SOLID STATE

1. INTRODUCTION

Solid state is a state of matter besides liquid and gaseous state. In case of solids the inter molecular forces are very strong and empty spaces between the atoms/ions/ molecules is very less. That is why they have a fixed shape and volume.

1.1 Characteristic Properties of Solids

Solids are characterised by the following properties

- High density
- Low compressibility
- Rigidity
- Definite shape and volume.

2. CLASSIFICATION OF SOLIDS

Solids are broadly classified on the basis of following parameters.

- based on various properties
- based on bonding present in building blocks.

2.1 On the basis of various properties

Based on their various properties solids can be classified as

- Crystalline solids
- Amorphous solids.

Crystalline solids have a regular structure over the entire volume and sharp properties whereas amorphous solids have irregular structure over long distances and properties are not that sharp. Various differences are listed in table below

Property	**Crystalline solids**	**Amorphous solids**
Shape	They have long range order	They have short range order.
Melting point	They have definite melting point	They do not have definite melting point.
Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
Compressibility	They are rigid and incompressible	These may be compressed to some extent
Cutting with a sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces	They give irregular cleavage i.e. they break into two pieces with irregular surface
Isotropy and Anisotropy	They are anisotropic	They are isotropic
Volume change	There is a sudden change in volume when they melt.	There is no sudden change in volume on melting.
Symmetry	They possess symmetry	They do not possess any symmetry.
Interfacial angles	They possess interfacial angles.	They do not possess interfacial angles.

2.2 Based on bonding

There are various type of solids based on type of bonding present in their building blocks. Various types of solids along with their properties are given in the table below.

The different properties of the four types of solids are listed in Different Types of Solids

Type of Solid	**Constituent**	**Bonding**	**Examples**	**Physical**	**Electrical**	**Melting**
(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)	

3. STRUCTURE OF CRYSTALLINE SOLIDS

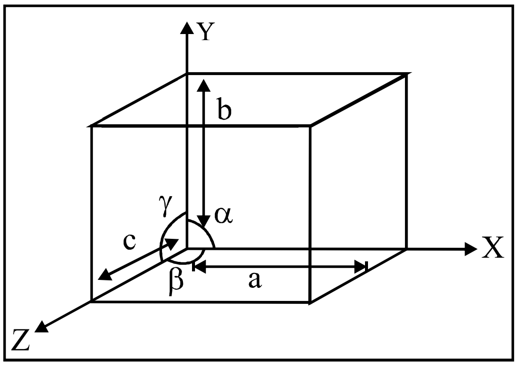
3.1 Crystal lattice and Unit Cell

The regular array of the building blocks (atoms/ions/ molecules) inside the crystalline solid is called "Crystal Lattice".

The smallest part or crystal lattice which can be repeated in all directions to generate entire crystal lattice is called "Unit Cell".

In unit cell the atoms of ions or molecules are represented by small spheres. Various lattices are formed by variation in following parameters :

- The edge length along 3 axes - a, b, c
- The interfacial angles - α, β, γ.
- Location of atom/ions w.r.t each other in crystal lattice.



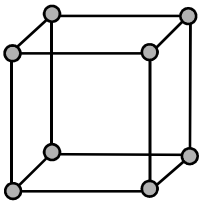
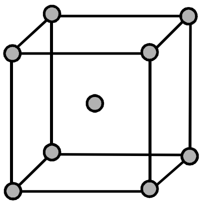
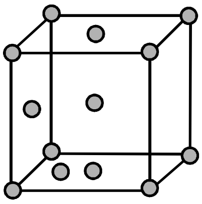
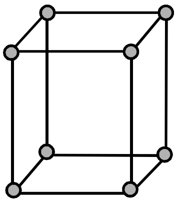
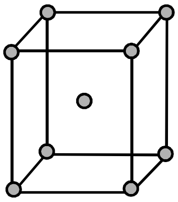
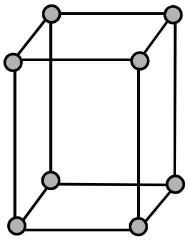
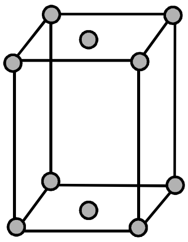
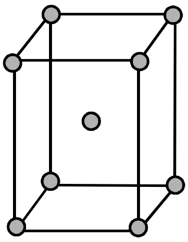
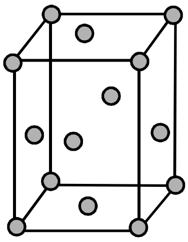
3.2 Primitive Unit Cells and Bravais Lattices

