

THE SOLID STATE

Solids are substances having definite shape and definite volume. In solids, the particles are closely packed and the force of attraction between the particles is strong. So solids are rigid and incompressible. Their constituent particles (atoms, molecules or ions) have fixed positions and can only vibrate about their mean positions.

Classification of solids

On the basis of orderly arrangement of particles, solids can be classified into two – Crystalline solids and Amorphous solids

1. Crystalline solids

In these solids, the constituent particles have a well ordered arrangement throughout the solid, i.e., they have a long range order. They consist of a large number of small crystals. They have a definite geometrical shape, melting point and heat of fusion.

E.g.: Quartz, Diamond, Graphite, fullerene, NaCl, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ice, naphthalene, SiC etc.

2. Amorphous solids

In these solids, the ordered arrangement of constituent particles is only at some portions of the solid, i.e., they have only a short range order. The structure of these solids is similar to that of liquids. They have no definite geometrical shape, melting point and heat of fusion.

E.g.: Plastic, Glass (quartz glass), Rubber, amorphous silica, coal, charcoal, coke, PVC etc.

Like liquids amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are also called *pseudo solids* or *super cooled liquids*.

Glass panes fixed to windows or doors of old buildings are slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Amorphous solids on heating become crystalline at some temperature. Some glass objects from ancient civilizations are found to become milky in appearance due to some crystallization.

Anisotropic and isotropic substances

Solids in which the physical properties like electrical conductance, refractive index etc are different when measured in different directions are said to be anisotropic in nature. This is due to the different arrangement of particles in different directions. Crystalline solids are anisotropic.

Solids in which the physical properties are same along any direction are said to be isotropic in nature. This is due to the irregular arrangement of particles along different directions. Amorphous solids are isotropic.

Differences between Crystalline solids and Amorphous solids

Properties	Crystalline solids	Amorphous solids
Orderly arrangement of particles	Long range order	Only short range order
Geometrical shape	Definite characteristic geometrical shape	No definite Geometrical shape
Melting point	Definite m.p	No definite m.p
Heat of fusion	Definite	Not definite
Mode of cleavage	Give regular cleavage on cutting	Give irregular cleavage on cutting
Nature	True solids	Pseudo solids
Isotropy/anisotropy	Anisotropic in nature	Isotropic in nature

Classification of Based on the nature of particles and binding force

On the basis of nature of particles and binding force between the particles, crystalline solids are classified into four types- *molecular solids*, *ionic solids*, *metallic solids* and *covalent solids*.

1. **Molecular Solids:** Here the constituent particles are molecules. These are further sub-divided into three:
 - i. *Non-polar molecular solids:* Here the constituent particles are either atoms like Ar, He etc. or non-polar molecules like H_2 , Cl_2 , I_2 etc and the binding force between the particles is London dispersion forces or weak van der Waal's forces. These are soft solids and are non-conductors of electricity. They have low melting points and are usually liquid or gaseous state at room temperature and pressure.
 - ii. *Polar molecular solids:* Here the constituent particles are polar molecules like HCl, CO_2 , SO_2 etc. and the binding force between the particles is relatively stronger dipole-dipole interactions. These are soft and non-conductors of electricity. Their melting points are higher than those of non-polar molecular solids. Most of them are gases or liquids at room temperature and pressure.
 - iii. *Hydrogen bonded molecular solids:* Here the constituent particles are molecules which contain atoms like H and F, O or N. The binding force between the particles is strong hydrogen bond. They are non-conductors of electricity and are volatile solids or soft solids at room temperature and pressure. E.g.: H_2O , NH_3 etc.
2. **Ionic Solids:** Here the constituent particles are ions and the binding force between the particles is strong electrostatic force of attraction (ionic bond). They are hard and brittle and have high m.p & b.p. They are electrical insulators in the solid state, since the ions are not free to move about. But in the molten or solution state, the ions become free to move about and they conduct electricity. E.g.: NaCl, KCl, $CaCl_2$ etc.
3. **Metallic Solids:** They contain a large number of metal ions which are surrounded by a sea of electrons. The particles are held together by strong electrostatic force of attraction (metallic bond). Due to the presence of a large number of free electrons, they are good conductors of heat and electricity, malleable and ductile and show metallic lustre. E.g. All metals
4. **Covalent or Network Solids:** Here the constituent particles are atoms and the binding force between the particles is strong covalent bond. They are very strong and brittle, have extremely high melting point and are electrical insulators. E.g. Diamond, Silicon Carbide (SiC , commonly known as Carborundum), Quartz, Graphite etc.

