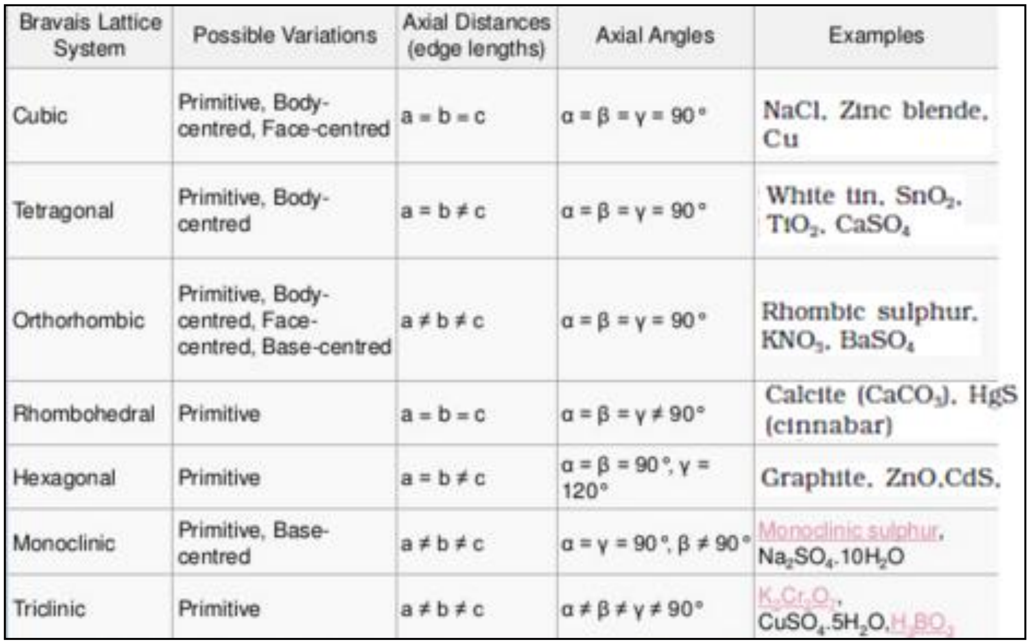
Note: Number of lattice point in Primitive = 8, FCC =14, BCC= 9

7. Different parameters of Cubic System:



Unit Cell	No. of atoms per unit cell	Distance b/w nearest neighbour (d)	C.N.	Radius (r)
Simple Cubic	1	a	6	a / 2
Face centred cubic	4	$\frac{a}{\sqrt{2}}$	12	$\frac{a}{2\sqrt{2}}$
Body centred cubic	2	$\frac{\sqrt{3}}{2}a$	8	$\frac{\sqrt{3}}{4}a$

8. Crystal Systems: There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called **Bravais Lattices**. On the basis of the axial distances and the axial angles b/w the edges, the various crystals can be divided in to seven systems. These are listed in below table-



Bravais Lattice System	Possible Variations	Axial Distances (edge lengths)	Axial Angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, Base-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Graphite, ZnO,CdS,
Monoclinic	Primitive, Base-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$,H_3BO_3

9. Packing Efficiency: Packing efficiency is the percentage of total space filled by the particles.

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

(i) Packing Efficiency in Simple (Primitive) cubic Lattice: In Primitive cubic lattice, atoms are located only on the corners of the cube and the atoms touch each other along the edges. If ‘a’ is the cube edge and ‘r’ is the radius of the atom so

$r = a / 2$

Volume of unit cell (V) = a^3

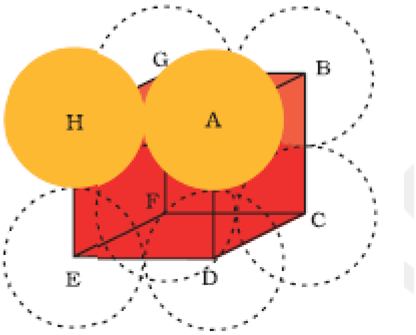
Since one atom is present in a simple unit cell, so its volume (v) = $4 / 3\ \pi r^3$

$$v = 4/3\ \pi\ (a / 2)^3$$

$$v = \frac{\pi a^3}{6}$$

$$\text{So Packing efficiency} = \frac{v}{V} \times 100$$

$$= \frac{\pi a^3/6}{a^3} \times 100 \quad = 52.40\%$$



The spheres are in contact with each other along the edge of the cube.