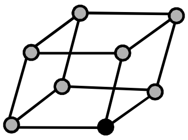
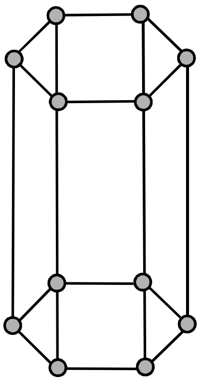
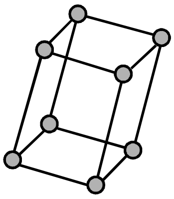
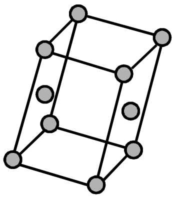
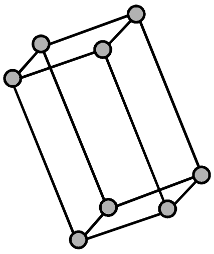
In all, there are seven types of unit cells and there can be some sub types of unit cells. These seven unit cells are called **Primitive Unit Cells** or **Crystal Habits.** Which are listed in table below

Crystal System	Axial distances	Axial angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Copper, Zinc blende, KCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sn (White tin), SnO_2, TiO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, $CaCO_3$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monoclinic sulphur, $PbCrO_2$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Graphite, ZnO
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$CaCO_3$ (Calcite), HgS (Cinnabar)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

For these 7 types of unit cells, 14 types of Lattices exist in nature. These 14 Lattices are called "Bravais Lattices."

SOLID STATE

Crystal system		Space lattice			Examples
Cubic a = b = c Here a, b and c are parameters (dimensions of a unit cell along three axes) size of crystals depend on parameters. $\alpha = \beta = \gamma = 90^\circ$ α β and γ are sizes of three angles between the axes.	**Simple :** Lattice Points at the eight corners of the unit cells. 	**Body Centered :** Points at the eight corners and at the body centre. 		**Face Centered :** Points at the eight corners and at the six face centres. 	Pb, Hg, Ag, Au, Cu, ZnS, diamond, KC*l*, NaC*l*, Cu_2O, CaF_2 and alumns. etc.
Tetragonal a = b ≠ c, $\alpha = \beta = \gamma = 90^\circ$	**Simple :** Points at the eight corners of the unit cell. 	**Body Centered :** Points at the eight corners and at the body centre 			SnO_2, TiO_2, ZnO_2, $NiSO_4$ $ZrSiO_4$, $PbWO_4$, white Sn etc.
Orthorhombic (Rhombic) a ≠ b ≠ c $\alpha = \beta = \gamma = 90^\circ$	**Simple :** Points at the eight corners of the unit cell. 	**End Centered :** Also called side centered or base centered. Points at the eight corners and at two face centres opposite to each other. 	**Body Centered:** Points at the eight corners and and at the body centre 	**Face Centered :** Points at the eight coreners and at the six face centres. 	KNO_3, K_2SO_4, $PbCO_3$, $BaSO_4$ rhombic sulphur, $MgSO_4$. $7H_2O$ etc.

Rhombohedral or Trigonal a = b = c, $\alpha = \beta = \gamma \neq 90^\circ$	**Simple :** Points at the eight corners of the unit cell 		$NaNO_3$,$CaSO_4$ calcite, quartz As, Sb, Bi etc.
Hexagonal a = b ≠ c, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	**Simple :** Points at the twelve or Points at the twelve corners of the unit cell out corners of the haxagonal lined by thick line. prism and at the centres of top and bottom faces. 		ZnO, PbS, CdS, HgS, graphite, ice, Mg, Zn, Cd etc.
Monoclinic a ≠ b ≠ c, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	**Simple :** Points ath the eight corners of the unit cell 	**End Centered :** Point at the eight corners and two face centres opposite to the each other. 	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $CaSO_4.2H_2O$, monoclinic sulphur etc.
Triclinic a ≠ b ≠ c $\alpha \neq \beta \neq \gamma \neq 90^\circ$	**Simple :** Points at eight corners of the unit cell. 		$CaSO_4$. $5H_2O$, $K_2Cr_2O_7$, H_3BO_3

We will focus majorly on cubic unit cells and their arrangements.