Graphite has exceptional properties i.e., it is soft and good conductor of electricity. In graphite carbon atoms are arranged in different layers and each atom is covalently bonded to three adjacent carbon atoms. The fourth electron is free to move about between different layers. So Graphite is a good conductor of electricity. The different layers are held together by weak van der Waal's force of attractions. So each layer can slide over the other and hence it is soft and used as a good lubricant.

Crystal lattice

The regular three dimensional arrangements of constituent particles of a crystal in space is called *crystal lattice* or *space lattice*.

The important characteristics of a crystal lattice are:

- (a) Each point in a lattice is called lattice point or lattice site.
- (b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
- (c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

There are only **14** possible three dimensional lattices. These are called **Bravais Lattices**.

Unit cell

A unit cell is the smallest repeating unit of a crystal lattice which, when repeated in three dimension we get a whole crystal. Or, it is the building block of a crystal. A unit cell is characterised by its edge lengths (a, b and c) and angle between the edges – α (between b and c), β (between a and c) and γ (between a and b). Thus a unit cell is characterised by 6 parameters – a, b, c, α , β and γ .

Unit cells can be broadly divided into two - primitive and centred unit cells.

1. Primitive Unit Cells:

Here the constituent particles are present only at the corners of the unit cell.

2. Centred Unit Cells:

Here the constituent particles are present at the corners and other positions of the unit cell. These are of three types:

- Body-centred unit cells:** Here the constituent particles are present at the body centre and at the corners of the unit cell.
- Face-centred unit cells:** Here the constituent particles are present at the centre of each faces and at the corners of the unit cell.
- End-centred unit cells:** Here the constituent particles are present at the centre of any two opposite faces and at the corners of the unit cell.

Seven types of crystal systems and their possible variations

Crystal Systems	Possible variations	Edge lengths	Axial angles	Examples
Cubic	Primitive, body-centred, face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende (ZnS), Cu
Tetragonal	Primitive, body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, TiO_2 , SnO_2 , CaSO_4
Orthorhombic	Primitive, body-centred, face-centred, end-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Monoclinic	Primitive, end-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS
Rhombohedral or trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (Cinnabar)
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Calculation of Number of atoms in a unit cell (z)

1. Primitive cubic (Simple Cubic) unit cell:

Here atoms are present only at the corners of the cube. Each corner atom is shared by 8 unit cells.

Therefore, contribution to one unit cell = $1/8$

Since each unit cell has 8 atoms at the corners, the total number of atoms in one unit cell = $8 \times 1/8 = 1$

So for a primitive (simple cubic) unit cell, $z = 1$

2. Body-centred cubic (bcc) unit cell:

Here the particles are present at the corners of the cube and also one atom at the body centre.

The number of atoms at the corner = $8 \times \frac{1}{8} = 1$

The atom present at the centre of the body is not shared by other atoms.

So the number of atoms at the body-centre = 1

Therefore, total number of atoms in the unit cell = $1+1=2$

So, for a bcc, $z = 2$

3. Face-centred cubic (fcc) unit cell:

Here the atoms are present at the corners and also at the centre of each faces. Each corner atom is shared by 8 unit cells and each face centre atom is shared by 2 unit cells.

Number of corner atoms = $8 \times \frac{1}{8} = 1$

Number of face-centre atoms = $6 \times \frac{1}{2} = 3$

Therefore, total number of atoms = $1+3 = 4$

So, for an fcc, $z = 4$

Close packing in solids

In solids the particles are closely packed. In close packed structures the particles are considered as hard spheres. Solids are three dimensional and the 3 dimensional structure can be obtained by the following three steps:

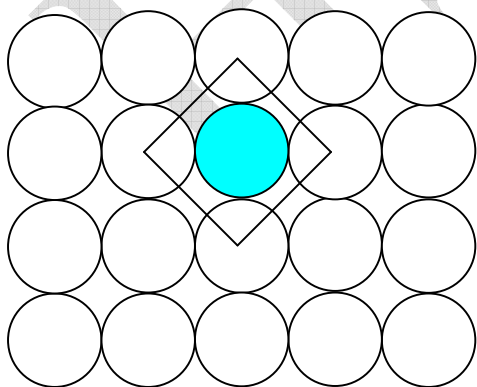
1. Close packing in One Dimensions

Here the spheres are arranged in a row touching each other. In this arrangement each sphere is in contact with 2 adjacent spheres. Therefore, co-ordination number of each sphere is 2.

