



Solid State

Solid:

A form of matter which possesses rigidity, do not flow and hence they have a definite shape and a definite volume is called solid.

Classification of solids:

On the basis of the nature of order present in the arrangement of their constituent particles (atoms, ions or molecules), solids are classified as crystalline and amorphous.

A. Crystalline solids:

A crystalline solid is a homogeneous solid in which the constituent particles (atoms, ions or molecules) are arranged in a definite repeating pattern.

They are further classified as:

a. Isomorphous form (Iso-same, renorphous-form):

Two or more substances having the same crystal structure are said to be isomorphous.

e.g.

- NaF and MgO (atoms in the ratio 1 : 1)
- Cr_2O_3 and Fe_2P_3 (atoms in the ratios 2 : 3)

b. Polymorphous / Allotropic form (Poly-many, morphous-form):

A single substance that crystallises in two or more forms under different conditions is called polymorphous.

e.g.

- Carbon has two polymorphous forms i.e. Graphite and diamond.
- Sulphur has two polymorphous form i.e. Rhombic and Monoclinic sulphur.

B. Amorphous solid/Pseudo solids/ Super cooled solids:

The substances that appear like solids but do not have well developed perfectly ordered crystalline structure are called amorphous (no form) solids.

e.g.

Jar, glass, plastic, rubber, butter, starch, cellulose, proteins etc.

Distinguish between crystalline solids and amorphous solids:

S.N.	Property	Crystalline Solids	Amorphous Solids
1.	Geometry	They have definite geometry.	They have no definite geometry.
2.	Shape	They have regular shape.	They have irregular shape.
3.	Melting point	They have sharp melting point.	They do not sharp melting point.
4.	Solid	They are true solids.	They are pseudo solid/super cooled liquids.
5.	Arrangement of particles	They have long range order.	They have short range order.
6.	Cleavage property clean cleavage.	When cut, they undergo surface of two pieces.	When cut, they undergo irregular
7.	Directional nature of properties	They are anisotropic i.e. have different physical properties in all directions.	They are isotropic. i.e. have same physical properties in all directions.
8.	Heat of fusion	Heat of fusion values are definite.	Heat of fusion values are not definite.
9.	Examples	Cu, Ag, ZnS, NaCl, KNO_3 etc.	Glass, Rubber, Plastics etc.

Glass:

Glass is an optically transparent material produced by fusing together silicon oxide with sodium oxide, boron oxide and a trace amount of transition metal oxide is added to impart colour to the glass.

Types of glass	Composition
Pyrex glass	60 to 80% SiO_2 + 10 to 25% B_2O_3 , some amount of Al_2O_3 .
Soda lime glass	75% SiO_2 + 15% Na_2O + 10% CaO .
Red glass	Trace amount of gold and copper.
Yellow glass	UO_2 .
Blue glass	It contain CoO or CuO .
Green glass	It contain Fe_2O_3 , or CuO .

• Classification of Crystalline solid:

Crystalline solid are classified into four main types depending on nature of bonds:

1. Molecular solids
2. Ionic solids
3. Metallic solids an
4. Covalent solids

Sr. No	Types of solid	Constituent particles	Nature of binding	Examples	Physical nature	Electrical conductivity	Melting point	Other characteristics
1.	Molecular solids	Molecules	Weak forces					Low density And volatile, low enthalpies of fusion and vaporization.
	i) non polar	Atoms of noble gas or non-polar molecules	London dispersion forces	$\text{Ar}, \text{H}_2, \text{I}_2, \text{S}$ $\text{Solid } \text{CO}_2$ (dry ice) CH_4	Soft	Insulator	Very low	
	ii) Polar	Polar molecules	Dipole-dipole attractions	HCl, SO_2	Soft	Insulator	Low	
	iii) Hydrogen	Molecules bounded H linked to F, O or N	Hydrogen containing	$\text{H}_2\text{O}(\text{ice}),$ bonding	Generally NH_3 , some are hard	Insulator soft or	Low	
2.	Ionic solids (W.Kossel) negative ions	Positive and electrostatic forces of attraction	Coulombic or CaF_2	$\text{NaCl}, \text{LiF}, \text{MgO}, \text{ZnS}$	Hard but brittle	Insulators in solid state but conductors in molten state or aqueous solution	High	Soluble in polar solvents, insoluble in nonpolar solvents. High enthalpies of fusion and vapourisation.
3.	Metallic solids (Drude and Lorentz)	Positive ions In a sea of mobile electrons.	Metallic bonds	All metals and alloys	Hard	Conductor in solid state as well as molten state	Fairly high	Malleable and ductile and possess luster, high enthalpies of fusion.
4.	Covalent solids (G.N. Lewis)	Atoms	Covalent bonds	Dimond. SiO_2 Graphite	Hard Soft	Bad Good	High	Moderate enthalpies of fusion.