Therefore, 52.4% of unit cell is occupied by atoms and the rest 47.6% is empty space.

(ii) Packing Efficiency in hexagonal close packed (hcp) & cubic close packed (ccp) or FCC:

In Δ ABC

$$AC^2 = b^2 = BC^2 + AB^2$$

$$= a^2 + a^2 = 2a^2 \text{ or}$$

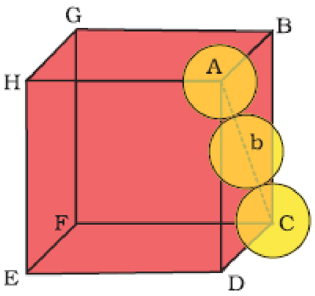
$$b = \sqrt{2}a$$

If r is the radius of the sphere, we find

$$b = 4r = \sqrt{2}a$$

$$\text{or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$$

(we can also write, $r = \frac{a}{2\sqrt{2}}$)



We know that each unit cell in ccp structure has 4 atoms so the total volume (v) of four atoms is $= 4 \times 4 / 3\ \pi r^3$

And total volume of the unit cell (V) = a^3 or $\left(2\sqrt{2}r\right)^3$

$$\text{Packing Efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100\ \%}{\text{Total volume of the unit cell}}$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{\left(2\sqrt{2}r\right)^3}\%$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3}\% = 74\%$$

Therefore, 74% of unit cell is occupied by atoms and the rest 26% is empty space.

(iii) Packing Efficiency in Body Centred Cubic Structures: In this case the Atom at the centre will be in touch with other two atoms diagonally arranged.

In Δ EFD,

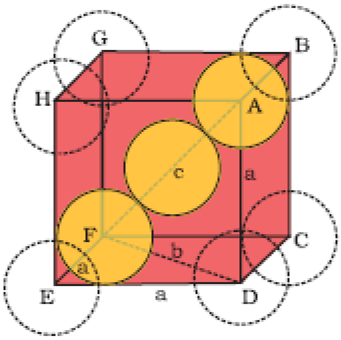
$$b^2 = a^2 + a^2 = 2a^2$$

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

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$



The length of body diagonal ‘c’ is equal to 4r, where ‘r’ is radius of atom (sphere). While all the three atoms along the touch each other diagonally so

$$c = 4r = \sqrt{3}a$$

$$a = \frac{4r}{\sqrt{3}}$$

$$r = \frac{\sqrt{3}}{4}a$$

In this type structure, the total numbers of atoms is 2, so the volume of occupied by two atoms (spheres) is, $v = 2 \times 4 / 3\ \pi r^3$.

And the total volume (V) of the unit cell is = $a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{\left[\left(4/\sqrt{3}\right)r\right]^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{64/\left(3\sqrt{3}\right)r^3}\% = 68\%$$

Therefore, 68% of unit cell is occupied by atoms and the rest 32% is empty space.

10. Density of Unit Cell: Suppose edge of a unit cell of a cubic crystal is ‘a’ and‘d’ is the density of the substance and M is the molar mass, then in case of cubic crystal,

Volume of unit cell = a^3

Mass of unit cell = No. of atoms in unit cell x Mass of each atom = z x m

Mass of each atom (m) = Molar mass (M) / Avogadro Number (N_A)

So Mass of unit cell = $\frac{z \times M}{N_A}$

Therefore, Density of unit cell (d) = $\frac{\text{mass of unit cell}}{\text{volume of unit cell}}$

$$d = \frac{z.M}{a^3 N_A}$$

Where d is in gm/cm^3 and a is in cm.

11. Coordination Number: It is defined as the number of particles immediately adjacent to each particle in the crystal lattice. In simple cubic lattice, CN is 6, in BCC, CN is 8, FCC lattice, CN is 12 and in HCP lattice, CN is 12.
High pressure increases the CN and high temperature decreases the CN.

