Revision Notes

Class 12 Chemistry

Chapter 1 – Solid State

INTRODUCTION

Apart from liquid and gaseous states, solid state is a state of matter. Solids have very strong intermolecular interactions, and there are very few vacant spaces between the atoms/ions/molecules. As a result, they have a predetermined shape and volume.

Characteristic Properties of Solids

The following properties come under the category of solids:

- Solids have high density.
- Solids have low compressibility.
- Solids are rigid in nature.
- Solids have definite shape and volume.

CLASSIFICATION OF SOLIDS

On the basis of the following parameter, solids are broadly classified as:

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

On the basis of various properties

On the basis of the various properties of solids, they can be classified as:

- Crystalline solids
- Amorphous solids

Amorphous solids have an uneven structure over long distances and lack sharp properties, whereas crystalline solids have a regular structure throughout the entire volume and sharp qualities. The table below shows the many differences.

Property	Crystalline solids	Amorphous Solids
Shape	Crystalline solids have a long range order.	Amorphous solids have a short range order.
Melting point	Crystalline solids tend to have definite melting points.	Amorphous solids do not have a definite melting point.
Heat of fusion	Crystalline solids have a definite heat of fusion.	Amorphous solids do not have a definite heat of fusion.
Compressibility	Crystalline solids are rigid and incompressible.	Amorphous solids may be compressed to some extent.
Cutting with a sharp edged tool	Crystalline solids tend to break into two pieces with plane surfaces.	Amorphous solids give irregular cleavage, that means they break into two pieces with irregular shape.
Isotropy and Anisotropy	Crystalline solids are anisotropic.	Amorphous solids are isotropic.
Volume change	When crystalline solids melt, there is a sudden change in their volume.	On melting there is no sudden change in the volume of amorphous solids.
Symmetry	Crystalline solids possess symmetry.	Amorphous solids do not possess any symmetry.
Interfacial angles	Crystalline solids have	Amorphous solids do not have

	interfacial angles.	interfacial angles.

Based on bonding

Solids are classified according to the sort of bonding present in their building units. The table below lists many types of solids as well as their properties.

The different properties of the four types of solids are listed as:

Type of Solid	**Constituent**	**Bonding**	**Examples**	**Physical**	**Electrical**	**Melting**
Molecular Solids						
Non Polar	Molecules	Dispersion or London forces	Ar , CCl_4 , H_2 , I_2 , CO_2	Soft	Insulator	Very low
Polar	Molecules	Dipole-Dipole interactions	HCl, SO_2	Soft	Insulator	Low
Hydrogen Bonded	Molecules	Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
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	High

					solutions.	
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
Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz) SiC, C (diamond) $C_{(graphite)}$	Hard Soft	Insulators Conductor	Very High

STRUCTURE OF CRYSTALLINE SOLIDS

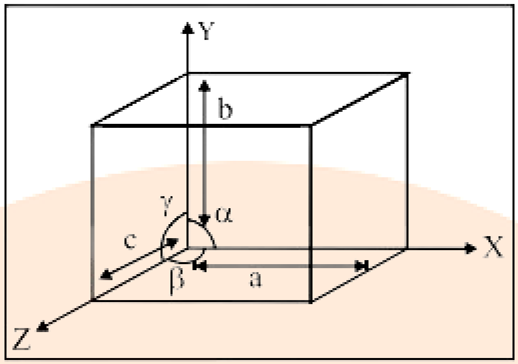
Crystal Lattice and Unit Cell

The crystalline solid regular array of building pieces (atoms/ions/molecules) is known as the "Crystal Lattice."

"Unit Cell" refers to the smallest component of a crystal lattice that can be repeated in all directions to form the full crystal lattice.

Small spheres represent the atoms of ions or molecules in a unit cell. Variations in the following parameters produce several lattices:

- The edge along the 3 axis – a, b, c.
- The interfacial angle - α, β, γ
- Location of atoms/ions with respect to each other in crystal lattice.