• **Allotropic modification of carbon:**

- i. Diamond
- ii. Graphite
- iii. Fullerene

I. Diamond:

Occurrence :

It occurs in nature. It can also be prepared artificially.

Structure:

- i. In diamond, carbon is sp^3 -hybridised.
- ii. Each carbon is tetrahedrally linked to four neighbouring carbon atoms through four strong C-C, sp^3-sp^3 , σ -bonds.
- iii. This network extends in three dimensions to form a giant network of covalent solid.

• **Properties:**

i. Purity:

Diamond is the purest form of carbon.

ii. Bond length:

C-C bond length in diamond are 1.54 Å (154 pm).

iii. Hardness:

It is the hardest substance known with high density and melting point.

iv. Conductivity:

Diamond is a bad conductor of electricity. Since all the electrons are firmly held in C-C, σ -bonds.

v. Transparency:

It is transparent. Because of its high refractive index (2.5) diamond can reflect light.

Uses:

- i. Diamond is used for cutting glass, making borers for rock drilling and for making abrasives.
- ii. When diamond is cut and polished, brilliant light is refracted from its surface. That is why diamond is used for making precious gems and jewellery.

Graphite:

Occurrence :

It occurs in nature and can also be manufactured artificially by heating coke to 3273-3300 K in an electric furnace.

Structure:

- i. In graphite, carbon is sp^2 -hybridized.
 - ii. Each carbon is thus linked to three other carbon atoms forming hexagonal rings.
 - iii. The remaining half filled unhybridized $2p_z$ orbital is for π bonding so that layers of C atoms are formed.
 - iv. Graphite has a two dimensional sheet like (layered) structure consisting of a number of benzene rings fused together.
 - v. The various sheets or layers are held together by weak van der Waal's forces of attraction.
 - vi. The distance between any two successive layers is 3.40 Å (340 pm).
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Properties:**i. Purity:**

Graphite is also the purest form of carbon.

ii. Bond length:

The C-C bond length in graphite are 1.415 Å (141.5 pm)

iii. Softness:

Graphite is a soft and a good lubricating agent because in graphite any two successive layers are held together by weak forces of attraction, one layer can slip over the other.

iv. Conductivity:

Graphite is a good conductor of heat and electricity because in graphite only three electrons of each carbon are used in making hexagonal rings and fourth valence electron of each carbon is free to move.

v. Opacity:

Graphite is a black substance and possesses a metallic lustre.

Uses:

- i. In making electrodes.
- ii. Cores lead pencils.
- iii. Moderator in atomic reaction.

3. Fullerenes:**Discovery:**

Third crystalline allotrope of carbon called fullerenes was discovered collectively by three scientists namely K.E. Smalley and R.F. Curl and H.W. Kroto. For this discovery, these scientists shared the 1996 Nobel prize in chemistry.

Composition:

C_{2n} where $(n > 30)$.

Preparation:

By evaporation of graphite using a powerful laser.