12. Bragg's Equation: $n\lambda = 2d \sin\theta$

Where n = Order of reflection (generally $n = 1$)
λ = Wave length of X-ray
d = Spacing of the crystal layers (path difference)
θ = Angle b/w incident ray and the scatter plane

13. Close Packing in Crystals:

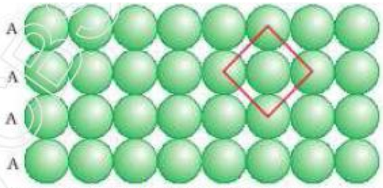
(1) Close Packing in One Dimension: Each sphere is in contact with two of its neighbors. Coordination number is 2.

One dimensional close packing of spheres

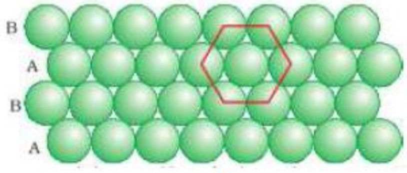
(2) Close Packing in Two Dimensions: It can be obtained in two ways

(i) Square close packing (AAA type arrangement): Here the spheres of the second row are placed exactly above those of the first row. The arrangement is AAA type and the coordination number (CN) is 4. Space occupied by spheres is 52.4%

(ii) Hexagonal close packing (ABAB type arrangement): Here the spheres of the second row are placed above the first one in a staggered manner in such a way that its spheres fit in the depression of the first row. The arrangement is ABAB type and the coordination number is 6. Space occupied by spheres is 60.4%. Hence it is more efficient.



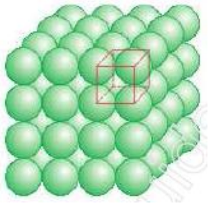
Square close packing (AAA type arrangement) in two dimension



Hexagonal close packing (ABAB type arrangement) in two dimension

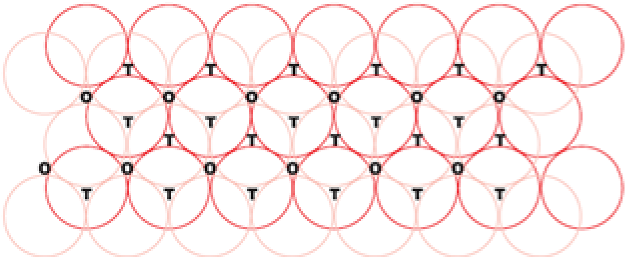
(3) Close Packing in Three Dimensions:

(i) Simple cubic lattice: It is 3D Close Packing which formed by 2D square close packed layers (AAA Type). Here the spheres of the upper layer are placed exactly over the first layer such the spheres of the layers are perfectly aligned horizontally and vertically. It has a AAAA type pattern. This kind of lattice is better known as a ***simple cubic lattice.***



(ii) Hexagonal close packed (HCP): If a two dimensional hexagonal layer, first which consider as A and the second layer which consider as B.

If placed the second layer over the first layer in such a way that the spheres of the second layer are placed in the depressions of the first layer. Due to this type arrangement of spheres, generate two types of voids which are known as tetrahedral voids (T) and octahedral voids (O).



Tetrahedral (T) and octahedral (O) voids generated due to the second layer placed in the depression of the first layer

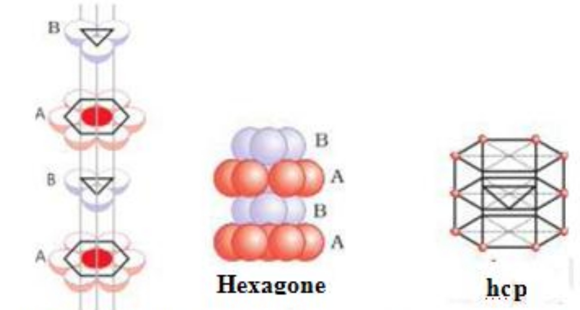
When, placing third layer over the second layer to covering the tetrahedral voids then a three dimensional close packing of ABAB pattern or ***hexagonal close packed (hcp)*** structure is obtained. Example-Molybdenum, Mg, Zn, He etc have hcp structure.