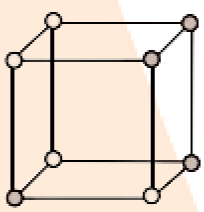
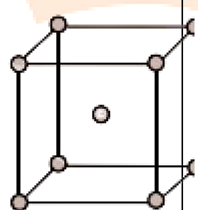
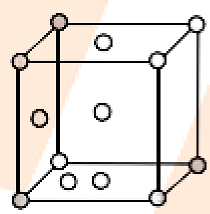
Primitive Unit Cells and Bravais Lattices

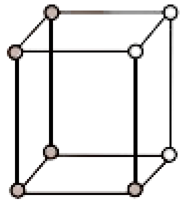
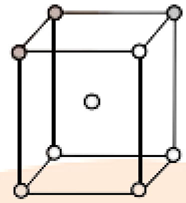
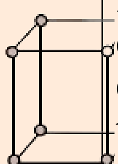
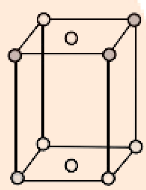
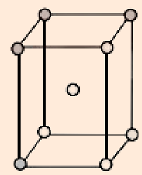
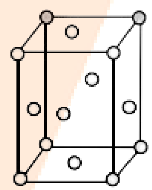
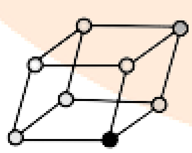
There are seven different types of unit cells, as well as various subtypes of unit cells. Primitive Unit Cells or Crystal Habits are the names given to these seven unit cells. The following are listed in the table below:

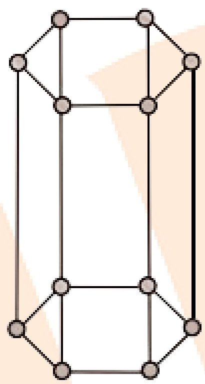
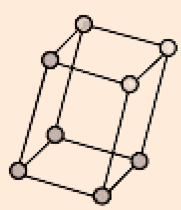
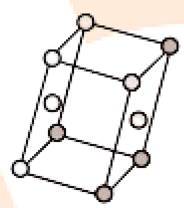
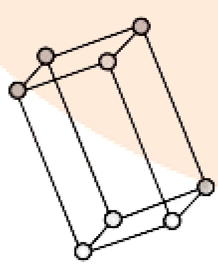
Crystal System	Axial Distance	Axial angles	Examples
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	Copper, Zinc blende, KCl
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	White tin, SnO_2, TiO_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	Rhombic sulphur, $CaCO_3$
Monoclinic	$a\neq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

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 named as "Bravais Lattices".

Crystal System		**Space Lattice**		**Examples**
Cubic $a = b = c$ Here a, b and c are the dimensions of a unit cell along three axes. $\alpha = \beta = \gamma = 9$ Here, α, β and γ are the 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 enters. 	Pb, Hg, Ag Au, Cu, ZnS Diamond, KCl NaCl, Cu_2O, CaF_2 and alumns, etc.
Tetragonal $a = b \neq c$	**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, $NiSO_4$

<table>
<tr><td>$\alpha = \beta = \gamma = 9$</td><td colspan="2"></td><td colspan="2"></td><td>$ZrSiO_4$,
$PbWO_4$
And white tin.</td></tr>
<tr><td>Orthorhombic:
$a \neq b \neq c$
$\alpha = \beta = \gamma = 9$</td><td>Simple: Points at the eight corners of the unit cell.
</td><td>End Centered: Also called side centered or base centered. Points at the eight corners and at two face centers opposite to each other.
</td><td>Body Centered: Points at the eight corners and at the body centre.
</td><td>Face Centered: Points at the eight corners and at the six face centres.
</td><td>KNO_3, K_2SO_4,
$PbCO_3$, $BaSO_4$
Rhombic sulphur, $MgSO_4.7H_2O$ etc.</td></tr>
<tr><td>Rhombohedral or Trigonal
$a = b = c$,
$\alpha = \beta = \gamma \neq 9$</td><td colspan="4">Simple: Points at the edge corners of the unit cell.
</td><td>$NaNO_3$, $CaSO_4$, calcite, quartz, As, Sb, Bi</td></tr>
<tr><td>Hexagon</td><td colspan="4">Simple: Points at the twelve or points at the twelve</td><td>ZnO, PbS, CdS ,</td></tr>
</table>