Structure:

- i. All the carbon atoms are equivalent and they undergo sp^2 hybridization. Each carbon atom forms three σ -bonds with other three carbon atoms. The remaining electron of each carbon is delocalized in molecular orbitals which, in turn, give aromatic character to the molecule.
- ii. C_{60} allotrope is most stable among all the fullerenes. It looks like a soccer ball and is sometimes called as bucky ball. It contains 12 five membered rings and 20 six membered rings.
- iii. Six-membered rings are fused both to other six-membered rings and five-membered rings, but the five-membered rings are connected only to six membered rings.
- iv. C_{70} fullerene, resembles a rugby ball. It consists of 12 five membered rings and 25 six-membered rings.
- v. It contains both single and double bonds with carbon-carbon distances of 145.3 and 138.3 pm respectively.

Applications:

- i. $K_{35}C_{60}$ behaves as superconductor below 18 K.
- ii. The tubes made from fullerene and graphite are called nanotubes.
- iii. These are used as high strength materials, conductors, semiconductors and molecular sensors.

- **Classify the following solids into different types:**

Sr.	Name of Solid	Type of Solid
i)	Plastic	Molecular solid
ii)	P ₄ molecule	Molecular solid
iii)	S ₈ molecule	Molecular solid
iv)	Iodine molecule	Molecular solid
v)	Tetra phosphorous decoxide	Molecular solid
vi)	Ammonium phosphate	Ionic solid
vii)	Brass	Metallic solid
viii)	Rubidium	Metallic solid
ix)	Graphite	Covalent solid
x)	Diamond	Covalent solid
xi)	NaCl	Ionic solid
xii)	Silicon	Covalent solid

- **Crystallography:**

The branch of science that deals with the study of structure, geometry and properties of crystal is called crystallography.

External features of the crystal:

- Face:**

The plane surfaces of the crystal are called faces.

- Edge:**

An edge is formed by the intersection of two adjacent faces.

- Interfacial angles:**

The angle between the perpendiculars to the two intersecting faces.

- **Crystal lattice or Space lattice:**

A regular arrangement of the constituent particles (atom, ions or molecules) of a crystal in three dimensional space is called crystal lattice or space lattice.

- **Parameter of unit cell:**

- Crystallographic axes: (Axial length)**

The position of a plans of the crystal in space is shown by the intercepts that it makes on three given lines called crystallographic axes.

From fig. there are different types of axes as

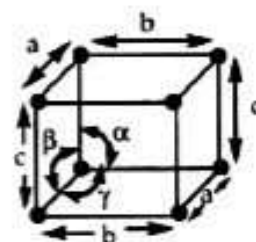
- Vertical line is called 'c' axis.
- The line running from right to left is called 'b' axis.
- The line running from front to rear is called 'a' axis.
- The point of intersection is called origin 'O'.

- Crystallographic angles: (Axial angle):**

- The angle between 'b' and 'c' axes is called ' α '.
- The angle between 'c' and 'a' axes is called ' β '.
- The angle between 'a' and 'b' axes is called ' γ '.

- **Bravais lattices:**

August Bravais (1850) observed that only 7 type of basic or primitive unit cells exist in the crystals. Each system is characterised by the relative lengths of edges i.e. a, b and c and the magnitudes of the angle α , β and γ . Bravais proved that lattice points can be arranged in maximum fourteen types. The arrangement is called Bravais Lattices.



Sr. No.	Crystal System (No. space lattice)	Lattice type	Edge length	Angle	Example	Maximum Symmetry
1.	Cubic (3)	Simple/primitive	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	CsCl	Nine planes, &
		Body centred	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	Li, Cr, CsCl	Thirteen axes, &
		Face centred	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Cu, Al, Ca, Ni	One centre
2.	Tetragonal (2)	Primitive	$a=b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO ₂	Five planes,
		Body centred	$a=b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ , CaSO ₄	& Five axes,
3.	Orthorhombic (4)	Primitive/Simple	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur	Three planes, Three axes
		Body centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO ₃	
		Face centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	BaSO ₄	
		End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	MgSO ₄ ·7H ₂ O	
4.	Monoclinic (2)	Primitive/Simple	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	Monoclinic S	One plane,
		End centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	Na ₂ SO ₄ ·10H ₂ O	& One axis
5.	Triclinic (1)	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , H ₃ BO ₃	No plane, & No axis
6.	Hexagonal (1)	Primitive	$a=b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	ZnO, BeO, CaS, SnS, Graphite	Seven planes, & Seven axes
7.	Rhombohedral (1) or trigonal	Primitive	$a=b=c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, HgS, NaNO ₃ , FeO ₃	Seven planes, & Seven axes

Three dimensional space lattice and unit cell :

In cubic unit cell there are four types of unit cell as.

a. Simple or Primitive cubic unit cell:

The unit cell in which constituents particles are present only at its corner.