(iii) Cubic Close Packed (ccp) or Face Centred Packed (fcc): When third layer is placed over the second layer in such a way that spheres covers the octahedral voids then a three dimensional pattern of ABCABC or ***Cubic Close Packed (ccp) or Face Centred Packed (fcc)*** is formed. Examples- Iron, Nickel and Copper have ccp structures.

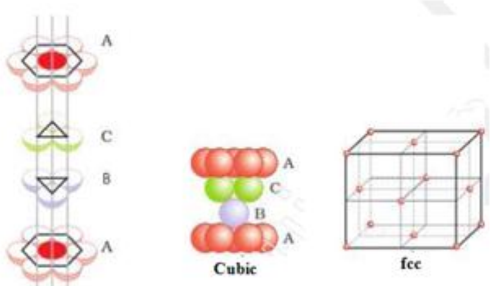
In both of them, the coordination number is 12 as each sphere is in contact with twelve spheres and 74% space is occupied in crystal by both types of arrangement.

(iv) Body centered cubic close packed (BCC): This is ABAB type pattern , the coordination number is 8 and 68% space is occupied in crystal.

Close packing efficiency of atoms in cubic structure decreases as: fcc > bcc > sc.



(a) **Hexagonal close packing** (b) Four layers of stacked spheres (c) Geometry of packing



(a) Cubic close packing (b) Four layers of stacked spheres (c) Geometry of packing

14. Voids or Hole: Empty or vacant space present between spheres of a unit cell is called void or space or hole or interstitial void. When particles are closed packed resulting in ccp or hcp structure, two types of voids are generated:

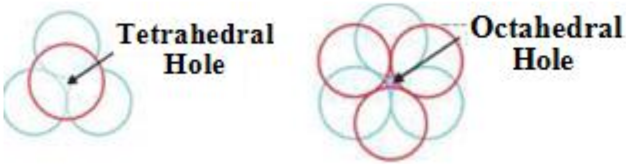
(i) Trigonal void: A simple triangular void in crystal is surrounded by three spheres is called a trigonal void. Coordination number of a trigonal void is 3 and the radius of void is 0.155 x r_{sphere}.

(ii) Tetrahedral void: A simple triangular void in crystal is surrounded by four spheres is called a tetrahedral void. Coordination number of a tetrahedral void is 4. There are 2 tetrahedral voids per atom in a crystal and the radius of void is 0.225 x r_{sphere}.

$$r_{void} = 0.225 \text{ x } r_{sphere}$$

(iii) Octahedral void: Void is surrounded by six spheres is called octahedral void. Coordination number of octahedral void is 6. There is one octahedral void per atom in a crystal and the radius of void is 0.414 x r_{sphere}.

$$r_{void} = 0.414 \text{ x } r_{sphere}$$



In a closed packed arrangement, the number of close packed spheres is N, then the number of voids can be calculated as

Number of octahedral voids = N

Number of tetrahedral voids = 2N

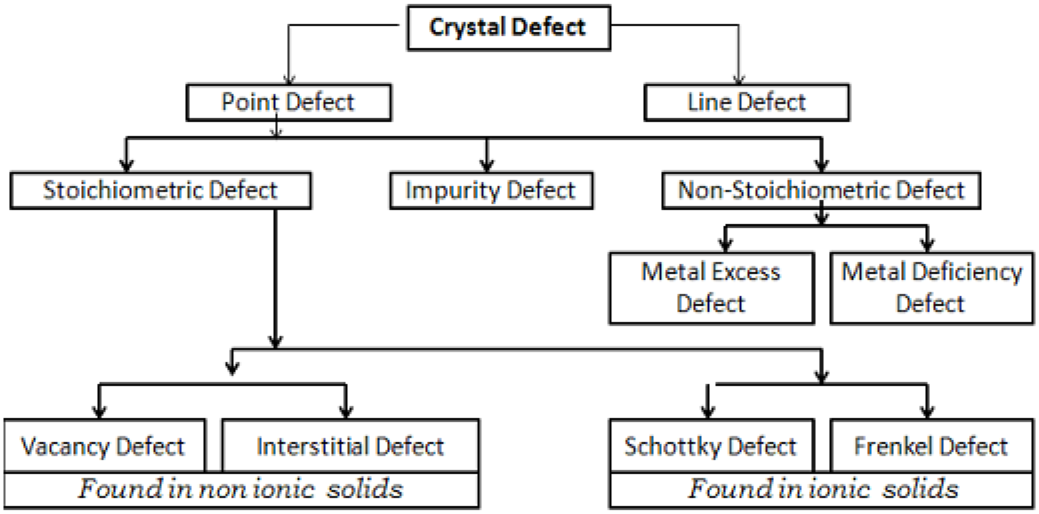
(iv) Cubic void: Void is surrounded by eight spheres is called octahedral void. Coordination number of cubic void is 8. The radius of void is 0.732 x r_{sphere}.

