6

The Solid State

Solids are the chemical substances which are characterised by definite 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.

Types of Solids

The solids are of two types : Crystalline solids and amorphous solids.

Distinction Between Crystalline and Amorphous Solids

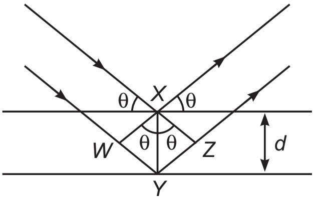
S.No.	Crystalline solids	Amorphous solids
1.	These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space.
2.	These are true solids.	These are super cooled liquids or pseudo solids.
3.	These have long order in arrangement of the particles.	These have short order in arrangement of particles.
4.	These are anisotropic in nature, i.e. their physical properties are different in different directions.	These are isotropic in nature i.e. their physical properties are same in all the directions.
5.	They have sharp melting points.	They melt over a certain range of temperature.
6.	They undergo a clean cleavage when cut.	They undergo irregular cleavage when cut.
7.	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.

Types of Crystalline Solids

Character	Ionic solids	Covalent or network solids	Molecular solids	Metallic solids
Constituent particles	Positive and negative ions	Atoms	Molecules	Positive metal ions (kernels) and free electrons
Bonding forces	Electrostatic or coulombic attraction	Covalent	van der Waals' Dipole-dipole	Metallic bonding
Melting point	High melting point	Very high melting point	Low melting point	Moderate to high melting point
Physical nature	Hard and brittle	Very hard	Very soft	Hard but malleable and ductile
Conductance	Conductors in aqueous solution or in molten state but insulators in solid state	Non-conductor	Insulator	Good conductor
Examples	NaCl, CaF_2, MgO, ZnS	Diamond, Silica, SiC	H_2O, CO_2, CCl_4, HCl, SO_2	Cu, Fe, Ag, Mg.

Note Molecular solids are further subdivided into non-polar molecular solids, polar molecular solids and hydrogen bonded molecular solids.

Structure Determination by X-ray Diffraction (Bragg's Equation)



When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. If the waves are in phase after reflection, the difference in distance travelled by the two rays (i.e. path difference) must be equal to an integral number of wavelength, $n\lambda$ for constructive interference.

Thus, path difference $= WY + YZ$

$$= XY \sin\theta + XY \sin\theta$$

$$= 2\,XY \sin\theta = 2d \sin\theta$$

$$\therefore \quad n\lambda = 2d \sin\theta$$

This equation is called Bragg's equation.

where, $n = 1, 2, 3 \ldots$ (diffraction order),

λ = wavelength of X-rays incident on crystal and

d = distance between atomic planes

θ = angle at which interference occurs.

Crystal Lattices

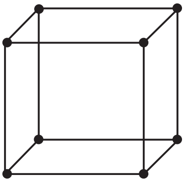
In three dimensional space, a regular arrangement and repeating pattern of the constituent particles of a crystal in which each particle is depicted as a point is known as **crystal lattice** or **space lattice**.

Unit Cell

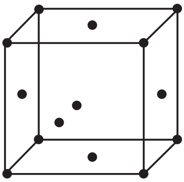
The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

Types of Unit Cell

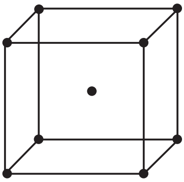
1. **Simple or primitive unit cell** In which the particles are present at the corners of unit cell only.



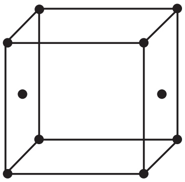
2. **Face centred unit cell** In which the particles are present at the corners as well as at the centre of each of six faces of unit cell.



3. **Body centred unit cell** In which the particles are present at the corners as well as at the centre of unit cell.



4. **End centred unit cell** In which the particles are present at the corners and at the centre of two opposite faces of unit cell.



Number of Particles Per Unit Cell

Unit cell	No. of particles and their contribution			Total
	Corner	Face	Centre	
Simple cubic	$8 \times \frac{1}{8}$	—	—	1
Face centred	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	—	4
Body centred	$8 \times \frac{1}{8}$	—	1	2
End centred	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$	—	2

Seven Crystal Systems and Possible Variations

There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called **Bravais Lattices,** on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axial distances.

Seven Crystal Systems

	Crystal system	Parameters of unit cell		Possible variation
		Axial distances or edge lengths	Angles	
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, body centred, face centred.
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body centred
3.	Rhombohedral or trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Primitive

	Crystal system	Parameters of unit cell		Possible variation
		Axial distances or edge lengths	Angles	
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Primitive, body centred, face centred.
4.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Primitive, body, face and end centred.
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Primitive and end centred.
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Primitive

Coordination Number (CN)

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 body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12.