The 8 particles at the 8 corner of the cube, represent atoms or ions. (Total eight points)

b. Body centred cubic unit cell:

The unit cell in which constituents particles are present at the centre of body in addition to the particles at its corner.

The 8 particles at the 8 corner of the cube and one more at the centre, represent atom or ions.

(Total $8 + 1 = 9$ points)

c. Face centred cubic unit cell:

The unit cell in which constituents particles are present at the centre of each face in addition to the particles at its corner.

The 8 particles at the 8 corner of the cube and 6 at the centre of 6 faces, represent atoms or ions.

(Total $8 + 6 = 14$ points)

d. Side centred or end centred unit cell:

The unit cell in which constituents particles are present at the centre of only one set of faces in addition to the particles at its corner.

The 8 particles at the 8 corner of the cube and 2 at the centre of upper and lower faces, represent atoms or ions. (Total $8 + 2 = 10$ points)

Contribution of particles in unit cell:

Contribution of a particles present at the corner of the cubic unit cell towards cell = $1/8$.

Contribution of a particles present on the face of the cubic unit cell towards the cell = $1/2$.

Contribution of a particle present within the body of the cubic unit cell towards the cell = 1

Contribution of a particle present at the end centre of the cubic unit cell towards the cell = $1/4$

Evaluation of Number of atoms in per unit cell:

Total number of constituent units (spheres) per unit cell =

$$\frac{1}{8} \times \text{occupied corners} + \frac{1}{2} \times \text{occupied face centres} + \text{occupied body centre} + \frac{1}{4} \times \text{occupied end centre}$$

A. Simple cubic unit cell:

Number of atoms (spheres) in one simple cubic unit cell = $\frac{1}{8} \times 8 + 0 + 0 + 0 = 1$ i.e. one atom per unit cell.

B. Body centred unit cell:

Number of atoms (spheres) in one simple cubic unit cell = $\frac{1}{8} \times 8 + 0 + 1 + 0 = 2$ i.e. two atoms per unit cell.

C. Face centred unit cell:

Number of atoms (spheres) in one simple cubic unit cell = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 + 0 + 0 = 4$ i.e. four atoms per unit cell.

Co-ordination number (C.N.) :

The number of particles surrounding a single particle in the crystal lattice is called co-ordination number that lattice or the number of nearest neighbours particles with which a given particle is in direct contact the crystal lattice of a substance is known as the co-ordination number of that lattice.

Crystal system	Simple Cubic	Body centred	Face centred	Hexagonal close packed
	SCC	BCC	FCC	HCP
CN	6	8	12	12

Structural relationship for cubic lattices:

Sr. No.	Particular entity	lattices		
		Simple Cubic	BCC	FCC
1.	No. of particles per unit cell	1	2	4
2.	Nearest neighbours or (CN)	6	8	12
3.	Distance between nearest neighbours (d) and (r)	$d = 2r$ a	$d = 2r \left[\frac{a\sqrt{3}}{2} \right] = 0.866a$	$d = 2r \left[\frac{a\sqrt{2}}{2} \right] = 0.707a$
4.	Atomic radius (r)	$\frac{a}{2} = 0.5a$	$\left[\frac{a\sqrt{3}}{4} \right] = 0.433a$	$\left[\frac{a\sqrt{2}}{4} \right] = 0.433a$
5.	Volume of atom (V)	$\frac{4}{3} \pi \left(\frac{a}{2} \right)^3$	$\frac{4}{3} \pi \left(\frac{a\sqrt{3}}{4} \right)^3$	$\frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3$
6.	Packing = $\frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$	$\left(\frac{\pi}{6} \right) = 0.524$ or 52.4%	$\left[\frac{\pi\sqrt{3}}{8} \right] = 0.68$ or 68%	$\left[\frac{\pi\sqrt{2}}{8} \right] = 0.74$ or 74%