15. Ionic Radii or Interionic distance in Unit Cell: Error less page 262

16. Limiting Radius Ratio: Error less page 262

17. Structure of different Ionic Crystals (About Fluorite and Anti fluorite): Allen 20 and Error less 263

18. Imperfections or defects in Solids: In a crystalline solid, the atoms, ions and molecules are arranged in a definite repeating pattern, but some defects may occur in the pattern. Derivations from perfect arrangement may occur due to rapid cooling or presence of additional particles. The defects in solids can be show as following flow chart-



The defects in solids are mainly of two types-

1) Point defects   2) Line defects.

1) Point Defects: Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects can be classified into three types-

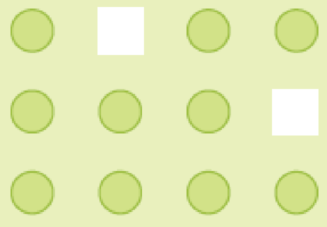
(i) Stoichiometric defects (ii) Impurity defects (iii) Non–Stoichiometric defects

(i) Stoichiometric Defect: These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types,

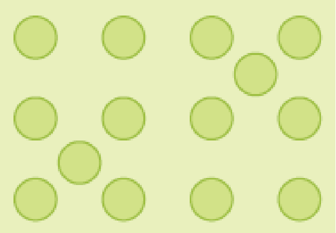
(A) Stoichiometric Defect for non-ionic solids: Non-ionic solids show two types of stoichiometric defects-

(a) Vacancy Defect: When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

(b) Interstitial Defect: When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.



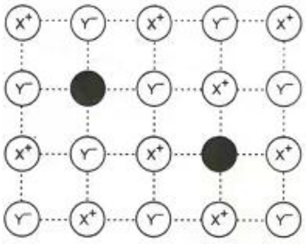
Vacancy defects



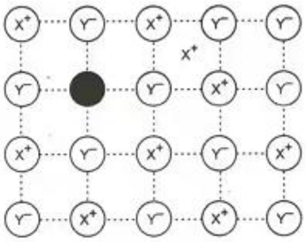
Interstitial defects

(B) Stoichiometric Defect for ionic solids: Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and Schottky defects.

Schottky defect	Frenkel defect
1. It is due to equal no. of cations and anions missing from lattice sites. 2. It results in decrease in density of crystal 3. This is found in the highly ionic compounds with having cations and anions of same sizes NaCl, CaCl	1. It is due to missing of ions [usually cations] from the lattice sites and these occupies interstitial sites. 2. It has no defect on the density of crystal. 3. This is found in crystal with low coordination no. Example:- AgI, ZnS etc.



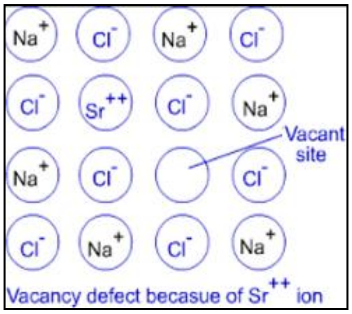
SCHOTTKY DEFECT OF CRYSTALS



FRENKEL DEFECT OF CRYSTALS

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

(ii) Impurity Defect: These defects arise when foreign atoms or ions are present in the ionic solids. For example, when molten NaCl containing a little amount of $SrCl_2$ is crystallized, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replace two Na^+ ions . It occupies the site of one ion and the other side remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions.