3.3 Cubic Unit Cells

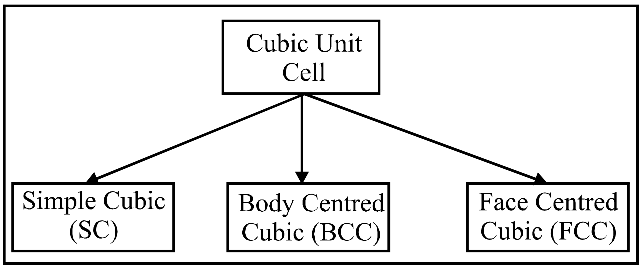
This is the most common unit cell. In a cubic unit cell there are following locations for the atoms or spheres

- Corners
- Body Centre
- Face Centres

Following are the contributions of a sphere kept at various locations.

Location	Contribution
Corners	1/8
Body Centre	1
Face Centre	1/2

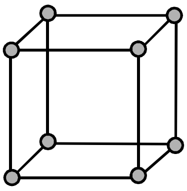
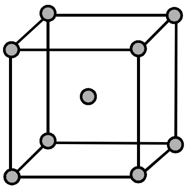
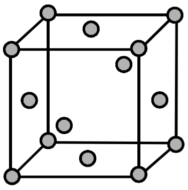
3.3.1 Types of cubic Unit Cells



These unit cells differ from each other in following factors.

- Location of spheres inside the unit cell.
- Rank of the unit cell (effective number of spheres inside a unit cell)
- Relation between edge length and radius of one sphere.
- Packing fraction (fraction of volume occupied by spheres in a unit cell)

The following parameters for all the 3 unit cells are listed is the table below :

Type of Cublic Crystal	No. of atoms at different locations			Structure	Rank	Packing	Relation b/w atomic radius and edge length (a)
	Corners	Body centre	Face centre				
Simple Cubic	8	–	–		1	52%	$r = a/2$
Body Centred	8	1	–		2	68%	$r = \frac{\sqrt{3}a}{4}$
Face Centred	8	–	6		4	74%	$r = \frac{\sqrt{2}a}{4}$

3.4 Density of cubic crystals

Density of cubic crystal is given by the following formula

$$\text{Density } \rho = \frac{M \times Z}{a^3 \times N_A}$$

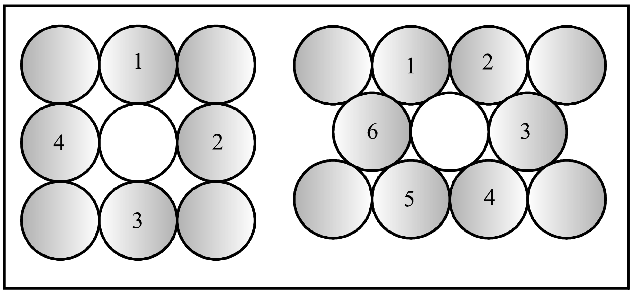
where, Z → rank of unit cell
M → Molar mass of solid
a → Edge length of unit cell
N_A → Avogadro Number.
Valume of Z will depend upon the type of unit cell.

3.5 Close packing in Solids : Origin of unit cells

Suppose we have spheres of equal size and we have to arrange them in a single layer with the condition that spheres should come in close contact with each other. Two types of layers are possible :

1. **Square Packing**
2. **Hexagonal Packing**

In square packing spheres are placed in such a way that the rows have a horizontal as well as vertical arrangement. In this case Co-ordination Number is 4.



Hexagonal packing is more efficient. Its Co-ordination Number is 6 and voids in the packing are smaller than square packing.

