By- Shailendra Shukla Sir

Chapter 1 SOLID STATE

(1) Crystalline and Amorphous Solids

Based on the nature of the order of arrangement of the constituent particles, solids may be of following two types-

(1) Crystalline solids (2) Amorphous solids

Differences between amorphous and crystalline solids-

	Crystalline solids	Amorphous solids
1	These solids have a definite crystalline structure and therefore, they have a definite geometrical shape.	These solids do not have a definite crystalline structure and therefore, they do not have a definite geometrical shape but have irregular shape.
2	These solids have long-range order in the arrangement of constituent particles	They have only short-range order in the arrangement of constituent particles.
3	These solids have sharp and characteristic melting point.	These solids do not have sharp melting point. On heating they gradually soften over a range of temperature then melt.
4	When these solids are cut with a sharp-edged tool, they split into two pieces with plane and smooth newly generated surfaces.	When cut with a sharp-edged tool, they split into two pieces with irregular shapes.
5	These solids have definite and characteristic heat of fusion.	These solids do not have definite heat of fusion.
6	These solids show anisotropism i.e. they have different properties such as refractive index, electrical resistance etc. in different directions. (Exception- solids having simple cubic structure).	These show isotropism i.e. have same properties in all the directions.
7	These are true solids e.g. NaCl, CsCl, ZnS etc.	These are pseudo solids or super-cooled liquids e.g. glass, plastic, rubber etc.

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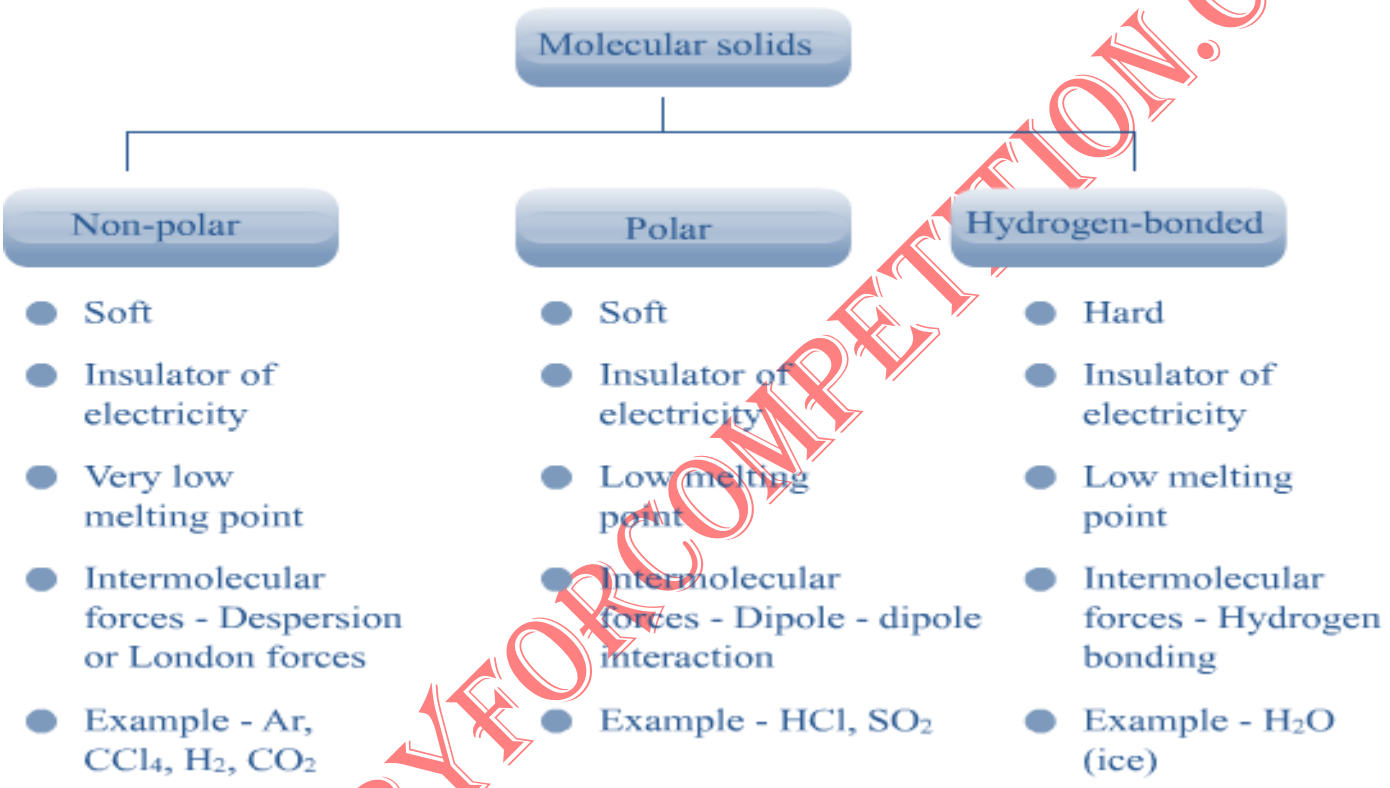
Classification of Crystalline Solids

