NEET Revision Notes Chemistry The Solid State

Introduction

Apart from liquid and gaseous states, a 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.

Property	Crystalline solids	Amorphous Solids
Shape	Crystalline solids have a long-	Amorphous solids have short-
Shape	range order.	range order.

The table below shows the many differences.

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Melting point	Crystalline solids tend to have definite melting points.	Amorphous solids do not have a definite melting point.
Heat of fusion	Crystalline solids has a definite heat of fusion.	Amorphous solids do not have 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, which means they break into two pieces with irregular shapes.
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 interfacial angles.	Amorphous solids do not have 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
Molecu lar						
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

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Hydrog en Bonded	Molecules	Hydrogen bonding	H ₂ O (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 solutions.	High
	Positive ions in a sea of delocalised electrons.	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleabl e and ductile	Conducors in solid state as well as in molten state.	Fairly high
Covale nt or networ k 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.

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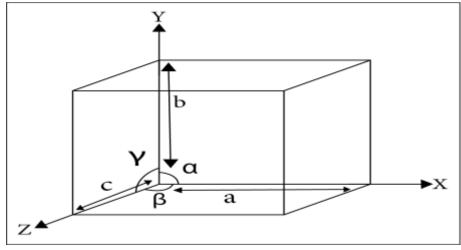


Image: The interfacial angles: alpha, beta, gamma.

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:

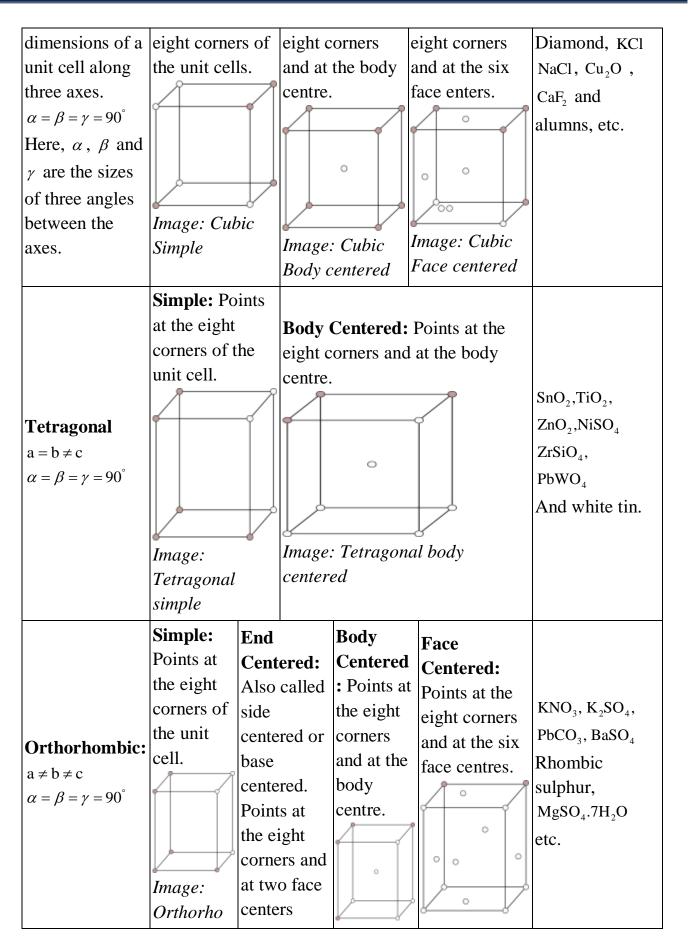
Crystal System	Axial Distance	Axial angles	Examples
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	Copper, Zinc blende, KCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	White tin, SnO_2 , TiO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	Rhombic sulphur, 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	Simple: Lattice points at the	Centerea:	Face Centered: Points at the	Pb, Hg, Ag Au, Cu, ZnS

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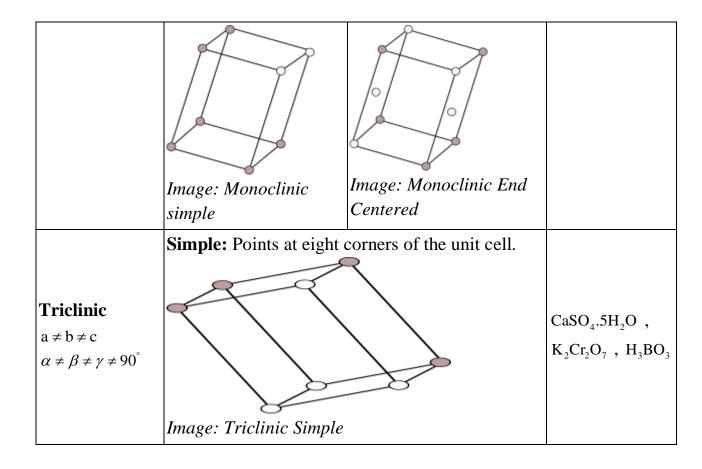


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	mbic simple	each other.	centered	Image: Orthorhombic face centered	
Rhombohedral or Trigonal a = b = c, $\alpha = \beta = \gamma \neq 90^{\circ}$	Image: Rho	ombohedral S	Simple	of the unit cell.	NaNO ₃ , CaSO ₄ , calcite, quartz, As, Sb, Bi
Hexagonal $a = b \neq c$, $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	Simple: Points at the twelve or points at the twelve corners of the unit cell out corners of the hexagonal lined by thick line, prism and at the centres of top and bottom faces.				ZnO, PbS, CdS , graphite, ice, Mg, Zn, Cd etc.
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^{\circ}$, $\beta \neq 90^{\circ}$	Simple: Po eight corne unit cell.		the eight co	ered: Point at orners and two s opposite to	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $CaSO_4.2H_2O$, monoclinic sulphur etc.

