Solid state

1. Characteristics of solids:

- They have definite mass, volumes and shapes.
- Regular order of their constituting particles.
- Strong forces of attraction between particles of solids.
- The properties depend on their arrangements.
- Intermolecular distances are short.

2. Classifications of solids:

S.No	Crystalline solids	Amorphous solids
1.	Definite shapes	Irregular shapes
2.	Melt at sharp temperature	Gradually soften over a range of temperature
3.	Anisotropic	Isotropic
4.	True solids	Super cooled liquids
5.	Long range of order	Short range order
6.	Definite heat of fusion	Do not have definite heat of fusion
7.	Eg: NaCl, Diamond	Eg. Glass, Rubber

3. Anisotropic:

This is arise from different arrangements of particles along different directions.

Electrical and optical properties are different.

isotropic:

This is arise from same arrangements of particles in all directions.

Identical electrical and optical properties.

4. Classification of Crystalline solids:

1. Ionic Solids: Such solids are formed by strong electrostatic forces between anion and cations.

Eg: NaCl

Characteristics:

- Hard and brittle
- High melting and boiling points
- Electrical insulator in solid state
- They conduct electricity in molten state

2. Covalent Solids: Such solids are formed by covalent bonds between adjacent atoms.

Eg: Diamond.

Characteristics:

- ✓ Very hard and brittle
- ✓ Extreme high melting point
- ✓ Insulators

3. Molecular Solids:

I. Non polar molecular solids: The molecular solids formed by non polar covalent bonds.
The atoms held by weak London forces.
Non conductors of electricity.
Eg: Naphthalene

II. Polar Molecular solids: The molecular solids formed by polar covalent bonds.
The atoms held by strong dipole-dipole interactions.
Non conductors of electricity.
Eg: Solid CO_2, Solid NH_3

III. Hydrogen bonded Molecular Solids: Such solids contain strong hydrogen bonding between the molecules.
Non conductors of electricity.
Eg: Water, Glucose.

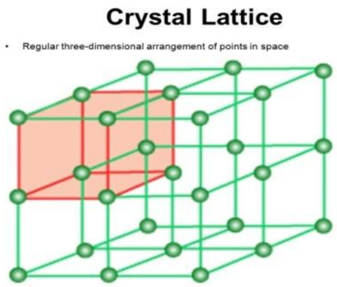
4. Metallic Solids: Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons.

High electrical and thermal conductivity.

Eg: Cu, Fe, and Zn.

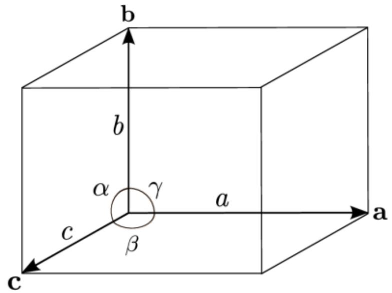
5. Crystal lattice:

The regular three dimensional arrangements of points in space.



6. Unit cell:

The smallest portion of a crystal lattice. It is repeated in different directions.

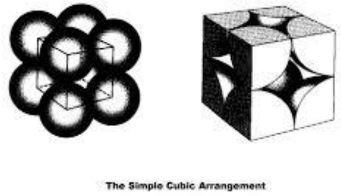


7. Number of atoms in a unit cell:

Simple Cubic Crystal (SCC):

Each cubic unit cell has 8 atoms in corners,

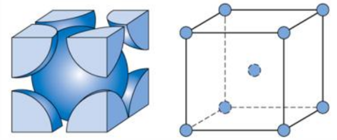
Total number of atoms in one unit cell $8 \times \frac{1}{8} = 1$ atoms.



Body Centred Cubic (bcc):

The total number of atoms in BCC unit cell = $\left(\frac{Nc}{8}\right) + \left(\frac{Nb}{1}\right)$

$= \frac{8}{8} + \frac{1}{1} = 2$ atoms

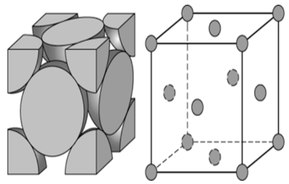


Face Centred Cubic (fcc):

The total number of atoms in FCC unit cell = $\left(\frac{Nc}{8}\right) + \left(\frac{Nf}{2}\right)$

$= \frac{8}{8} + \frac{6}{2}$

$= 1 + 3 = 4$ atoms



Calculate the density of unit cells:

Density of unit cell "ρ" = $\frac{\textbf{Mass of unit cell}}{\textbf{volume of unit cell}}$

Mass of unit cell = $\mathbf{n} \times \frac{M}{N}$

n = no. of atoms in unit cell

M= Molar mass

N = Avogadro number

Density of unit cell "ρ" = $\mathbf{nM / a^3N}$

Voids: The empty spaces between close packing of its constituting particles.