Based on the nature of intermolecular forces, crystalline solids are classified into four categories −

(1) Molecular solids (2) Ionic solids
(3) Metallic solids (4) Covalent solids

(1) Molecular solids

Constituent particles of these solids are molecules. They are further classified as follows-



(2) Ionic solids

- Constituent particles of these solids are oppositely charged ions.
- They are hard but brittle.
- They are insulators of electricity in solid state, but conductors in molten state and in aqueous solution.
- They have high melting point.
- In these solids the attractive forces are Coulombic or electrostatic forces.
- Examples − NaCl, MgO, ZnS

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(3) Metallic solids

- In metallic solids, positively charged metal ions remain held together in a sea of delocalized electrons.
- They are hard but malleable and ductile.
- They are conductors of electricity in solid state as well as molten state.
- They have fairly high melting point.
- In these solids metal atoms remain held together by metallic bonding.
- Examples − Fe, Cu, Mg etc.

(4) Covalent or network solids

- In these solids the constituent particles are atoms.
- They are hard (except graphite, which is soft).
- They are insulators of electricity (except graphite, which is a conductor of electricity).
- They have very high melting point and usually get decomposed before melting.
- In these solids constituent particles i.e. atoms remain held together by covalent bonding.
- Example − SiO_2 (quartz), SiC, diamond, graphite etc.

Crystal Lattice

The regular three-dimensional arrangement of constituent particles (atoms, ions or molecules) in space is called Crystal Lattice.

The position of constituent particles in a crystal lattice is called point.

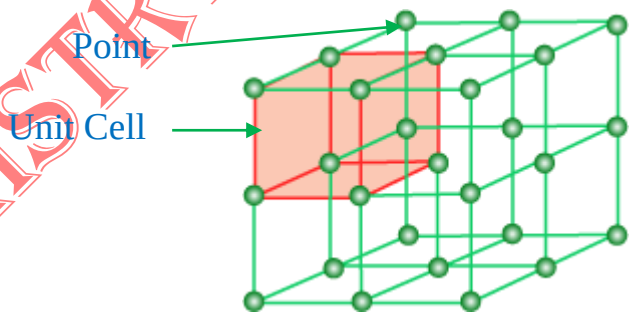


Fig.- Crystal Lattice

There are in all 7 Crystal systems and 14 possible three-dimensional crystal lattices called **Bravais lattices.**

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Characteristics of a crystal lattice

- Each point in a lattice is called lattice point or lattice site.
- Each lattice point represents one constituent particle (atom, molecule or ion).
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit Cell

The smallest unit which repeats again and over again three dimensionally to form a big crystal is called unit cell of the crystal.

The unit cell is smallest model of a big crystal and has all the properties of solid crystal. Its geometry decides the geometry of socrystal and its melting point, density, refractive index etc. correspond to those of solid crystal.

A unit cell is characterized by –

(i) Its dimensions along the three edges *a*, *b* and *c*

(ii) Angles between the edges α, β and γ



Fig.- A unit cell

For example, in simple cubic or primitive unit cell, all the sides and angles are equal i.e.