al $a = b \ne c$, $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	corners of the unit cell out corners of the hexagonal lined by thick line, prism and at the centres of top and bottom faces. 		graphite, ice, Mg, Zn, Cd etc.
Monoclinic $a \ne b \ne c$ $\alpha = \gamma = 90^{\circ}$, $\beta \ne 90^{\circ}$	**Simple:** Points at the eight corners of the unit cell. 	**End Centered:** Point at the eight corners and two face centres opposite to each other. 	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $CaSO_4.2H_2O$, monoclinic sulphur etc.
Triclinic $a \ne b \ne c$ $\alpha \ne \beta \ne \gamma \ne 9$	**Simple:** Points at eight corners of the unit cell. 		$CaSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3

The focus will primarily be on cubic unit cells and their arrangements.

Cubic Unit Cells

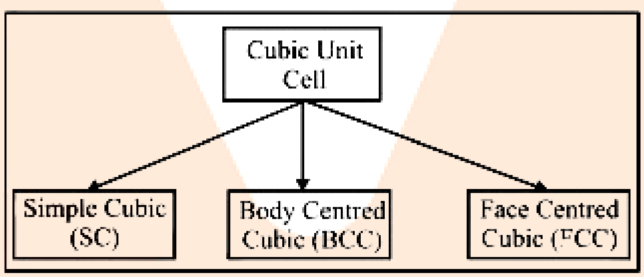
The most common unit cell is this one. The atoms or spheres in a cubic unit cell can be found at the following locations.

- Corners
- Body centre
- Face centres

The contributions of a sphere stored at various locations are as follows:

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

Types of Cubic Unit Cells

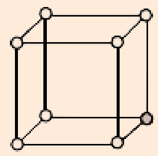
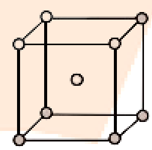
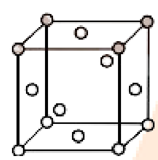


The following factors distinguish these unit cells from one another:

- The positions of the spheres within the unit cell.
- The unit cell's rank (effective number of spheres inside a unit cell).
- The relationship between the radius and the edge length of a single sphere.

- Fractional packing (fraction of volume occupied by spheres in a unit cell).

The following parameters are provided in the table below for all three unit cells:

Type of Cubic Crystal	**No. of atoms at different locations**			**Structure**	**Rank**	**Packing**	**Relation b/w atomic radius and edge length (a)**
	Corners	**Body Centres**	**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%	$r = \frac{\sqrt{2}a}{4}$

Density of Cubic Crystals

By the following formula, the density of the cubic crystal is given:

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

Where, Z is the rank of the unit cell, M is the molar mass of the solid, a is the edge length of the unit cell, N_A is the Avogadro number.

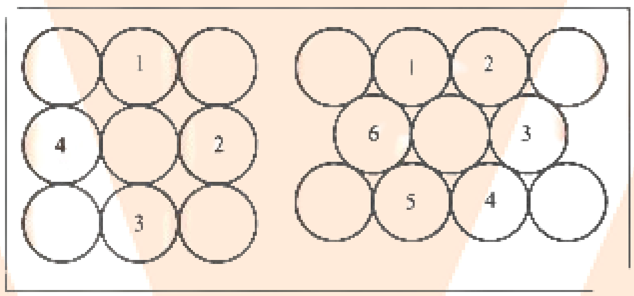
The volume of Z will depend on the type of unit cell.

Close packing in solids: Origin of unit cells

Assume we have a set of spheres of identical size that we must arrange in a single layer with the requirement that the spheres be in close proximity to one another. There are two sorts of layers that can be used:

- Square Packing
- Hexagonal Packing

Spheres are arranged in square packing in such a way that the rows are both horizontal and vertical. The Co-ordination number is 4 in this situation.