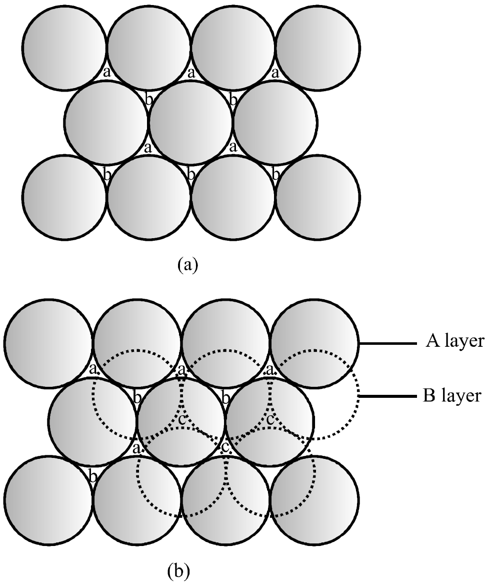
If we place another layer on square packing then there are following possibilities :

1. A similar layer placed just above foundation layer that is the spheres of the second layer coming just above the spheres of the first layer and layers get repeated. If first layer is termed A the packing in this case is AA... type and the unit cell is **simple cubic.**
2. On other hand if spheres of second layer are placed in depressions of first layer we get **BCC unit cell** and ABAB ..... type of packing.

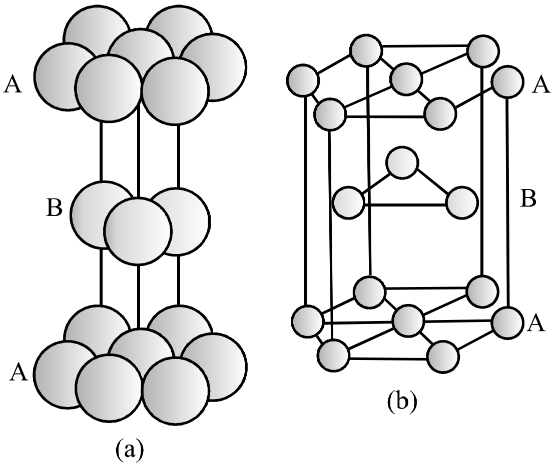
Arrangements based on hexagonal foundation layer are as follows :

If we put 2^{nd} layer in depressions of first hexagonal layer A two types of voids are created. X type of voids are those which are hollow and through voids of layer A and layer B. While Y type of voids are those voids of layer B which are exactly above spheres of layer A. If we place the spheres of 2nd layer on Y voids then we are repeating layer 1 and ABABAB.... type packing is obtained. In this arrangement hexagonal unit cell is obtained and packing is called **Hexagonal Close Packing** (HCP). The efficiency of this packing is 74%.

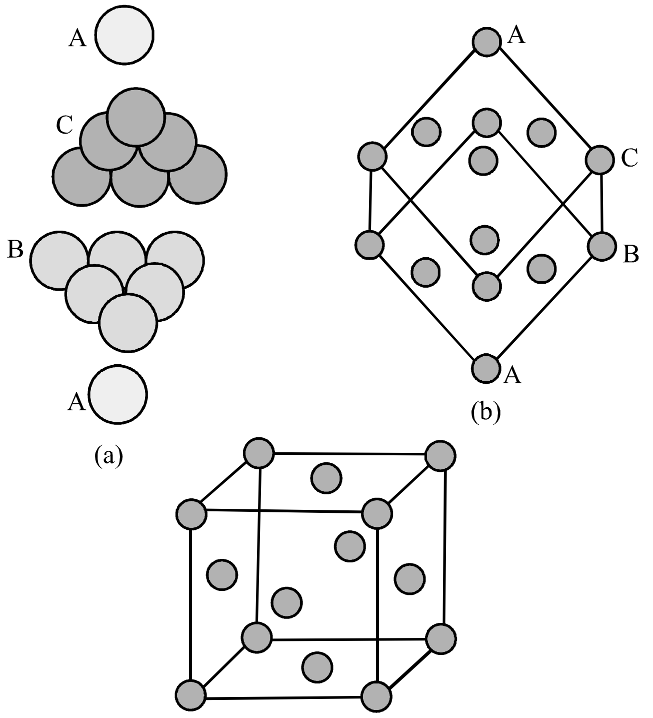
If the 3rd layer is placed on X-type of voids then a new layer C is obtained and then the arrangement will be repeated. We will obtain ABCABCABC..... type of packing. The unit cell for this arrangement is **FCC** and the packing effeciency is 74%.