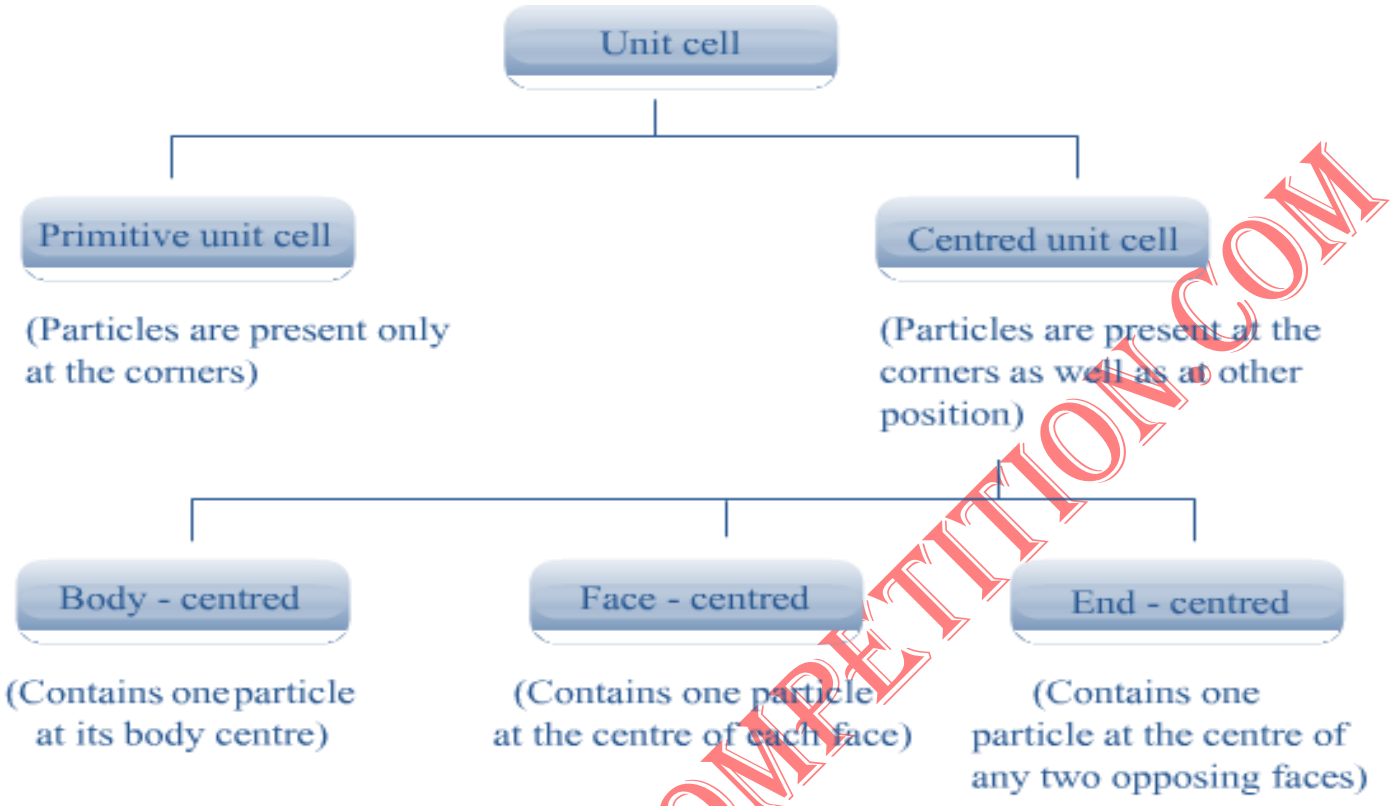
$$a = b = c$$

and $$\alpha = \beta = \gamma = 90^0$$

Similarly, other unit cells also have characteristic values of these parameters.

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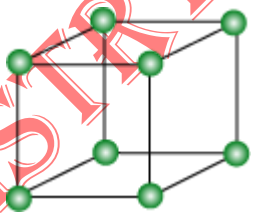
Classification of unit cells

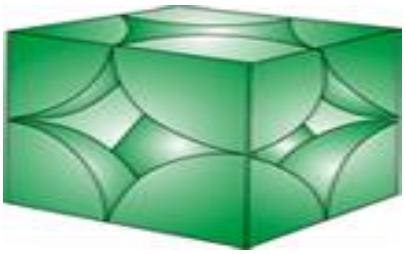


Types of Cubic Unit Cells and Number of Atoms per Unit Cell

(1) Primitive or Simple Cubic Unit Cell

Such unit cells in which constituent particles are present only at all the corners of the cube are called primitive or simple cubic (sc) unit cells.





Simple Cubic Unit Cell **Total number of atoms in one unit cell**

Here, each constituent particle (say atom) present at corner is equally shared by eight cubes and gives its one-eighth contribution to each cube.