7. % of void	47.6 %	32 %	26 %
8. Density	$\frac{M}{a^3 \times N_A}$	$\frac{2M}{a^3 \times N_A}$	$\frac{4M}{a^3 \times N_A}$
9. Empty space	$\left(8 - \frac{4}{3}\pi\right)r^3 = 3.81r^3$	$\left(\frac{4}{3} - \frac{8\pi}{3}\right)r^3 = 3.941r^3$	$\left(8 - \frac{16}{3}\pi\right)r^3 = 5.87r^3$

• **The characteristics and Examples of Different Crystal Structure:**

Property	hcp	ccp	bcc
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	ABABA	ABCABCA	ABABA
Available space occupied	74%	74%	68%
Vacant space	26%	26%	32%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard, brittle	Malleable and ductile	

• **Radius ratio:**

Definition:

The limiting value of a ratio of radius of cation to that of anion for given co-ordination number is called radius ratio.

Expression:

Let r^+ and r^- be the radius of cations and anions respectively then-

Radius ratio = r^+ / r^-

• **Radius ratio rule for ionic compounds:**

The relationship between the radius ratio and co-ordination number and structural arrangement are called radius ratio rule.

- If the value of ratio of r^+ / r^- is equal to the expected value then ionic structure becomes stable.
- If the value of r^+ / r^- is less than or greater than expected then ionic becomes unstable.

• **Radius ratio and structural arrangement:**

Sr. No.	Limiting value of radius ratio (r^+ / r^-)	Coordination no. of cation	Structural arrangement	Example
1.	0 - 0.155	2	Linear	-
2.	0.155 - 0.225	3	Planar triangular	B_2O_3
3.	0.225 - 0.414	4	Tetrahedral	ZnS
4.	0.414 - 0.732	6	Octahedral	NaCl
5.	0.732 - 1.00	8	Cubic	csc

• **Ionic solids are hard and brittle :**

- The ionic solids are formed by molecules containing positively charged, small in size cations and negatively charged relatively bigger atoms.
- Thus the electrostatic forces of attraction between nearest neighbouring ions are very strong. Which are responsible for holding very strongly particles together. Thus ionic solids are hard.
- When a force is applied, the layer of ions slip over one another and repel. This breaks the crystal.
- Thus ionic solids are brittle.

• **Solids are lighter than water.**

- Ice has hexagonal three dimensional crystal structure formed by intermolecular hydrogen bonding, which leaves more empty space i.e. unoccupied.

- b. The structure of liquid water and solid ice are almost identical.
- c. However on melting of ice some of the hydrogen bonds are broken and some of the empty spaces are occupied by the water molecule i.e. hexagonal crystalline structure of solid ice collapses while liquid water molecules becomes closed packed.
- d. Thus the density of liquid water is more than ice. Hence ice floats on water.

• **Packing in solids:**

The space occupied by constituents particles in unit cell is called packing in solids.

• **Voids or empty space:**

The unoccupied empty space in unit cell is called by void or empty in unit cell. In three dimensional closed packing of constituents particle shows following two types of voids.

• **Tetrahedral voids:**

Each sphere in the second layer rest on the hollow in the three following sphere in the first layer.

- i. The vacant space surrounded by four neighbours in tetrahedral disposition in the crystal lattice is formed, called a tetrahedral void.
- ii. In a close packed structure, the number of tetrahedral voids is doubled the number of constituents particles. This is because every void has four particles and there are eight voids around each particle.

• **Octahedral void :**

Three touching spheres in the second layer rest on the hollow in the three touching spheres in the first layer.

- i. Then vacant space surrounded by six nearest neighbours in octahedral disposition in the crystal lattice is called an octahedral void.
- ii. A close packed structure, the number of octahedral voids is the same as the number of constituent particles. This is because every void has six particles and there are six voids around each particle.

• **Voids of ionic compound:**

In case of ionic compounds, it is found that the bigger ions (usually anions) are present in the packing whereas smaller ions (usually cations) occupy the voids.