Packing of second layer (b) on first layer (a)



ABABA .... or hcp arrangement of spheres. Metals like magnesium, zinc, etc. adopt this type of arrangement.



(a) (b)

ccp arrangement
(c)

ABCABCA ... or ccp arrangement of spheres

4. VOIDS

4.1 Definition

The empty spaces inside a spheres are called “voids”. The size and shape of voids depends upon the type of unit cell and packing.

4.2 Radius Ratio

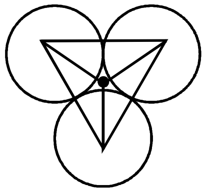
The size of void is expressed in terms of radius ratio of a sphere that can be exactly fit in the void to the radius of surrounding spheres. This expressed as :

$$\text{Radius ratio} = \frac{r}{R}$$

4.3 Types of voids

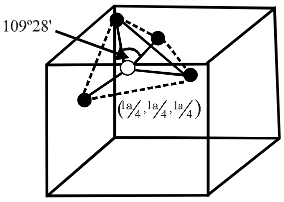
4.3.1 Trigonal void

It is a void formed of equal radii and touching each other as shown in figure.

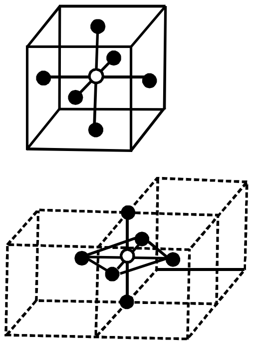
Figure	Key Points
 Trigonal Void	* Radius Ratio $\frac{r}{R} = 0.155$ * Smallest void * Co-ordination no. = 3

4.3.2 Tetrahedral Void

It forms by contact of 4 spheres and is positioned at the centre of tetrahedron formed by contact of 4 spheres.

Figure	Key Points
 An atom occupying a tetrahedral void	* Radius ratio $\frac{r}{R} = 0.225$ * No. of voids in FCC crystal = 8 * Position : at a distance $\frac{a\sqrt{3}}{4}$ from every corner. * Co-ordination no. = 4

4.3.3 Octahedral Void

Figure	Key Points
	* Radius ratio $\frac{r}{R} = 0.414$ * No. of voids in FCC crystal = 4 * Positions : Body centre Edge centres * Rank = 4 * Co-ordination No. = 6

4.3.4 Cubic Void

This void forms by close contact of 8 spheres

Key Points

- * Radius Ratio = $\frac{r}{R} = 0.732$
- * No. of voids in cubic crystal = 1
- * Postion : at body centre
- * Co-ordination number = 8
- * Rank = 1

It is clear from above details that

Trigonal < Tetrahedral < Octahedral < Cubic
void void void void

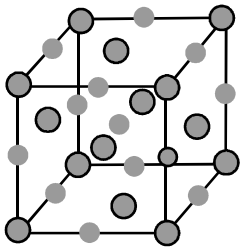
5. CLASSIFICATION OF IONIC STRUCTURES

Ionic compounds are formed by the simultaneous arrangement of cations and anions in lattice/unit cell. The larger of two species occupies major positions in a unit cell and the smaller ones occupy voids according to their size. Which is decided on the bases of radius ratio (r_+/r_-). The various ratios are listed below.

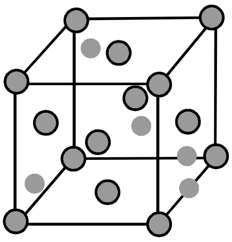
Limiting Radius Ratios,	**$x = r_+/r_-$**	**C.N.**	**Shape Example**
$x < 0.155$	2	Linear	BeF_2
$0.155 \le x < 0.225$	3	Planar Triangular	$AlCl_3$
$0.225 \le x < 0.414$	4	Tetrahedron	ZnS
$0.414 \le x < 0.732$	6	Octahedron	NaCl
$0.732 \le x < 0.999$	8	Body Centred Cubic	CsCl

Based on these ratio ranges, ionic crystal are classified into 5 categories which are as follows