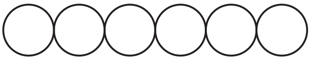
High pressure increases CN and high temperature decreases the CN.

Close Packing in Crystals

Packing in solids may be divided into the following categories :

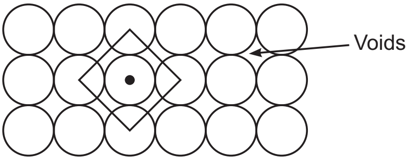
One Dimensional packing of constituent particles

In one dimensional close packing arrangement, the coordination number is 2.

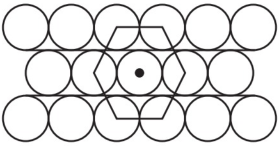


Two Dimensional Packing of Constituent Particles

(i) **Square Close Packing** When atoms arranged in a row is stacked with atoms arranged in another row exactly one over another is known as square close packing. Coordination number in square close packing is 4. This is also known as *AAA*...type arrangement space occupied by spheres is 52.4%.

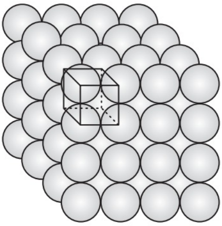


(ii) **Hexagonal Close Packing** This is generated by placing spheres of the second row in the depressions of first row. Coordination number in hexagonal closed packing is 6. This is also known as *ABAB*...type arrangement space occupied by spheres is 60.4%. Hence, it is more efficient.



Three Dimensional Packing of Constituent Particles

(a) **Three dimensional closed packing from two dimensional square close packed layers** When two dimensional square close packed layers are arranged exactly one over the other they constitute a three dimensional close packing. The arrangement is known as *AAA* arrangement.



(b) **Three dimensional close packing from two dimensional hexagonal close packed layers** When hexagonal close packed layers are stacked kone over another, they form three dimensional close packing.

- (i) **Hexagonal close packing** When third layer is placed over second layer in such a way that they constitute tetrahedral void. The arrangement is called *ABAB* pattern.
- (ii) **Cubic close packing** When the third layer is placed over second layer in such a way that sphere covers octahedral voids. The arrangement is called *ABABC* pattern.

In both these arrangements 74% space is occupied.

Coordination number in hcp and ccp arrangement is 12 while in bcc arrangement, it is 8.

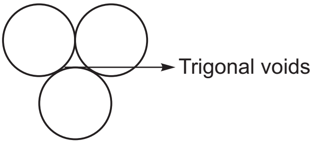
Close packing of atoms in cubic structure = fcc> bcc> scc

All noble gases have ccp structure except He (hcp structure).

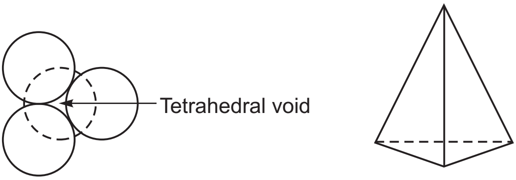
Void or Space or Holes

Empty or vacant space present between spheres of a unit cell, is called void or space or hole or interstitial void. When particles are close packed resulting in either ccp or hcp structure, three types of voids are generated:

Trigonal voids exist in two dimensional arrangement.

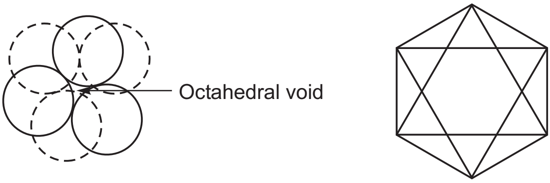


Tetrahedral voids are holes or voids surrounded by four spheres present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.



$r_{\text{void}} = 0.225 \times r_{\text{sphere}}$ (for tetrahedral voids)

Octahedral voids are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.



$r_{\text{void}} = 0.414 \times r_{\text{sphere}}$ (for octahedral voids)

The number of octahedral voids present in a lattice is equal to the number of close packed particles.
The number of tetrahedral voids present in a lattice is twice to the number of close packed particles.

Packing Efficiency or Packing Fraction

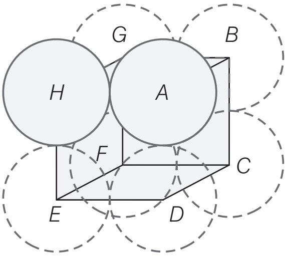
The percentage of total space filled by the particles.

(i) **Primitive cubic unit cell** Atoms touch each other along edges.