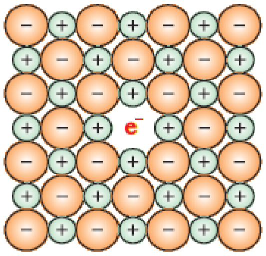
Vacancy defect becasue of Sr^{++} ion

(iii) Non-Stoichiometric Defect: Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. Types of non-stoichiometric defects are as follows:

(A) Metal excess defect: This may occur by following two ways-

(a) Metal excess defect due to anionic vacancies: When a negative ion may be missing from its lattice site, this empty lattice site is called a hole. To maintain electrical neutrality this site is occupied by an electron. The hole occupied by an electron is called the F-centre or Farbenzenter centre. The F- centre is responsible for the color of the crystals.

Example: When NaCl is heated in an atmosphere of Na vapours. The excess of Na atoms deposit on the surface of NaCl crystal then Cl^- ions diffuse to the surface where they combine with Na^+ ions which become due to losing electrons. These electrons loses by Na atom are diffuse back into the crystal and occupy the vacant site created by Cl^- ions and imparts Yellow colour to NaCl crystal



An F-centre in a crystal

(b) Metal excess defect due to presence of extra cations at interstitial sites: In this defect an extra positive ion (cation) occupies interstitial position in the lattice and the free electron is trapped in the vicinity of the interstitial cation. In this way crystal remains neutral. For example when ZnO is heated it loses oxygen and turns yellow due to following

$$ZnO \rightarrow Zn^{+2} + (1/2)\ O_2 + 2e^-$$

The excess Zn^{2+} ions move to interstitial sites and the electrons moves to neighbouring interstitial sites.

(B) Metal deficiency defect due to cation vacancy: It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from $Fe_{0.93}O$ to $Fe_{0.96}O$.
In crystal of FeO, some Fe^{2+}cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

15. Electrical Properties of Solids: Solids are classified in to three groups on the basis of their electrical conductivities-

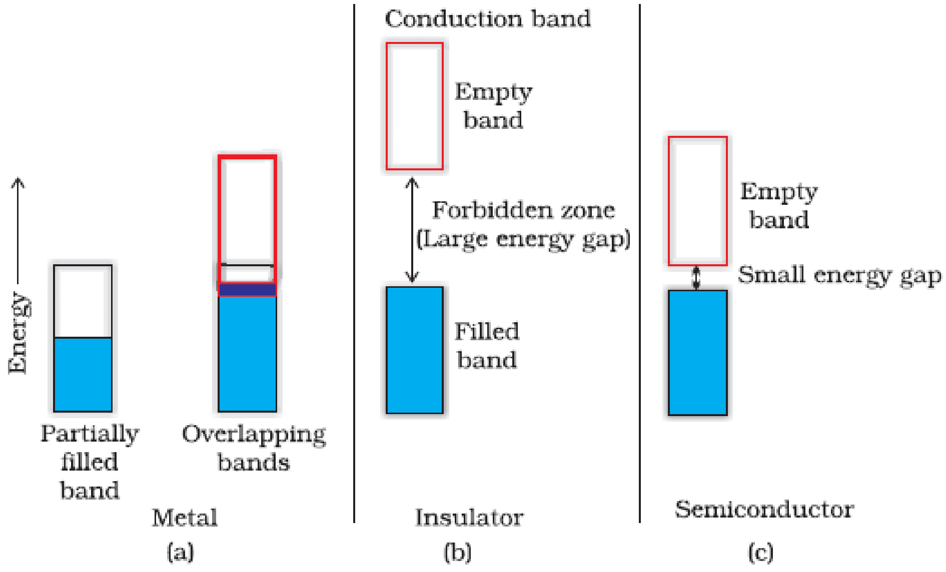
(i) Conductors: The solids with conductivities ranging between 10^4 to 10^7 $ohm^{-1}m^{-1}$ are called conductors. Metals have conductivities in the order of 10^7 $ohm^{-1}m^{-1}$ is good conductors.