Hence, Total number of atoms per unit cell in simple cubic structures,

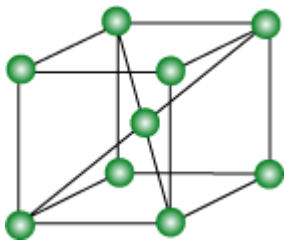
$$N = 1/8 \times (\text{Total no. of atoms at corners})$$
$$= 1/8 \times 8$$
$$= 1$$

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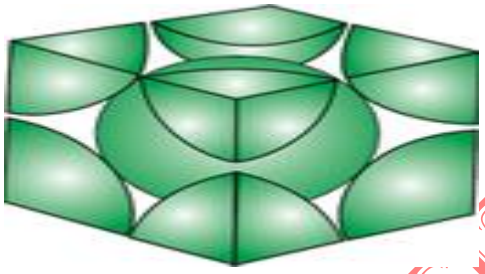
Thus, there is only one constituent particle (say atom) per unit cell in simple cubic structures.

(2) Body-Centred Cubic (bcc) Unit Cell

Such unit cells in which constituent particles are present at all the corners as well as at the body centre of the cube are called body centred cubic (bcc) unit cells.



bcc unit cell



Total number of atoms per unit cell

Here, each constituent particle (say atom) present at corner is equally shared by eight cubes and gives its one-eights contribution to each cube while that present at body centre gives its entire contribution to same cube .

Hence, Total number of atoms per unit cell in simple cubic structures,

N = 1/8 ×(Total no. of atoms at corners) + 1(atom at body centre)

= 1/8× 8 + 1

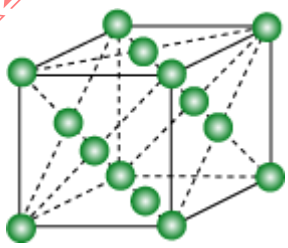
= 1+1

= 2

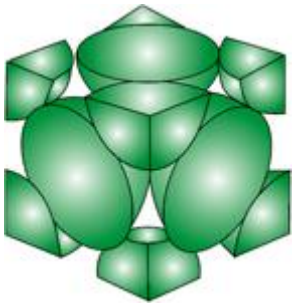
Thus, there are in all two constituent particles (say atom) per unit cell in bcc structures.

(3) Face-Centred Cubic (fcc) Unit Cell

Such unit cells in which constituent particles are present at all the corners as well as at the faces of the cube are called face centred cubic (fcc) unit cells.



fcc Unit cell



Total number of atoms per unit cell

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Here, each constituent particle (say atom) present at corner is equally shared by eight cubes and gives its one-eights contribution to each cube while that present at faces are equally shared by two cubes and gives its one-half contribution to each cube.

Hence, Total number of atoms per unit cell I fcc structures,

$$N = 1/8 \times (\text{Total no. of atoms at corners}) + 1/2(\text{ Total no. atom at faces })$$
$$= 1/8 \times 8 + ½ \times 6$$
$$= 1+3$$
$$= 4$$

Thus, there are in all four constituent particles (say atom) per unit cell in fcc structures.

Closed-Packed Structures

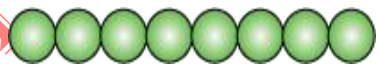
Such packing of constituent particles (atoms, ions or molecules) where maximum available space gets occupied and minimum space remains unoccupied is called close packing of constituent particles.

The structures having close packing of constituent particles are called closed packed structures.

Here, the number of nearest neighbours of a constituent particle is called coordination number of respective constituent particle.

(1) Close-Packing in One dimension

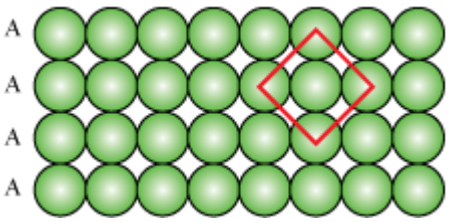
Here, the particles are arranged in a row, touching each other.



Coordination number = 2

(2) Close-Packing in Two Dimensions

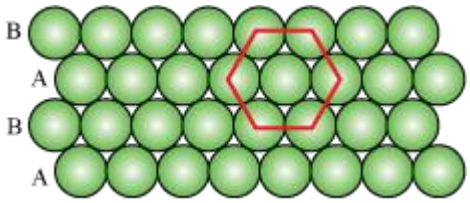
(a) Square close-packing (AAA type arrangement)- Here, particles show both horizontal and vertical alignment i.e. the particles in the second row are exactly above those in the first row.



Coordination number = 4

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(b)Hexagonal close-packing (ABAB type arrangement of rows)- Here, the particles in the second row are placed in the depressions of the first row. Thus, the particles in the third row are aligned with those in the first row. It is more efficient than square close-packing.