It is more efficient to pack hexagonally. It has a Coordination number of 6 and has fewer voids than square packing.

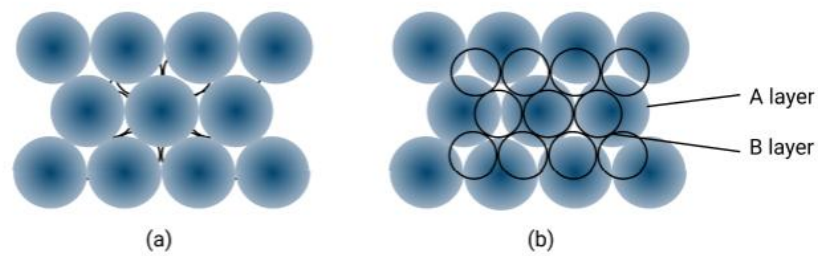
If we add another layer to the square packing, we can do the following:

- A comparable layer is placed just above the foundation layer, with the second layer's spheres appearing just above the first layer's spheres, and the layers are repeated. If the first layer is designated as A, the packing is of the type AA, and the unit cell is simple cubic.
- On the other hand, we get BCC unit cells and ABAB type of packing when spheres from the second layer are inserted in depressions from the first layer.

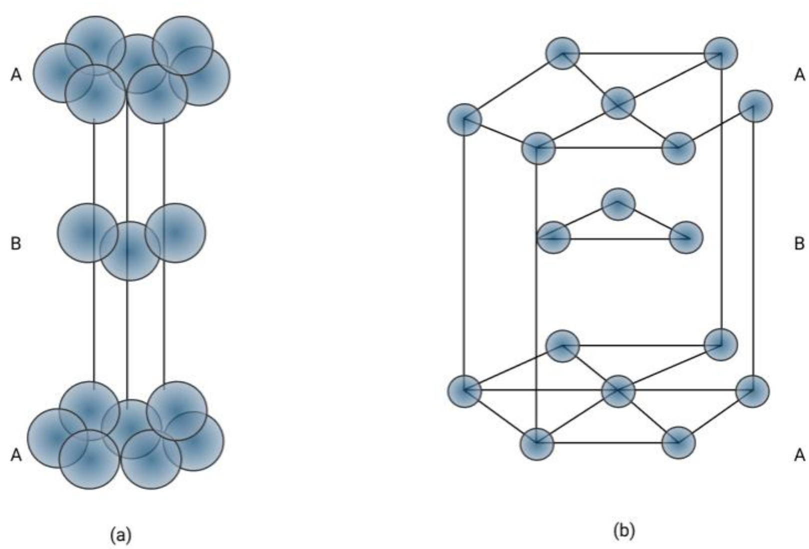
The following are examples of hexagonal foundation layer arrangements:

When we place the second hexagonal layer A in the depressions of the first hexagonal layer A, we get two sorts of voids. Hollow and through voids of layer A and layer B are the X kind of voids. Layer B voids that are directly above spheres in layer A are referred to as Y type voids. When the spheres of the second layer are placed over Y voids, layer 1 is repeated, and ABABAB type packing is obtained. The hexagonal unit cell is obtained in this arrangement, and the packing is known as hexagonal close packing (HCP). This packing has a 74 percent efficiency.

When the third layer is applied to X-type voids, a new layer C is created, and the process is repeated. Packing of the ABCABCABC type will be obtained. The FCC unit cell is used in this design, and the packing efficiency 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.

VOIDS

Definition

Voids are the empty spaces inside a sphere. The amount and shape of voids is determined by the unit cell and packing used.