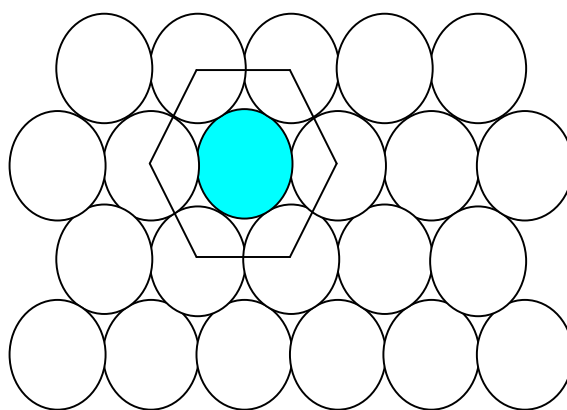
2. Close packing in Two Dimensions

Here the spheres are arranged in two directions – length-wise and breadth-wise. This can be done in two different ways.

- Square close packing:** Here the spheres of second row are placed exactly above those of the first row. In this arrangement, each sphere is in contact with four adjacent spheres. So the co-ordination number of each sphere is 4. When we join the centres of these spheres, we get a square. So this close packing is called square close packing in two dimensions.
- Hexagonal close packing:** Here the spheres of the second row are placed in the depressions of the first row, the spheres of the third row are placed in the depressions of the second row and so on. In this arrangement, each sphere is in contact with six adjacent spheres. So the co-ordination number of each sphere is 6. When we join the centres of these spheres, we get a hexagon. So this close packing is called hexagonal close packing in two dimensions.



Square close packing



Hexagonal close packing

Hexagonal close packing is more efficient than square close packing in two dimensions. This is because in Hexagonal close packing maximum space is occupied by spheres.

3. Close packing in Three Dimensions

Here the particles are arranged in layers. This can be possible in two ways.

i. *Three dimensional close packing from two dimensional square close-packed layers:*

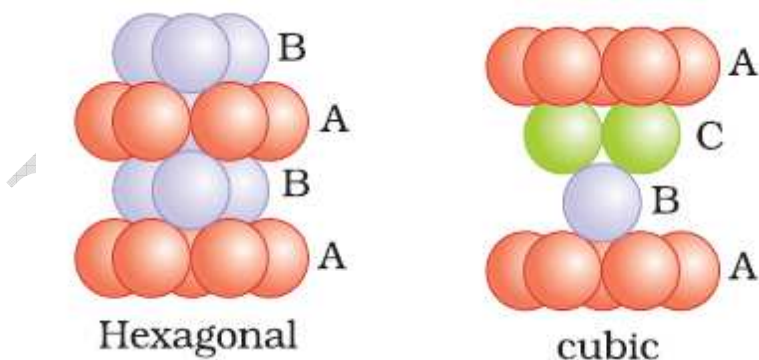
Here the spheres of the second layer are placed exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. The spheres of the third layer are placed exactly above those of the second layer and so on. If the arrangement of the spheres in the first layer is denoted as 'A', all the layers are of 'A' type. So this arrangement forms AAA..... type pattern. The lattice thus generated is the simple cubic lattice and its unit cell is the primitive cubic unit cell.

ii. *Three dimensional close packing from two dimensional hexagonal close-packed layers:*

Here the first layer is arranged as hexagonal manner. The second layer is placed above the depressions of the first layer. On placing the second layer there arises two types of voids (vacant spaces) above the second layer – tetrahedral voids and octahedral voids. Thus when we place the third layer over the second there are two possibilities:

➤ *Covering tetrahedral voids:* Here the spheres of the third layer are placed above the tetrahedral voids of the second layer. In this arrangement, the spheres of the third layer are vertically above those of the first layer, i.e. the first layer and the third layer are identical. If we call the first layer as 'A' and the second layer as 'B', then the third layer will be 'A', the fourth layer will be 'B' and so on. This will form the pattern ABAB..... This type of close packing is called **Hexagonal close packing (hcp) in three dimensions**. This type of arrangement is found in metals like Mg, Zn etc.

➤ *Covering octahedral voids:* Here the spheres of the third layer are placed above the octahedral voids of the second layer. In this arrangement, the third layer is different from the first or the second layer. But the spheres of the fourth layer are vertically above those of the first layer, i.e. the first layer and the fourth layer are identical. If we call the first layer as 'A', the second layer as 'B', and the third layer as 'C', then the fourth layer will be 'A', the fifth layer will be 'B' and so on. This will form the pattern ABCABC..... This type of close packing is called **Cubic close packing (ccp) or face-centred cubic(fcc) packing in three dimensions**. This type of arrangement is found in metals like Cu, Ag etc.