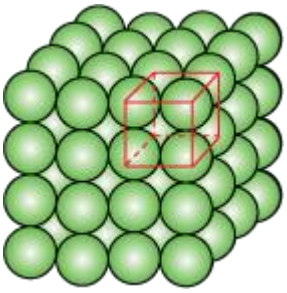
Coordination number = 6

(3) Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

(a) Stacking of square close-packed Layers (AAA type arrangement of layers)-It involves the stacking of two-dimensional square close-packed layers exactly one above another. Thus, the particles in the second layer are exactly above those in the first layer.

Here, the lattice generated is simple cubic lattice, and its unit cell is primitive or simple cubic unit cell.



Coordination number = 6

(b) Stacking of hexagonal close-packed layers- It involves the stacking of two-dimensional hexagonal close-packed layers one over another. Here, first layer contains two types of depressions one having apex upwards, while other having those downwards.

During the stacking of second layer only one of these two types of depressions can be covered. If the depressions having apex upwards are covered

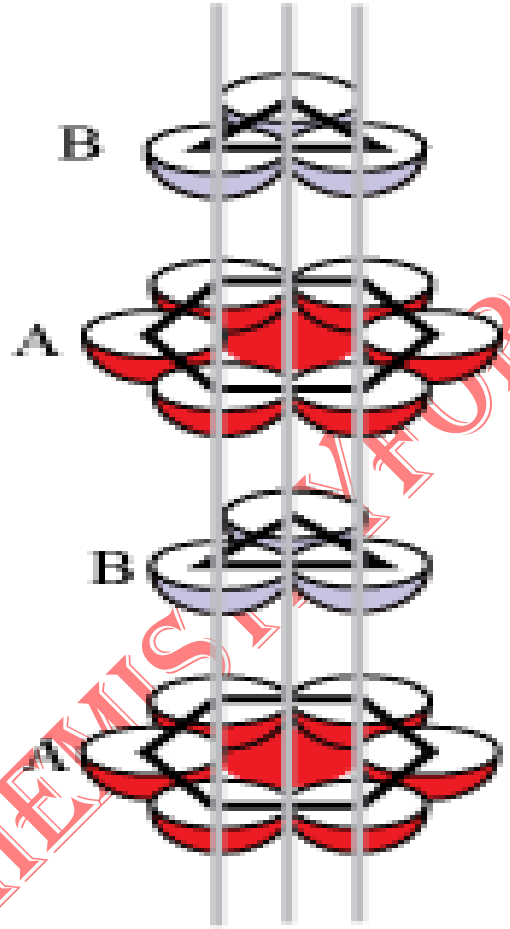
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during stacking of second layer then those having their apex downwards remain uncovered and vice versa. Thus, the two layers get differently aligned and a new type of depressions get formed just above the spheres of first layer.

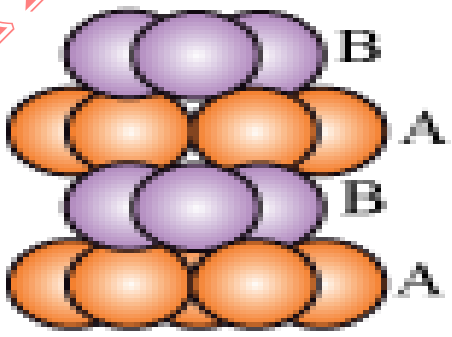
Here, if a particle in the second layer is placed above a void of the first layer then tetrahedral void is formed. However, if a void of the second layer is above the void of the first layer then octahedral void is formed.

During the stacking of third layer over the second layer following two cases may arise-

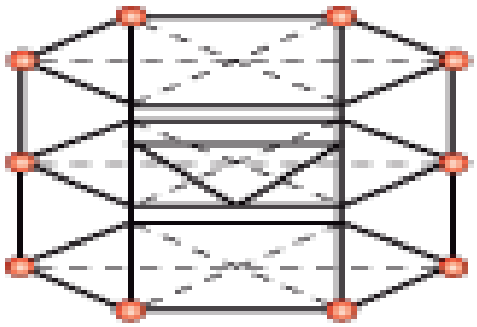
(i) Covering tetrahedral voids -If the spheres of third layer are placed above the newly formed depressions then the third layer becomes identical to first layer. Thus, ABABAB------ type of arrangement of layers is obtained where, each third layer is identical to the first layer. It results in a hexagonal close-packed (*hcp*) structure. For example, arrangement of atoms in Mg and Zn.