Ex.

- i. If the cations are smaller in size, they may occupy tetrahedral voids (because they are smaller than octahedral voids) for all tetrahedral voids, the ratio of cations to anion is 2:1.
- ii. If the cations are bigger in size, they may occupy octahedral voids (because they are smaller than tetrahedral voids) for all octahedral voids, the ratio of cations to anion is 1:1.

• **Number of void filled and formula of the compound:**

- i. Number of octahedral voids = Number of particles in the close packing = N
- ii. Number of tetrahedral voids = 2 x Number of particles in the close packing = 2 N

• **Defect in crystal structure:**

Any deviation from the perfectly ordered arrangement of constituents particles, called defect or imperfection.

• **Types of defects:**

There are two types of defects (a) line defect and (b) point effect

• **Line defects:**

The defect is due to the irregularity in a complex line, a row of lattice point of constituents particles is called line defect.

Point defects:

The defect is due to a fault produced in the arrangement of a point i.e. constituent particles like atom, ions or molecule in a crystalline solid is called point defect.

Types of point defects:

There are three types of point defects -

- a. Vacancy defect
- b. Interstitial defect
- c. Impurity defect.

A. Vacancy defect:

During the crystallization some of the places of the constituents particles remain unoccupied in crystal lattice and the defect generated is called vacancy defect (schottky defect).

Schottky defect:

The defect was noticed by German scientist Schottky in 1930.

The defect arises because of some vacancies are produced due to missing of cations and anions in the crystal lattice is called schottky defect.

Condition favouring Schottky defect:

The schottky defect is noticed in ionic compounds,

- a. With high co-ordination numbers.
- b. In which cations and anions have almost identical sizes.

Ex: Alkali metal halides such as NaCl, KCl, CsCl, KBr etc. normally show this defect.

Consequence of Schottky defect :

- i. The defect increases the electrical conductivity of the crystalline solid.
- ii. The presence of holes because of the missing ions lowers the density of the crystal.
- iii. Due to the presence of the large number of holes, the stability of the crystal decreases.
- iv. It also lowers its lattice energy.
- v. It does not change dielectric constant.

B. Interstitial defect or Frenkel defect:

This defect in the ionic crystals was discovered Frenkel in 1926.

Interstitial or Frenkel defect:

A defect occurs when a cation or anion from ionic solid leaves its regular site and moves to occupy a place between the lattice site i.e. interstitial position, the defect is called interstitial defect or **Frenkel defect**.

Conditions favouring Frenkel defect :

Generally it is observed in the ionic compounds:

- a. Crystal structure possess low co-ordination number.
- b. The anions are much larger than cations.

Consequences of Frenkel defect :

- i. The presence of this defect does not alter the density of solid.
 - ii. Frenkel are responsible for conduction of electricity in crystals.
 - iii. They are responsible for phenomenon of diffusion in solid.
 - iv. They decrease the stability of crystal.
 - v. They are also responsible to increase the dielectric constant of a crystal.
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Keep in mind:

AgBr has both Schottky as well as Frenkel defect.

C. Impurity defect:

When a regular cation of the crystal is replaced by some different cation or excess of cations sometimes occupy interstitial position then the defect is generated is called impurity defect.

Types of Impurity defect:

There are two types:

- i. Substitution impurity defect: If the impurity cation is substituted in place of regular cation then it is called substitution impurity defect.

Ex. Brass is a substitution alloy formed by substituting copper metal by zinc metal in the ratio 1:3.

- ii. **Interstitial impurity defect:**

If the impurity cation is present in the interstitial positions then it is called interstitial impurity defect.

Ex. Stainless steel is an interstitial alloy formed by introducing carbon atoms as impurity.

Electrical properties in solid:

On the basis of electrical conductivity, solids can be divided into three types:

- i. Metals
- ii. Non-metal
- iii. Semiconductors.

I. Metals:

These are the good conductors of heat and electricity because of a presence of delocalised or free electrons. Their conductivity 10^4 – $10^7 \text{ ohm}^{-1}\text{m}^{-1}$. Ex. Na, Al, Cu etc.