In both hcp and ccp 74% of the available space is occupied by spheres. So both are equally efficient.

Co-ordination Number

In a close packed arrangement the number of nearest neighbours with which a given sphere is in contact is called *the co-ordination number* of that sphere. In both hcp and ccp each sphere is in contact with 12 adjacent spheres. Thus the co-ordination number in both hcp and ccp is 12.

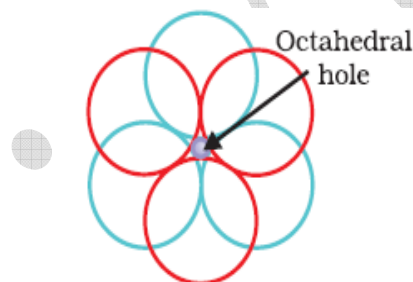
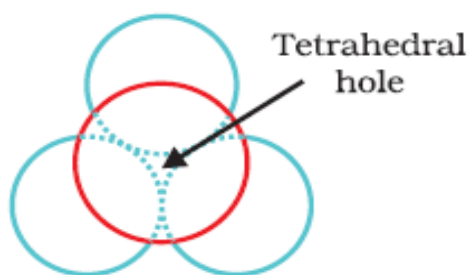
Interstitial voids

The vacant space in close packed arrangement is called *voids*. These are of two types- tetrahedral voids and octahedral voids.

Tetrahedral void: A void surrounded by *four* spheres in tetrahedral position is called tetrahedral void. In a close packed arrangement the number of tetrahedral voids is double the number of spheres, i.e. there are two tetrahedral voids per sphere.

Octahedral voids: A void surrounded by *six* spheres in octahedral position is called octahedral void. In a close packed arrangement the number of octahedral voids is equal to the number of spheres, i.e. there is only one octahedral void per sphere.

If there are N close packed spheres,
The number of tetrahedral voids = 2N and
The number of octahedral voids = N



Packing Efficiency

The percentage of the total space occupied by spheres (particles) is called packing efficiency.

$$\text{Packing Efficiency} = \frac{\text{Volume occupied by all the spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \%$$

Calculation of Packing Efficiency

1) In hcp and ccp structures

Consider a cube with edge length 'a' and face diagonal 'b'

$$\text{In } \triangle ABC, AC^2 = AB^2 + BC^2$$

$$\text{i.e. } b^2 = a^2 + a^2$$

$$\text{or, } b^2 = 2a^2$$

$$\text{or, } b = \sqrt{2}a$$

If 'r' is the radius of the sphere, then $b = 4r$

$$\therefore 4r = \sqrt{2}a$$

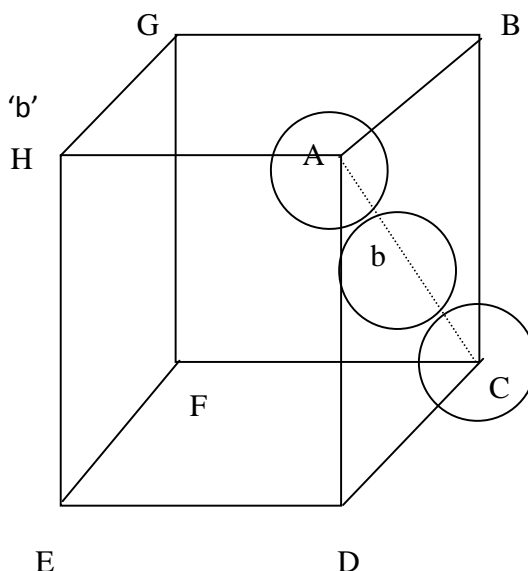
$$\text{Or, } a = 4r/\sqrt{2} = 2\sqrt{2}r$$

We know that, volume of a sphere = $(4/3)\pi r^3$

In ccp (fcc) or hcp, there four spheres per unit cell

$$\therefore \text{Volume of four spheres} = 4 \times (4/3)\pi r^3$$

$$\begin{aligned} \text{Volume of the cube} &= a^3 \\ &= (2\sqrt{2}r)^3 \end{aligned}$$



$$\text{Packing Efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \%$$

$$= \frac{4 \times \left(\frac{4}{3}\right) \pi r^3 \times 100}{(2\sqrt{2}r)^3} \%$$

$$= \frac{(16/3) \pi r^3 \times 100}{16\sqrt{2}r^3} \% = \underline{74\%}$$

2) In Body-centred cubic (bcc) structures:

Consider a cube with edge length 'a', face diagonal 'b' and body diagonal 'c'

From the figure it is clear that the atom at the centre is in contact with the other two atoms diagonally placed.