Radius Ratio

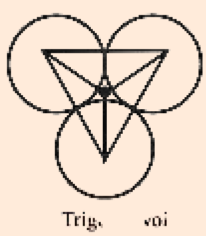
The radius ratio of a sphere that can be perfectly fit in the void to the radius of surrounding spheres is used to determine the size of the void. This is written as:

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

Types of voids

Trigonal Void

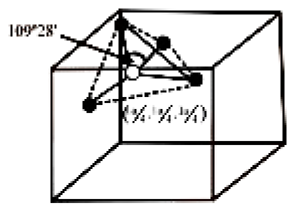
It is the void formed of equal radii which touches each other as shown in the figure.

Figure	**Key Points**
	• Radius Ratio $\frac{r}{R} = 0.155$ • Smallest void • Coordination number is 3.

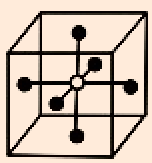
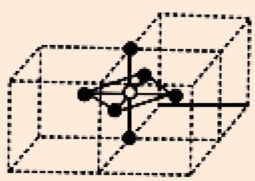
Tetrahedral Void

It is formed by the contact of four spheres and is located in the centre of a tetrahedron formed by the contact of four spheres.

Figure	**Key Points**

	• Radius ratio $\frac{r}{R} = 0.225$ • Number of voids in FCC crystals is 8. • Position at a distance: $\frac{a\sqrt{3}}{4}$ from every corner. • Coordination number is 4.

Octahedral Void

Figure	**Key Points**
 	• Radius ratio $\frac{r}{R} = 0.414$ • Number of voids in FCC crystals is 4. • Positions: Body centre and edge centre. • Rank is 4. • Coordination number is 6.

Cubic Void

The voids formed by the close contact of eight spheres.

The following are the key points:

- Radius ratio is equal to $\frac{r}{R} = 0.732$
- Number of voids in a cubic crystal is 1.
- Position is at the body centre.

- Coordination number is 8.
- Rank 1.

It is clear from the above details that:

Trigonal < Tetrahedral < Octahedral < Cubic

CLASSIFICATION OF IONIC STRUCTURES

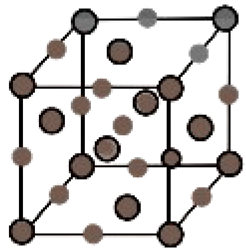
The simultaneous arrangement of cations and anions in a lattice/unit cell produces ionic compounds. The larger of two species takes up major places in a unit cell, while the lesser species takes up vacancies in proportion to their size. Which is determined by the radius ratio. Below is a list of the various ratios.

Limiting Radius Ratio $x = \frac{r_+}{r_-}$	**C. N.**	**Shape**	**Example**
$x < 0.155$	2	Linear	BeF_3
$0.155 \leqslant x \leqslant 0.225$	3	Planar Triangular	$AlCl_3$
$0.225 \leqslant x \leqslant 0.414$	4	Tetrahedron	ZnS
$0.414 \leqslant x \leqslant 0.732$	6	Octahedron	NaCl
$0.732 \leqslant x \leqslant 0.999$	8	Body centred cubic	CsCl

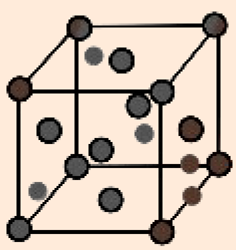
On the basis of these ratio ranges, the ionic crystal is classified into five categories which are as follows:

NaCl **Type Structure**

Figure	**Key Points**

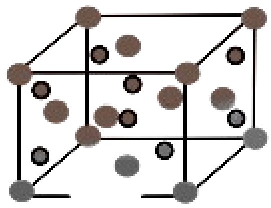
 Rock salt structure	• Cl^- occupy corners and face centres and Na^+ occupy octahedral voids in FCC crystal. • Effective formula is Na_4Cl_4 • Coordination number of Na^+ is 6. • Coordination number of Cl^- is 6. • Distance b/w the nearest neighbour $[r_{Na^+} + r_{Cl^-} = \frac{a}{2}]$