Hence, $d = a$ or $r = \frac{a}{2}$ (r = radius of atom and a = edge length)

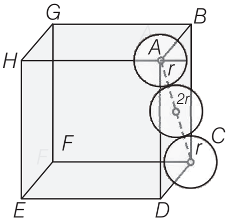
Therefore,

$$\text{PF} = \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.524 \text{ or } 52.4\%$$



Simple cubic unit cell, the spheres are in contact with each other along the edge of the cube

(ii) **Face centred cubic unit cell** Atoms touch each other along the face diagonal.



Cubic close packing, or face centred cubic unit cell other sides are not provided with spheres for sake of clarity

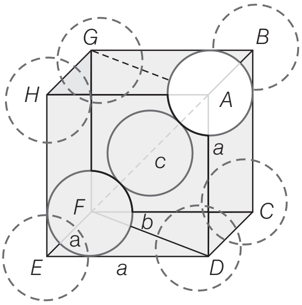
Hence, $d = a/\sqrt{2}$

or $r = \sqrt{2}a/4$ ($\because$ Length of face diagonal $= \sqrt{2}a$)

Therefore, $$\text{PF} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74 \text{ or } 74\%$$

The packing efficiency of hcp and ccp structures is also 74%.

(iii) **Body centred cubic unit cell** Atoms touch each other along the body diagonal.



Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries)

Hence, $d = \sqrt{3}a/2$

or $r = \sqrt{3}a/4$ ($\because$ Length of body diagonal $= \sqrt{3}a$)

Therefore, $$\text{PF} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68 \text{ or } 68\%$$

The packing efficiency of hcp and ccp structure is also 74%.

Density of Unit Cell (d)

$$\text{Density of unit cell} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

$$d = \frac{Z \cdot m}{a^3} = \frac{ZM}{a^3 \times N_A} \text{ kg/cm}^3$$

$$\left[\text{Mass of an atom } (m) = \frac{M}{N_A}\right]$$

(The density of the unit cell is same as the density of the substance.)

where, d = density of unit cell, M = molecular weight

Z = number of atoms per unit cell, N_A = Avogadro number

a = edge length of unit cell.

The Structure of Ionic Crystals

The **ionic radius ratio** of cation and anion play a very important role in giving a clue to the nature of the crystal structure of ionic substance.

The ratio r_+ to r_- is called radius ratio.

$$\text{Radius ratio} = \frac{\text{radius of positive ion}}{\text{radius of negative ion}} = \frac{r_+}{r_-}$$

Radius Ratio and Crystal Structure

S. No.	Radius ratio (r_+ / r_-)	Coordination number	Shape	Crystal structure	Example
1.	< 0.225	2 or 3	Linear or triangular	Linear or triangular	B_2O_3
2.	0.225–0.414	4	Tetrahedral	ZnS type (sphalerite)	CuCl, CuBr, HgS, BaS
3.	0.414–0.732	4 or 6	Squar planar or octahedral	NaCl type	MgO, NaBr, CaS, KBr, CaO, AgCl
4.	0.732 or more	8	Cube	CsCl type	CsI, CsBr, NH_4Br, TlBr

Ionic crystals may be of two types:

(i) AB type and (ii) A_2B or AB_2

Structure of Ionic Crystals

Ionic crystal type	Cation occupy	Anion form	Coordination number
NaCl (Rock salt structure) type	All octahedral voids	fcc unit cell	6 : 6
CsCl type	Body centre	simple cubic unit cell	8 : 8
ZnS (Sphalerite structure) type	Alternate tetrahedral voids	fcc unit cell	4 : 4
CaF_2 (Fluorite structure) type	Alternate body centre	simple cubic unit cell	8 : 4
Na_2O (Antifluorite structure) type	All tetrahedral sites	fcc unit cell	4 : 8

On applying pressure, NaCl structure (6 : 6 coordination) changes into CsCl structure (8 : 8 coordination) and reverse of this occur at high temperature (760 K).

Imperfections 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. Deviations from perfect arrangement may occur due to rapid cooling or presence of additional particles.

The defects are of two types, namely **point defects** and **line defects.**

The irregularities or deviations from ideal arrangement in entire rows of lattice points is called **line 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 :

(1) stoichiometric defects (2) impurity defects

(3) non-stoichiometric defects.

1. Stoichiometric Defect

These are point defects that do not disturb the stoichiometry of the solid. They are also called **intrinsic** or **thermodynamic defects**.

(a) **In non ionic solids**, two types of defects are present:

Vacancy Defect When some of the lattice sites are vacant, crystal is said to have vacancy defect and results in decrease in density of substance.

Interstitial Defect When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect and results in increase in density of substances.

(b) **In ionic solids**, basically these are of two types, Frenkel defect and Schottky defect.