In $\triangle EFD$,

$$FD^2 = EF^2 + ED^2$$

$$\text{i.e. } b^2 = a^2 + a^2 = 2a^2$$

$$\text{or, } b = \sqrt{2}a$$

In $\triangle AFD$,

$$AF^2 = AD^2 + FD^2$$

$$\text{i.e. } c^2 = a^2 + b^2$$

$$= a^2 + 2a^2 = 3a^2$$

$$\text{Or, } c = \sqrt{3}a$$

But, $c = 4r$ (where r is the radius of the particle)

$$\therefore 4r = \sqrt{3}a$$

$$\text{Or, } a = 4r/\sqrt{3} \quad (\text{also } r = \sqrt{3}a/4)$$

In a bcc, the no. of atoms present per unit cell = 2

$$\text{Volume of 2 spheres} = 2 \times \left(\frac{4}{3}\right) \pi r^3$$

$$\text{Volume of the cube} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

$$\therefore \text{Packing Efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \%$$

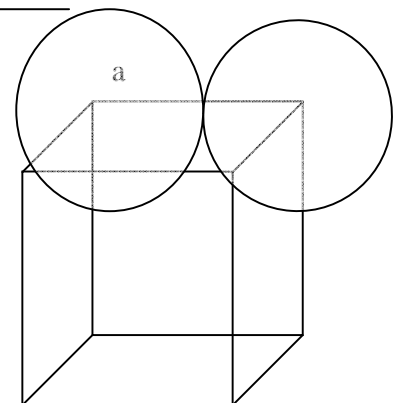
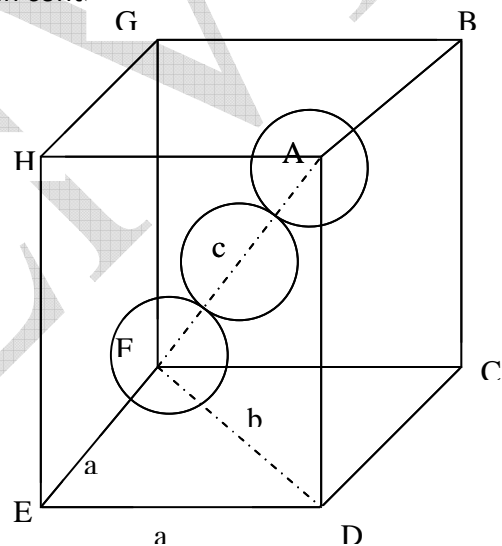
$$= \frac{2 \times \left(\frac{4}{3}\right) \pi r^3 \times 100}{\left(\frac{4r}{\sqrt{3}}\right)^3} \%$$

$$= \frac{(8/3) \pi r^3 \times 100}{64/(3\sqrt{3})r^3}$$

3) In simple cubic structures:

Consider a cube with edge length 'a' and the radius of the particle 'r'. Here the edge length is related to the radius of the particle as $a = 2r$

$$\text{The volume of the cubic unit cell} = a^3 = (2r)^3 = 8r^3$$



A simple cubic unit cell contains only one particle.

Volume of one sphere = $(4/3) \pi r^3$

$$\text{Packing Efficiency} = \frac{\text{Volume occupied by the spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \%$$

$$= \frac{(4/3) \pi r^3 \times 100}{8r^3} \%$$

$$= \pi/6 \times 100 \% = \underline{\underline{52.4\%}}$$

Calculation of Density of the unit cell (Solid)

Consider a cubic unit cell with edge length 'a'. Then volume of the unit cell = a^3 .

Let 'M' be the atomic mass of the element in the unit cell (i.e. mass of Avogadro number (N_A) of atoms).

Then mass of one atom = M / N_A .

Let the number of particles present per unit cell = z

Then mass of the unit cell = $z \times M / N_A$

Density of the unit cell = $\frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

$$\text{i.e. density (d)} = \frac{z \times M / N_A}{a^3} \quad \text{Or, } d = \frac{z \cdot M}{N_A \cdot a^3}$$

Imperfections in solids (Crystal Defects)

The deviation from the regular orderly arrangement of particles of a solid is termed as **imperfections or crystal defects**. The crystal defects are broadly classified into two – point defects and line defects.