ZnS **Type Structure**

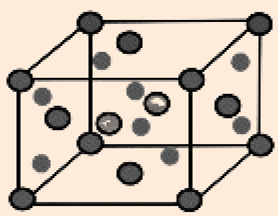
Figure	**Key Points**
 Zinc Blende Structure	• S^{2-} ions occupy main positions and Zn^{+2} ions are present in alternate tetrahedral voids in FCC crystal. • Effective formula is Zn_4S_4 • The Coordination of Zn^{+2} is 4. • Coordination number of S^{2-} is 4. • $r_{Zn^{+2}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$

Fluorite Type Structure

Figure	**Key Points**

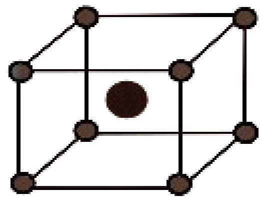
	• Ca^{+2} ions occupy main positions and F^{-} ions occupy tetrahedral voids in FCC crystal. • Effective formula is Ca_4F_8 . • The Coordination number of Ca^{+2} is 8. • Coordination number of F^{-} is 4. • $r_{Zn^{+2}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$

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. • The Coordination number of Li^{+} is 4. • Coordination number of O^{2-} is 8. • $r_{Li^{+}} + r_{O^{2-}} = \frac{a\sqrt{3}}{4}$

$CsCl$ **Type Structure**

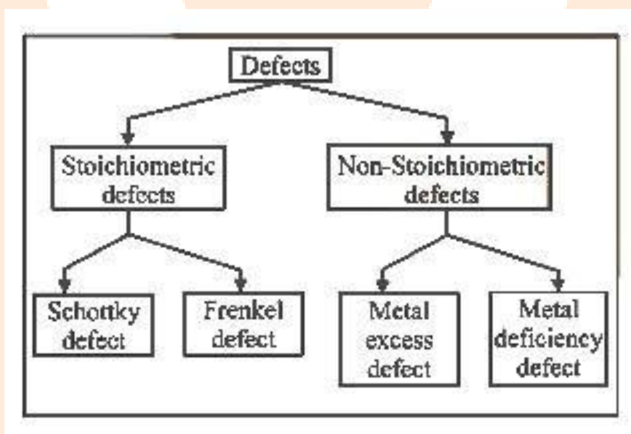
Figure	Key Points

 Cesium Halide structure	• Cl^- ions simple cubic locations (corners) and Cs^+ ions occupy body centre in BCC lattice. • Effective lattice is $CsCl$. • The Coordination number of Cs^+ is 8. • Coordination number of Cl^- is 8. • $r_{Cs^+} + r_{Cl^-} = \frac{a\sqrt{3}}{4}$

IMPERFECTIONS IN SOLIDS

In a crystal structure sometimes some imperfections or defects occur:

Classification of defects

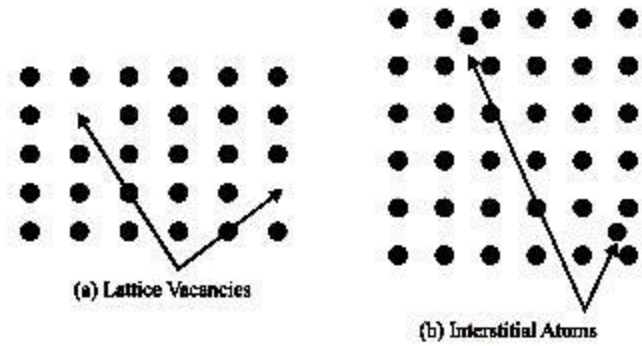


Vacancies

This type of defect occurs when the positions that should contain atoms or ions are vacant.

Interstitial Sites

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

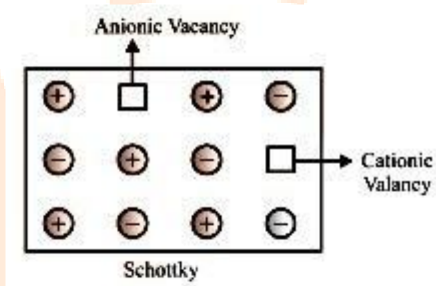


Stoichiometric Defects

The stoichiometry of solids are not disturbed by these defects.