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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

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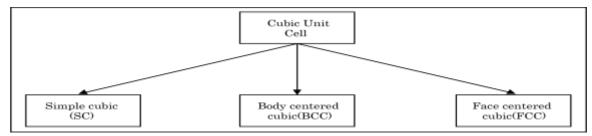


Image: Cubic unit cells

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	No. of atoms at different locations		Structure	Donk	Packing	Relation b/w atomic radius	
Crystal	Corner s	Body Centres	Face Centre		Kalik	I acking	and edge length (a)
Simple Cubic	8	_	_	Image: Simple cubic structure	1	52%	r = a/2
Body Centred	8	1	-	Image: Body Centred structure	2	68%	$r = \frac{\sqrt{3a}}{4}$
Face Centred	8	-	6		4	74%	$r = \frac{\sqrt{2a}}{4}$



Image: Face Centred	
structure	

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 Coordination number is 4 in this situation.

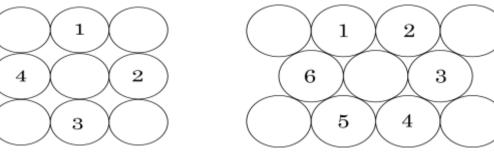


Image: Square packing

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.

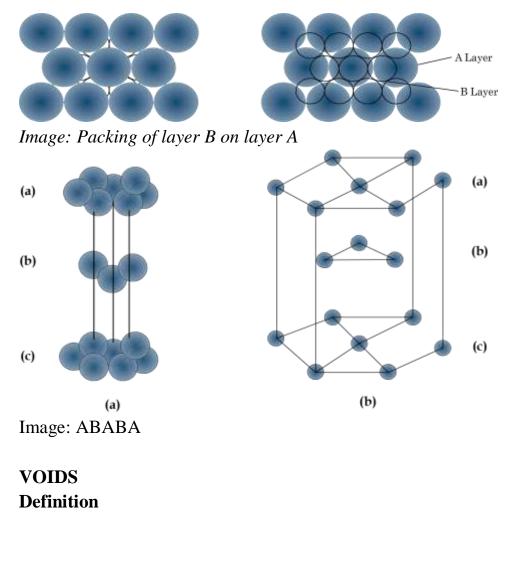
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• On the other hand, we get BCC unit cells and ABAB type of packing when spheres from the second layer are inserted in depressions from the first layer.

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%.



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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 touch each other as shown in the figure.

Figure	Key Points
\bigcirc	Radius Ratio
	$\frac{r}{R} = 0.155$
	Smallest void
Image: Trigonal 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
Image: tetrahedral void.	 Radius ratio r/R = 0.225 Number of voids in FCC crystals is 8. Position at a distance: a√3/4 from every corner. Coordination number is 4.

Octahedral Void:

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Figure	Key Points
Image: Octahedral void 1 Image: Octahedral void 2	 Radius ratio ^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 are 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

Imperfections in solid:

In a crystal structure sometimes some imperfections or defects occur:

Classification of defects

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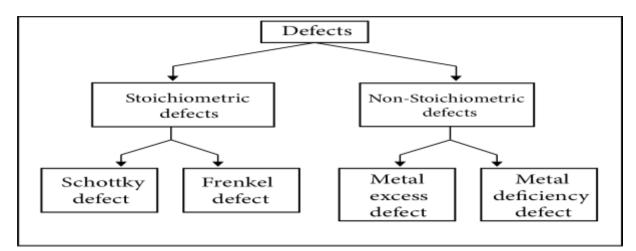


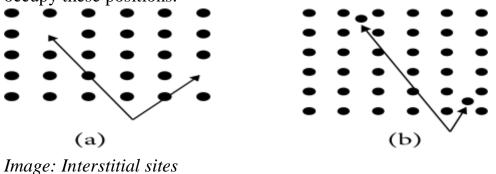
Image: Classification of defects

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.



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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.

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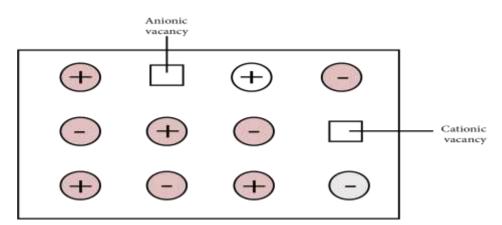


Image: Schottky Defects

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.

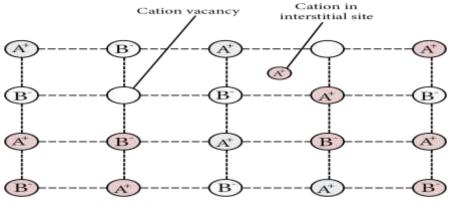


Image: Frenkel defect

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

Non-Stoichiometric Defects

The compounds with these flaws have combined 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

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Farbenzenter, which means colour. This defect looks like Schottky defect and can be seen in crystals with Schottky defect. Examples: NaCl, KCl etc.

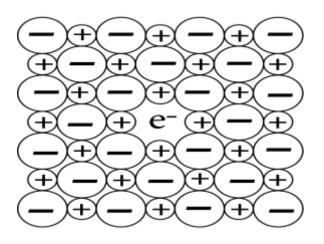


Image: F in a crystal

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.

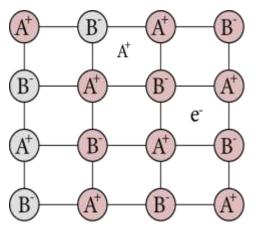


Image: Metal Excess Defect Cation

Metal Deficiency 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.