The imperfection around a point (an atom) in a crystalline substance, it is termed as **point defect**.

The imperfection along a row is termed as **line defect**.

Point defects

Point defects can be classified into three types: Stoichiometric defects, Non-stoichiometric defects and Impurity defects.

1. Stoichiometric defects:

These are point defects which do not disturb the stoichiometry of the solid. They are also called *intrinsic or thermodynamic defects*, because these defects can also develop when a substance is heated. These are of two types – vacancy defects and interstitial defects.

a. **Vacancy defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This defect decreases the density of the solid.

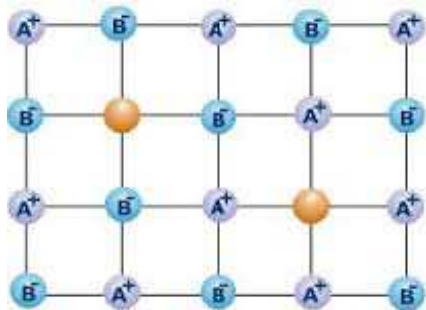
b. **Interstitial defect:** When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the solid.

The above two types of defects are shown by *non-ionic solids*.

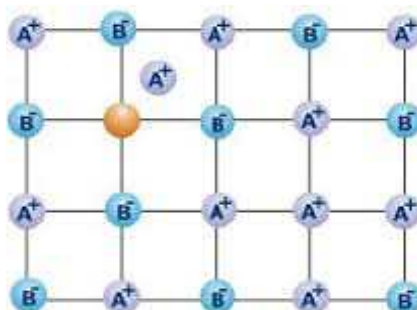
Ionic solids show two types of stoichiometric defects – **Schottky defect and Frenkel defect**.

i. **Schottky defect:** It is basically a vacancy defect. It arises due to the missing of equal number of anions and cations from the lattice site. It is shown by ionic crystals in which the anionic and cationic sizes are almost equal. NaCl, KCl, CsCl, AgBr etc. show Schottky defect. Due to this defect the density of the solid decreases.

ii. **Frenkel defect:** It is a stoichiometric defect arising due to the misplacing of an ion (generally a cation) from the lattice site to the interstitial site. It is also called dislocation defect. This type of defect is shown by ionic solids in which there is a large difference in the size of the ions. E.g. ZnS, AgCl, AgBr, AgI etc. This defect does not change the density of the solid.



Schottky Defect



Frenkel Defect

b) **Non-Stoichiometric defects:** These are point defects which change the stoichiometry of a solid. These defects are of two types:

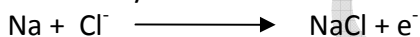
i) Metal excess defect and ii) Metal deficiency defect

i) **Metal excess Defect:**

Here the number of cations is greater than the number of anions. This arises in two ways:

- **Metal excess defect due to anionic vacancies:** Here some of the anions are missing from the lattice site. The electrical neutrality is maintained by occupying electrons in the anionic sites. These electrons are called **f-centres** because they give colour to the crystal.

This defect is shown by alkali metal halides. For example when NaCl is heated in an atmosphere of sodium vapour, some sodium atoms are deposited at the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combines with Na atom to form NaCl.

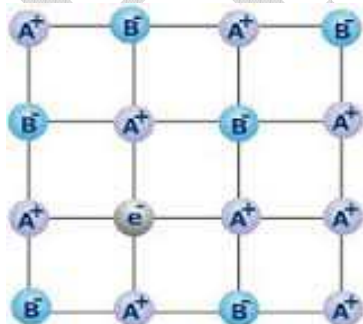


The electron so formed diffuse into the crystal and occupies the anion vacancy. These electrons absorb light energy and get excited. As a result the crystal becomes yellow in colour. Similarly, *excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet.*

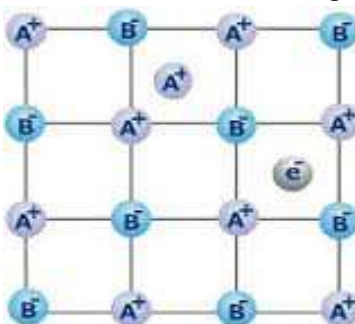
- **Metal excess defect due to extra cations at interstitial sites:** Here some cations occupy the interstitial sites. The electrical neutrality is maintained by occupying some electrons in adjacent interstitial sites. E.g. When ZnO crystals are heated, the white coloured crystals becomes yellow. This is because on heating, the crystal loses oxygen as follows:



The Zn ions now move to the interstitial sites and the electrons to neighbouring interstitial sites.