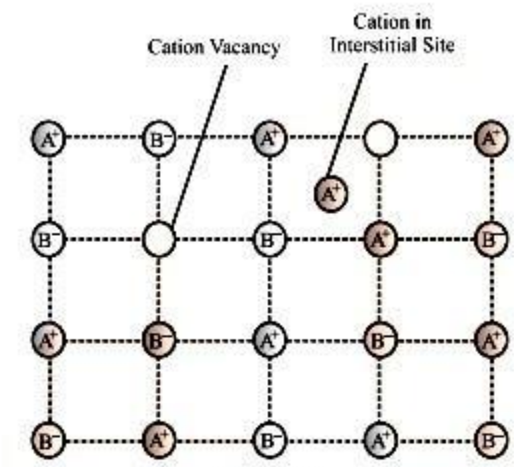
Schottky Defects

In ionic solids, it's a vacancy defect. Electrical neutrality is maintained because the number of missing cations and anions is equal. The density of the substance is reduced as a result of this flaw. Ionic compounds with almost identical cation and anion sizes demonstrate the flaw. Examples are: KCl, NaCl, AgBr etc.



Frenkel Defect

The smaller ion is relocated from its typical position to an interstitial region in ionic solids. At its original place, it causes a vacancy defect, and at new locations, it causes an interstitial defect. Dislocation defect is another name for it. It has no effect on the solid's density. Ionic compounds with a considerable disparity in ion size are examples of this type of defect.



A Frenkel defect

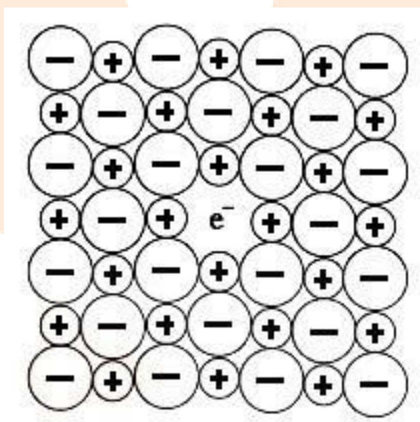
Note: Silver bromide $(AgBr)$ shows Schottky and Frenkel defects both.

Non Stoichiometric Defects

The compounds with these flaws have combining components in a different ratio than their stoichiometric formulas require.

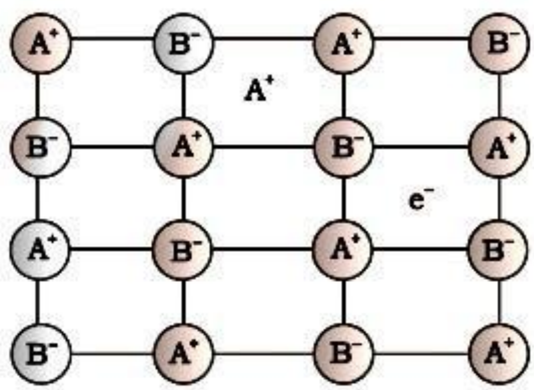
Metal Excess Defect

Due to anionic vacancies: It's possible that the anion is absent from its lattice position, leaving an electron behind to keep the charge balanced. The F centre is the electron-containing site. They provide the crystal colour; F stands for Farbenzenter, which means colour. This defect looks like schottky defect and can be seen in crystals with schottky defect. Examples: $NaCl, KCl$ etc.


An F centre in a crystal

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

To maintain electrical neutrality, an additional cation may be present in one interstitial site while an electron is present in another interstitial site. This is a flaw that is similar to the Frenkel defect and can be discovered in crystals with the Frenkel defect.



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

Metal Deficieny Defect

When metal has a fluctuating valency, this is a defect. FeO , for example, is generally found in compositions ranging from $Fe_{0.93}O$ to $Fe_{0.96}O$. Some Fe^{+2} cations are missing from FeO crystals, but the loss of positive charge is compensated for by the existence of the requisite amount of Fe^{+3} ions.