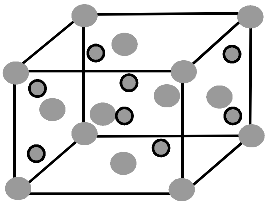
5.1 NaCl Type Structure

Figure	**Key Points**
 Rock Salt Structure	* Cl^- occupy corners and face centres and Na^+ occupy octhedral voids in FCC crystal. * Effective formula = Na_4Cl_4 * Co-ordination No. of $Na^+ = 6$ * Co-ordination No of $Cl^- = 6$ * Distance b/w nearest neighbours $[r_{Na^+} + r_{Cl^-} = \frac{a}{2}]$

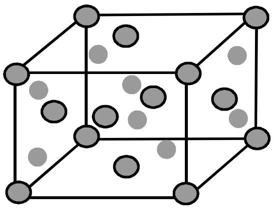
5.2 ZnS type Structure

Figure	**Key Points**
 Zinc Blende Structure	* S^{2-} ions occupy main positions and Zn^{+2} ions are present in alternate tetrahedral voids in FCC crystal. * Effective formula = Zn_4S_4 * Co-ordination of $Zn^{+2} = 4$ * Co-ordination No. of $S^{2-} = 4$ * $r_{Zn^{+2}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$

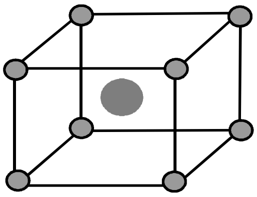
5.3 Fluorite Type Structure

Figure	**Key Points**
 Fluorite Structure	* Ca^{+2} ions occupy main positions and F^- ions occupy tetrahedral voids in FCC crystal. * Effective formula = Ca_4F_8 * Co-ordination no. of $Ca^{+2} = 8$ * Co-ordination no. of $F^- = 4$ * $r_{Zn^{+2}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$

5.4 Anti Fluorite structure

Figure	Key Points
 Anti-Fluorite Structure	* Common in alkali oxides like Na_2O, Li_2O etc. * O^{2-} ions occupy FCC and Li^+ ions occupy the tetrahedral voids * C.N. of $Li^+ = 4$ * CN of $O^{2-} = 8$ * $r_{Li^+} + r_{O^{2-}} = \frac{a\sqrt{3}}{4}$

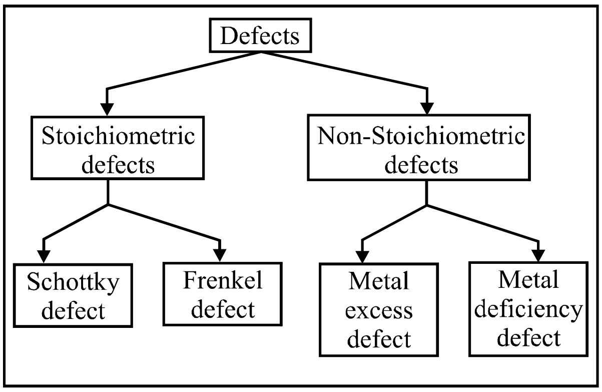
5.5 CsCl Type Structure

Figure	Key Points
 Cesium Halide Structure	* Cl^- ions simple cubic Locations (corners) and Cs^+ ions occupy body centre in BCC lattice * Effective formula = CsCl * Co ordination no of $Cs^+ = 8$ * Co ordination no. of $Cl^- = 8$ * $r_{Cs^+} + r_{Cl^-} = \frac{a\sqrt{3}}{2}$.

6. IMPERFECTIONS IN SOLIDS

Sometimes some defects or imperfections occur in crystal structure.

6.1 Classification of defects

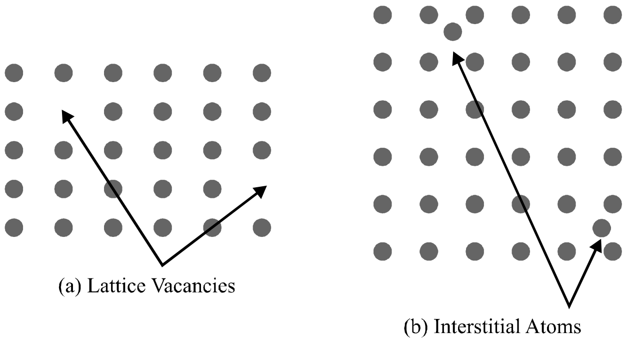


6.2 Vacancies

These are defects that occur when positions that should contain atoms or ions are vacant.