II. Non-metal:

These are poor conductor of electricity because of absence of free electrons.

Their conductivity 10^{-20} – $10^{-10} \text{ ohm}^{-1}\text{m}^{-1}$.

- iii. Semiconductors: Their conductivity lies in between metals and insulators.

Their conductivity 10^{-6} – $10^{-4} \text{ ohm}^{-1}\text{m}^{-1}$.

Conductivity:

- a. In metallic crystals valence band and conduction band are close to each other and a very little energy is required to excite electrons from valence band into conduction band. In conduction the electrons are delocalised and are free to move from one end to end of the metal acts as a good conductors.
- b. In non-metals, the spacing between valence band and conduction band is relatively more hence large amount of energy is required to promote electrons valence band to conduction band. This relatively more amount of energy is not available. Hence electrons remain in valence band and thus cannot move freely, do not conduct heat and electricity, acts as an insulator.
- c. In semiconductor, the spacing between valence band and conduction band is very small hence the electrons from valence band can be excited to conduction band on slight heating. Thus conduction band contain free electrons to conduct electricity.

As temperature increases, more and more electrons available in conduction band thus the conductivity of semiconductor increases.

Semiconductors :

The solid whose conductivity lies in between metals and insulators, called semiconductor .

Types:

There are two main types of semiconductors:

I. n-type semiconductor (Electron rich or donor impurities) :

The conductor which are formed by adding impurity atoms containing more valence electrons than the atoms of the parent in insulator are called n-type semiconductor.

Explanation:

- a. As a Si atom is substituted by an atom of 'As' then four of the electrons in arsenic form covalent bonds with surrounding Si atoms and the fifth electron remains free.
- b. This extra electron delocalised and can conduct electricity.

This type of conductivity is known as n-type semiconductor where 'n' stands for negative because electrons are responsible for semiconducting behaviour.

Ex. Doping of a silicon (or Ge) with group-15 elements such as P, Sb or Bi also give n-type semiconductors.

p-type semiconductor (electron deficient impurities):

The conductors which are formed by adding impurity atoms containing lesser number of valence electrons than the atoms of the parent insulator element called p-type semiconductor.

Explanation:

- a. As a 'Si' atom is substituted by atom of 'B' then three electrons in boron form three covalent bonds and is unable to form fourth bond to complete the network structure of Si.
- b. As a result, some sites are left empty and gives rise to electrons deficiencies, are called electron vacancies or positive holes because the net charge at these sites is positive.
- c. When electric field is applied, a valence electrons on adjacent Si atom, jumps in the hole and this migration of positive hole continues and current is carried throughout the crystal.

This types of conduction is called p-type semiconduction because 'p' stand for holes (positive charge) appears to be responsible for the semiconducting properties.

Ex. Doping of a silicon (or Ge) with group-13 elements such as In, Al or Ga also give p-type semiconductor

Some examples of 'n' and 'p' type semiconductors:

I. B doped with Si :

'B' is 13 group element and 'Si' is a 14 group element. When B is doped with 'Si' then electron will free. Therefore it is a n-type semiconductor.

II. As doped with Si :

'As' is 15 group element and 'Si' is 14 group element. When 'As' is doped with 'Si' then electron will free. Therefore it is a n-type semiconductor.

III. P doped with Si :

'P' is a 15 group element and 'Si' is a 14 group element. Hence when 'P' is doped with 'Si' then electron will free. Therefore it is n-type semiconductor.

IV. Ge doped with In:

'Ge' is 14 group element and 'In' is 13 group element. Hence when 'Ge' is doped with 'In' then an electron deficient hole is created. Therefore, it is p-type semiconductor.