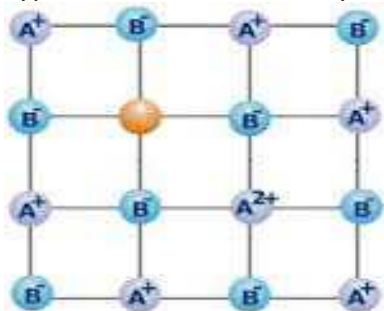
Metal excess Defect
due to anion vacancy



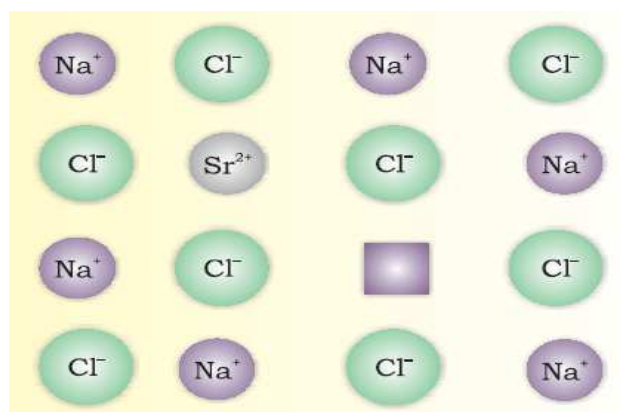
Metal excess Defect
due to extra cation

ii) **Metal deficiency Defect:**

Here the number of cations is smaller than the number of anions. This mainly arises due to cation vacancies. This type of defect is commonly shown by transition metal compounds. E.g. FeO



c) **Impurity Defects:** It is the defect arising due to the presence of foreign particles in a crystal. For example if molten NaCl containing a little amount of SrCl_2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} . Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal to the number of Sr^{2+} ions. Another similar example is a solid solution of CdCl_2 and AgCl .



Properties of solids

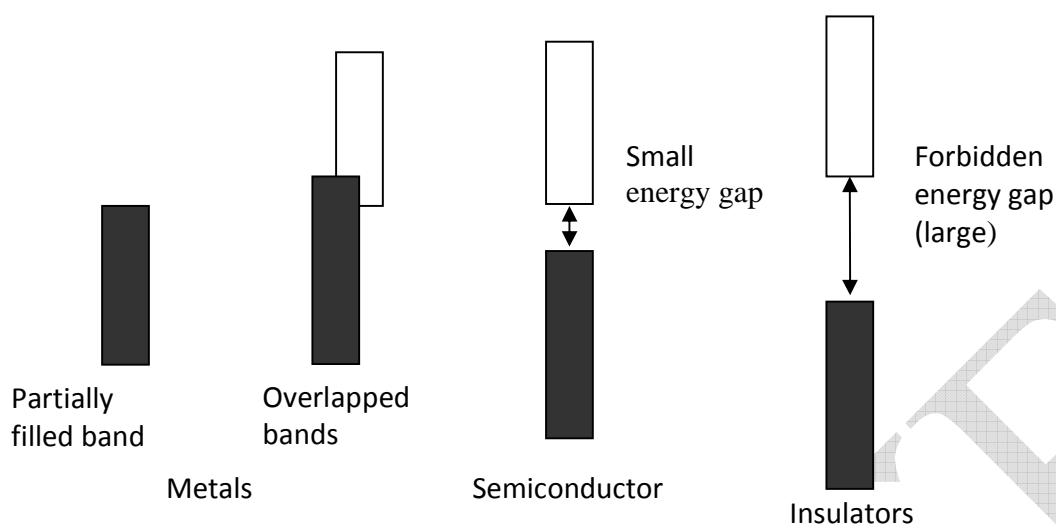
1) **Electrical properties:** Based on the electrical conductivity, solids are classified into three types:

- Conductors:** They are solids which allow the passage of electricity through them. Their conductivity ranges from 10^4 to $10^7 \text{ ohm}^{-1}\text{m}^{-1}$. Metals have conductivities in the order of $10^7 \text{ ohm}^{-1}\text{m}^{-1}$.
- Semi-conductors:** They are solids which allow the passage of electricity only partially. Their conductivity ranges from 10^4 to $10^{-6} \text{ ohm}^{-1}\text{m}^{-1}$.
- Insulators:** They are solids which do not allow the passage of electricity through them. Their conductivity ranges from 10^{-10} to $10^{-20} \text{ ohm}^{-1}\text{m}^{-1}$.