Coordination number of unit cells:

Simple cubic , coordination number = 6.

In bcc, coordination number = 8.

In fcc, coordination number = 12.

Packing efficiency:

The percentage of total space filled by the particles.

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

Simple cubic:

$$\text{Packing efficiency} = \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100$$

$$= \frac{\pi}{6} \times 100$$

$$= 52.36\%$$

$$= 52.4\ \%$$

Body centred cubic:

Therefore,

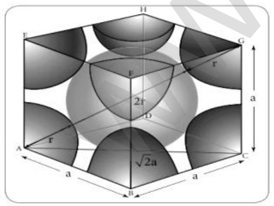
$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell (volume of cube)}} \times 100$$

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

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}} r^3} \times 100$$

$$= 68\ \%$$

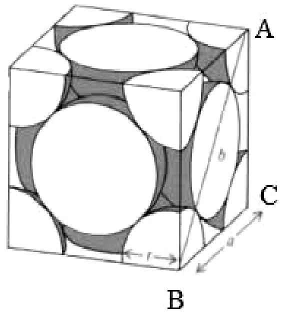
Packing efficiency $= 68\ \%$



Face centred cubic:

$$\text{Packing efficiency} = \frac{\left(\text{Volume occupied by 4 spheres in the unit cell}\right)}{\left(\text{Total volume of the unit cell}\right)} \times 100$$

$$= \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}\, r)^3} \times 100\% = 74\%$$



Unit cell	Packing efficiency
fcc	74%
bcc	68%
Simple cubic	52%

Radius ratio: The ratio between radius of cation and anion in crystals.

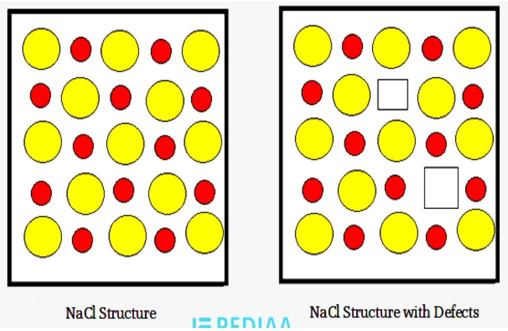
Radius ratio $\left(\frac{r_+}{r_-}\right)$	Coordination number	Structure	Example
< 0.155	2	linear	—
0.155 – 0.225	3	planar triangular	B_2O_3
0.225 – 0.414	4	tetrahedral	CuCl, CuBr
0.414 – 0.732	6	octahedral	NaBr, KBr
0.732 – 1	8	bcc	CsI, CsBr

Crystals Defects (or) Imperfections in Crystals:

Point defects: The deviations from ideal arrangements around an atom in a crystalline substance.

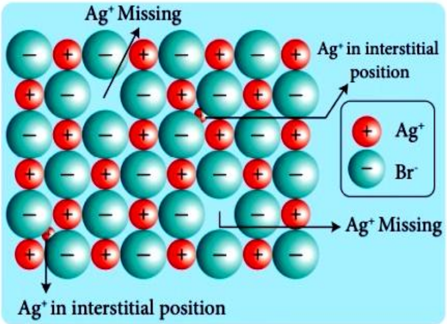
1.Schottky defects:

Ex: NaCl, KCl



- Missing of anions and cations from their positions.
- Cation and anion are of almost similar size.
- Decrease the density of the substance.
- Electrical neutrality is still maintained.
- Stoichiometric defects.

2.Frankel defects:



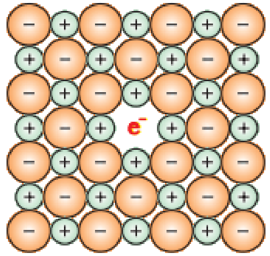
Frenkel Defect

Ex: AgBr, AgCl, ZnS

- ➢ The smaller ion is dislocated from normal site to its interstitial site.
- ➢ Cation and anion are differ in size.
- ➢ Doesnot change in density.
- ➢ Electrical neutrality is still maintained.
- ➢ Anion is much larger than cation.

3. Metal excess defects:

Ex: NaCl, KCl



An F-centre in a crystal

- ✓ This is due to metal halides are heated in metal vapours.
- ✓ NaCl is heated in Na vapour Na^+ ions become excess.
- ✓ Cl^- ions leave the normal site.
- ✓ Anionic site occupied by unpaired electrons (F- centre).
- ✓ NaCl- Yellow colour, KCl- Violet, LiCl- Pink.
- ✓ Non-stoichiometric defects.

4. Metal deficiency defects: Ex: FeO

- This is due to crystals in which their cations show variable oxidation states.
- Missing of cation in lower valence.
- Another lattice site occupied by a cation in higher valencies.
- Electrical neutrality is maintained.
- Non-stoichiometric defect.