Magnetic Properties:

Due to the spinning motion of electrons around the nucleus, a spinning charge generates a magnetic field and hence spinning electrons as like tiny magnets.

a. Diamagnetism:




Substances which are repelled by external magnetic field [diamagnetic (TiO_2 , NaCl)]

b. Paramagnetism:

Substances which are weakly attracted by magnetic field [paramagnetic (TiO , VO_2)]

c. Ferromagnetism:

Substances which are strongly attracted by magnetic field [Ferromagnetic (Fe, CO, Ni)]

Sr. Properties	Information	Magnetic	Example Alignment	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons		Benzene, NaCl, TiO ₂ , V ₂ O ₅ , etc.	Insulators.
2. Paramagnetic	Have unpaired electron, weakly attracted in magnetic field. They cannot be permanently magnetized.		O ₂ , VO, CuO, TiO	Electronic devise.
3. Ferromagnetic	Have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetized.		Fe, Ni, COO, crO ₂	CrO ₂ is used in audio video tapes

Determination of magnetic property (Guoy's method) :

The method consists of weighing the substances in and out of magnetic field.

- If the substance is **diamagnetic** then it weightless in the magnetic field.
- If the substance is **paramagnetic** then it weight more in the magnetic field because the substance is pulled in magnetic field.
- If the substance is **ferromagnetic** then its weight more than that of paramagnetic in the magnetic field because the substance is more pulled in magnetic field.

Important Formulae

1. To calculate formula of compound:

- In a cube, there are 8 comers, 6 face centres, 12 edge centres and one body centres.
- Contribution towards unit cell :

$$\text{corner} = \frac{1}{8}, \text{face centre} = \frac{1}{2}, \text{edge centre} = \frac{1}{4}, \text{body centre} = 1$$

- Formula of the compound is same as the ratio of atoms in the unit cell.

2. To calculate the radius of cation exactly flitting into the void.

- Radius of cation in the tetrahedral void = 0.225 x Radius of anion
- Radius of cation in the octahedral void = 0.414 x Radius of anion

3. To calculate the radius of the cation that can be slipped into the void:

Radius ratio	0.155 - 0.225	0.225 - 0.414	0.414-0.732	0.732-1
C.N.	3	4	6	8
Structural arrangement	Planer triangular	Tetrahedral	Octahedral	BCC

Keep In mind:

- If the radius ratio for cation has exact value like 0.225, 0.414 then cation fitted exactly in void.

- b. If the radius ratio for cation has value intermediate between suppose 0.225 to 0.414 then cation can slipped into the void.

4. To calculate radius ratio:

$$\text{Radius ratio} = \frac{r^+}{r^-}$$

5. To calculate distance between nearest neighbouring atoms (d) :

a. For SCC: $d = a$ and $r = \frac{a}{2}$

b. For BCC: $d = \frac{\sqrt{3}}{2} a = 0.866 a$ and $r = \frac{\sqrt{3}}{4} a = 0.433 a$

c. For FCC: $d = \frac{a}{\sqrt{2}} = 0.707 a$ and $r = \frac{a}{2\sqrt{2}} = 0.3535 a$

6. To calculate density (ρ) of cubic system:

A. For cubic crystal of an element:

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

Where Z = number of atoms present per unit cell i.e. for SCC, $Z = 1$, BCC, $Z = 2$ and FCC, $Z = 4$

M = Atomic mass of an element in gmol^{-1} , a = Edge of cubic crystal in cm.

(Generally it is given pm, hence convert into cm)

N_A = Avogadro's number = 6.022×10^{23}

B. For cubic crystals of ionic compounds:

$$\rho = \frac{Z \times M}{a^3 \times N_A} \text{ g cm}^{-3}$$

Where

Z = number of formula unit present in one unit cell. M = Formula mass.

Keep in Mind:

For BCC structure of pure element, $Z = 2$ (molecular mass) of compound but for BCC structure of ionic compounds like NaCl, ($Z = 4$), CsCl, ($Z = 1$).

7. To calculate number of formula units:

$$\text{Number of formula units in 1 g of any compound} = \frac{N_A}{\text{molar mass}}$$

8. Relation between 'd' and 'a'

scc	bcc	fcc
$d = 2r$	$d = 2r$	$d = 2r$
$d = a$	$d = \frac{\sqrt{3}}{2} a$	$d = \frac{a}{\sqrt{2}}$

Where 'd' is distance between nearest neighbours and

'a' is edge length of cubic unit cell.