Conduction of Electricity in metals - Band Model

Metals conduct electricity in solid as well as in molten state. The conductivity of metals depends upon the number of valence electrons. The atomic orbitals of metals combine to form molecular orbitals, which are so closely spaced that they form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, the electrons can flow easily under an applied electric field and the metal shows conductivity.

If the gap between filled valence band and the unoccupied conduction band is large the electrons cannot jump to it and such substances act as insulators.



Conduction of Electricity in semi-conductors

In the case of semiconductors, the gap between the valence band and the conduction band is small. So some electron may jump from valence band to conduction band and show some conductivity. Their conductivity increases with rise in temperature, since more electrons can jump to the conduction band. Such semiconductors are also called *intrinsic semiconductors*. E.g.: Si, Ge etc.

The conductivity of intrinsic semiconductors is very low. Their conductivity can be increased by adding an appropriate impurity. The process is called *doping*. Addition of impurities creates electronic defects in them. Such semiconductors are called *extrinsic semiconductors*. Doping can be done by the addition of either *electron rich impurity* or *electron deficit impurity*.

a) Doping by electron rich impurity:

When a group 14 (which contains 4 electrons in the valence shell) element like Si or Ge is doped with a group 15 element (which contains 5 electrons in the valence shell) like P or As, four electrons are used for the formation of covalent bonds and the fifth electron becomes free. The presence of this delocalised electron increases the conductivity and hence silicon doped with electron rich impurities is called *n-type semiconductor*.

b) Doping by electron deficient impurity:

When a group 14 (which contains 4 electrons in the valence shell) element like Si or Ge is doped with a group 13 element (which contains 3 electrons in the valence shell) like B, Al, or Ga, the three electrons are used for the formation of covalent bonds and the fourth valence electron is missing. This creates an electron hole or electron vacancy. An electron from a neighbouring atom can come and fill the electron hole. So the position of the hole is moved in the direction opposite to that of the electron has moved. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes. It would appear as if electron holes are positively charged. This type of semiconductors are called *p-type semiconductors*.

A large variety of solids which have lattices similar to Ge or Si have been prepared by the combination of groups 13&15 or 12&16. E.g. for 13and15 group compounds are InSb, AlP & GaAs. They are used as semiconductors. E.g. for 12 and 16 group compounds are ZnS, CdS, CdSe & HgTe.

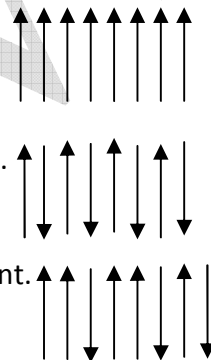
2) Magnetic properties

Every solid has some magnetic properties associated with it due to the presence of electrons. Each electron in an atom behaves like a tiny magnet. Electron being a charged particle and due to spin and orbital motions, has a permanent spin and orbital magnetic moment. The magnitude of this magnetic moment is

very small and is measured in the unit called Bohr Magnetron (μ_B). ($1 \mu_B = 9.27 \times 10^{-24} \text{ Am}^2$ (ampere-metresquare)).

Based on the magnetic properties, solids can be classified into **five** types.

1. **Diamagnetic Substances:** These are weakly repelled by an external magnetic field. Diamagnetism arises due to the presence of only paired electrons. Pairing of electrons cancels their magnetic moments and so they have no net magnetic moment. E.g.: H_2O , NaCl , Benzene (C_6H_6)
2. **Paramagnetic Substances:** They are weakly attracted by an external magnetic field. Paramagnetism is due to the presence of one or more unpaired electrons. They have a net magnetic moment. They lose their magnetism in the absence of external magnetic field. So they are temporary magnets.
Eg: O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} etc.
3. **Ferromagnetic Substances:** They are very strongly attracted by a magnetic field and can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. In the absence of an external magnetic field, these domains are randomly oriented. When the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains does not change even when the external magnetic field is removed and so they become permanent magnets.
Eg: Fe, Co, Ni, Gd (Gadolinium), CrO_2 etc.
4. **Anti-ferromagnetic Substances:** Here the domains are oppositely oriented and cancel each other. So they have no net magnetic moment.
Eg: MnO
5. **Ferrimagnetic Substances:** Here the domains are arranged in opposite directions but in unequal numbers. So they have a net magnetic moment.
Eg: Fe_3O_4 (magnetite) and ferrites like MgFe_2O_4 , ZnFe_2O_4 etc



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