(ii) Insulators: Solids with very low conductivities range b/w 10^{-20} to $10^{-10}ohm^{-1}m^{-1}$.

(iii) Semiconductors: Solids with conductivities in the intermediate range from 10^{-6} to $10^4ohm^{-1}m^{-1}$. Examples Si, Ge, Sn (grey), Cu_2O, SiC and GaAs.

Causes of conductance in solids (Band theory): A metal is characterized by a band structure. The highest filled band is called valence band and the lowest unoccupied band is called conduction band. The gap b/w the two bands is called forbidden band. The band structures in different solids can be explained as

- In case of conductors, the valence band and conduction band overlap.
- In case of insulators, the forbidden gap is very large and the electrons are unable to excite to the conduction band.
- In case of semiconductors, forbidden gap is small so some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temp, since more electrons can jump to the conduction band.



Types of Semiconductors:

(i) Intrinsic Semiconductors: Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

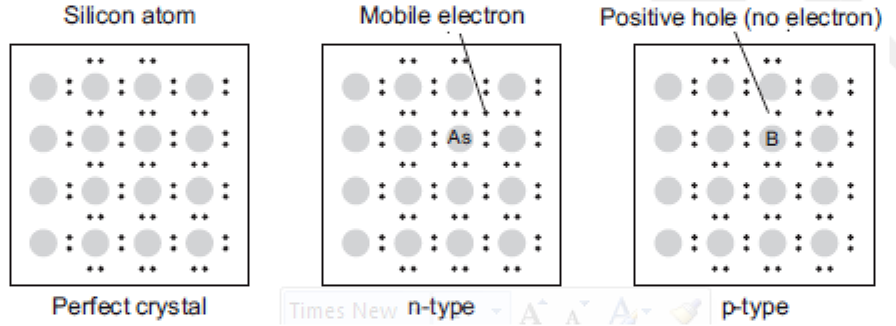
(ii) Extrinsic Semiconductors: When an appropriate impurity is added (dope) to an intrinsic semiconductor, it is called extrinsic semiconductors. Their electrical conductivity is high. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

Doping: The process of adding an appropriate amount of suitable impurity to increase the conductivity of semiconductors is known as doping.

Types of Extrinsic Semiconductors: There is two types-

(a) n·type semiconductors: They are formed when silicon is doped with electron rich impurity like group 15 elements (phosphorus). The increase in conductivity is due to the negatively charged electrons.

(b) p·type semiconductors: They are formed when silicon is doped with electron deficient impurity like group 13 elements (gallium). The increase in conductivity is due to the positively charged holes.



Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements

Application of n·type and p-type semiconductors:

- **Diode:** It is a combination of n-type and p-type semiconductors and is used as a rectifier.
- **Transistors:** They are made by sandwitching a layer of one type of semiconductor b/w two layers of the other type of semiconductor. The npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- **Photodiode:** These are diodes which are capable of converting light energy in to electrical energy and are used in solar cells.

16. Dielectric properties of Solids:

1) Piezoelectricity:

2) Pyroelectricity:

3) Ferroelectricity:

4) Antiferroelectricity:

17. Magnetic Properties of Solids: Solids can be divided into five categories on the basis of their response to magnetic field-

(i) **Diamagnetic Substances:** These are weakly repelled by the magnetic field and do not have any unpaired electron, e.g., TiO_2, V_2O_5, C_6H_6, NaCI, etc.

(ii) **Paramagnetic Substances:** These are weakly attracted by the magnetic field due to presence of one or more unpaired electrons. These lose magnetism in the absence of magnetic field, e.g., O_2, Cu^{2+}, Fe^{3+}, etc.

(iii) **Ferromagnetic Substances:** These are strongly attracted by the magnetic field and show permanent magnetism even till the absence of magnetic field e.g., Fe, Co and Ni.

(iv) **Anti-ferromagnetic Substances:** These substances have net magnetic dipole moment zero due to having equal number of parallel and anti-parallel magnetic dipoles, e.g., MnO, MnO_2, FeO, etc.

(v) **Ferrimagnetic Substances:** These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g., Fe_3O_4, ferrites, etc.