	Schottky defect	Frenkel defect
1.	It is due to equal number of cations and anions missing from the lattice sites.	It is due to the dislocation of ions (usually cations) from the lattice sites to occupy the interstitial sites.
2.	This results in the decrease in density of crystal.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number, e.g. NaCl, CsCl, etc.	This type of defect is found in crystal where the difference in the size of cations and anions is very large, e.g. AgCl, ZnS, etc.

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

2. Impurity Defect

It arises when foreign atoms or ions are present in the lattice. In case of ionic compounds, the impurity is also ionic in nature. When the impurity has the same charge as the host ion, it just substitutes some of the host ions. Impurity defects can also be introduced by adding impurity ions having different charge than host ions, e.g. molten NaCl containing a little amount of $SrCl_2$ is crystallised. In such cases,

cationic vacancies produced = [number of cations of higher valence × difference in valence of the host cation and cation of higher valence]

3. Non-Stoichiometric Defect

Non-stoichiometric crystals are those which do not obey the law of constant proportions. The number of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole is neutral.

Types of non-stoichiometric defects are as follows:

(i) **Metal excess defect due to anionic vacancies** Alkali halides like NaCl and KCl show this type of defect. F-centres are the sites from where anions are missing and the vacant sites are occupied by electrons. F-centres contribute colour and paramagnetic nature of the crystal [F stands for German word *Farbe* meaning colour].

Metal excess defect due to presence of extra cations at interstitial sites, e.g. zinc oxide is white in colour at room temperature. On heating, it loses oxygen and turns yellow.

$$\text{ZnO} \xrightarrow{\text{Heating}} \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2e^-$$

(ii) **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 $Fe_{0.96}O$.

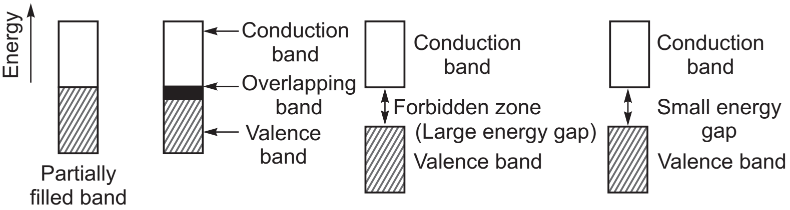
In crystal of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Electrical Properties of Solids

Solids can be classified into three types on the basis of their conductivities.

Classification of Solids on the Basis of Electrical Conductivity

Type of solid	Conductivity (ohm^{-1} m^{-1})	Reason of conductivity	Examples
Conductors	$10^4 - 10^7$ (Very high)	Motion of electrons	Metals like Ag, Al
Insulators	10^{-20} to10^{-10} (Very low)	Do not permit electricity to pass	Wood, rubber, bakelite
Semiconductors	$10^{-6} - 10^4$ (Moderate)	Motion of interstitial electrons or holes or both	Si, Ge, etc.



Conductors **Insulator** **Semiconductor**

> The electricity produced on heating a polar crystal is called **'pyroelectricity'**. When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called **'piezoelectricity'**.

Semiconductors

Electronic conductors having electrical conductivity in the range of $10^4 - 10^{-6}\ \Omega^{-1}\ \text{m}^{-1}$ are known as semiconductors, e.g. Si, Ge, Sn (grey), Cu_2O, SiC and GaAs.

Intrinsic Semiconductors

Pure substances that are semiconductors are known as intrinsic (undoped) semiconductors, e.g. Si, Ge.

Extrinsic Semiconductors

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

(i) ***n*-type semiconductors** Silicon or germanium doped with 15 group elements like phosphorus is called *n*-type semiconductor. The conductivity is due to the presence of negative charge (electrons).

(ii) ***p*-type semiconductors** Silicon or germanium doped with 13 group element like gallium is called *p*-type semiconductor. The conductivity is due to the presence of positive holes.

Some typical 13-15 compounds are InSb, AlP and GaAs and some typical 12-16 compounds are ZnS, CdS, CdSe and HgTe.

These exhibit electrical and optical properties of great use in electronic industry.

Magnetic Properties of Solids

Solids can be divided into different classes depending on their response to magnetic field.

Paramagnetic Substances

These are attracted by the magnetic field and have unpaired electrons. These lose magnetism in the absence of magnetic field,
e.g. O_2, Cu^{2+}, Fe^{3+}, etc.

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, NaCl, etc.

Ferromagnetic Substances

These are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field, e.g. Fe, Co, CrO_2 and Ni.

Anti-ferromagnetic Substances

These substances have net magnetic moment zero due to compensatory alignment of magnetic moments, e.g. MnO, MnO_2, FeO, NiO, Cr_2O_3 etc.

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 ($M^{2+}Fe_2O_4$), where M = Mg, Cu, Zn etc.