6.3 Interstitial sites

These are sites located between regular positions sometimes atoms or ions may occupy these positions.


(a) Lattice Vacancies

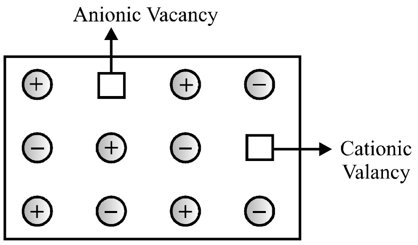
(b) Interstitial Atoms

6.4 Stoichiometric Defects

These defects do not disturb stoichiometry of solid substance.

6.4.1 Schottky defects

It is a vacancy defect in ionic solids. No. of missing cations and anions is equal so electrical neutrality is maintained. This defect decreases the density of the substance. The defect is shown by ionic substances in which cation and anion are of almost similar sizes. eq. KCl, NaCl, AgBr etc.

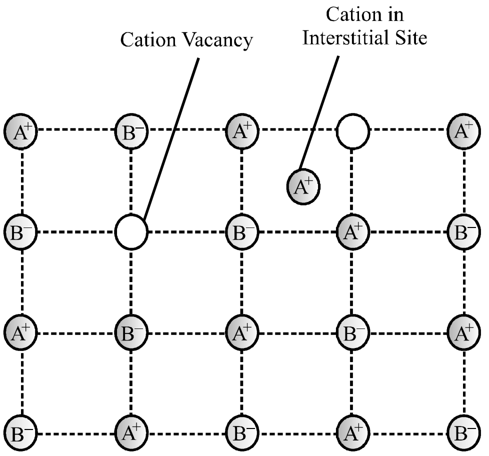


Schottky

6.4.2 Frenkel defect

In ionic solids the smaller ion is dislocated from its normal position to an interstitial site. It creates a vacancy defect at its original site and interstitial defect at new location. It is also called as dislocation defect. It does not change the density of solid.

This type of defect is shown by ionic substances in which there is a large difference in size of ions. eq ZnS, AgCl, AgBr etc.



A Frenkel defect

Note..

AgBr shows both Schottky and Frenkel defects.

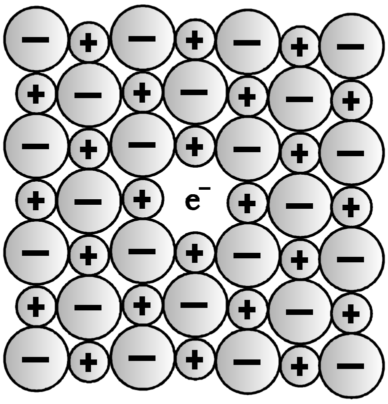
6.5 Non Stoichiometric Defects

The compounds having these defects contain combining elements in a ratio different from required by their stoichiometric formulae.

6.5.1 Metal Excess Defect

Due to anionic vacancies : The anion may be missing from its lattice site leaving an e^- behind so that charge remains balanced. The site containing electron is called F centre. They import colour to the crystal, F stands for **Farbenzenter** meaning colour.

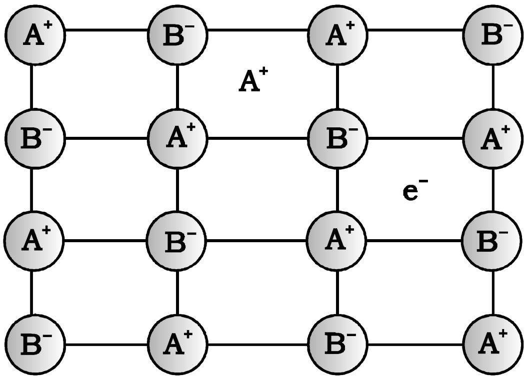
This defect is similar to schottky defect and is found is crystals having schottky defect eq. NaCl, KCl etc.



An F-centre in a crystal

Due to the presence of extra cations in the interstitial sites.

An extra cation may be present in interstitial site and an electron is present in another interstitial site so that electrical neutrality is maintained. This is similar to Frenkel defect and if found in crystal having Frenkel defect.



Metal excess defect caused by extra cation in the interstitial site.

6.5.2 Metal Deficiency Defect

This defect occurs when metal shows variable valency. eq. FeO is mostly found is varying compostions between $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals 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.