Hexagonal packing

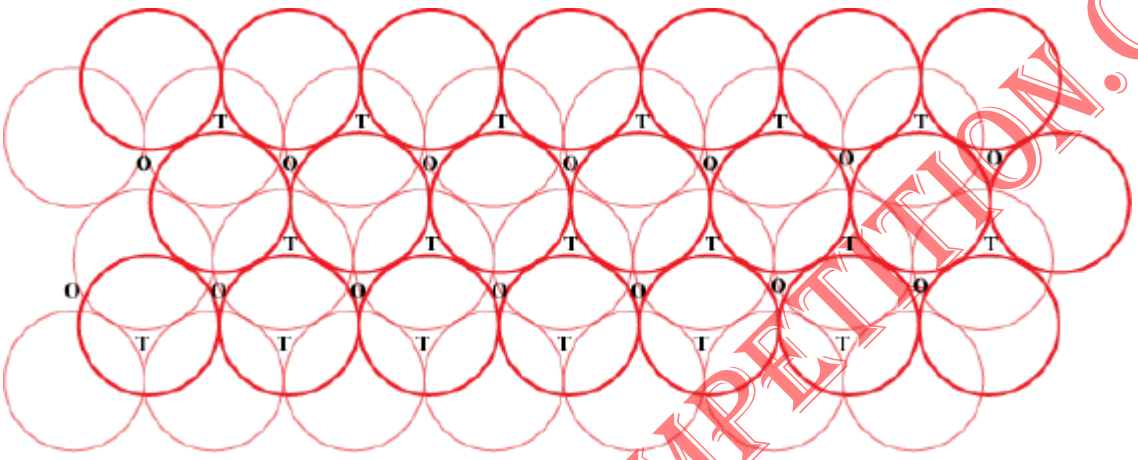


Hexagonal


hcp

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(ii) Covering octahedral voids - If the spheres of third layer are placed above the depressions remained uncovered during stacking of second layer then the new types of depressions remain uncovered and the third layer gets aligned differently with respect to first and second layers but each fourth layer becomes identical to the first layer. Thus, ABCABCABC ------ type of arrangement of layers is obtained. It results in a cubic close-packed (*ccp*) or face-centred cubic (*fcc*) structure. For example, arrangement of atoms in Cu and Ag metals.

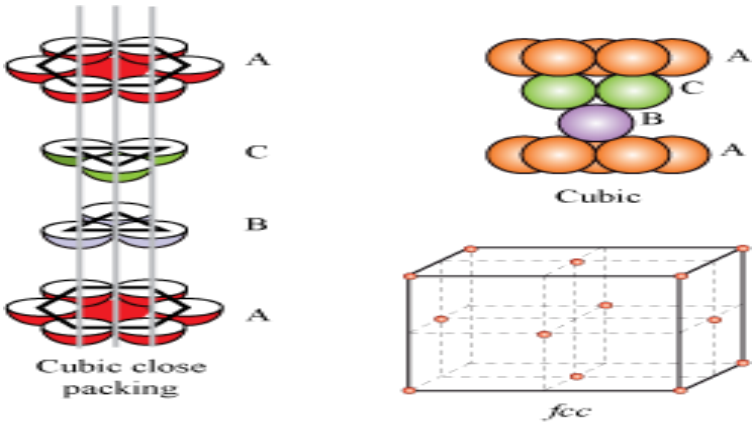


Here, T = Tetrahedral void
O = Octahedral void

Close Packed Structures (hcp and ccp) contain both tetrahedral and octahedral voids. Here, the number of tetrahedral voids is equal to the twice of the number of constituent particles packed while the number of octahedral voids is equal to the number of constituent particles packed. Thus, if n is the total number of constituent particles packed, then-

Total Number of octahedral voids formed = n

Total Number of tetrahedral voids formed = 2n



Coordination number in both *hcp* ad *ccp* structures is 12

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Both *hcp* and *ccp* structures are highly as well as equally efficient with packing efficiency of 74%.

Interstitial Sites or Voids

During packing of constituent particles in a solid crystal some of the space remains unoccupied. These unoccupied spaces are called Interstitial Sites or Voids.

Close Packed Structures (both *hcp* and *ccp*) contain following two types of voids-

(1)Tetrahedral Voids- Such voids around which the arrangement of constituent particles is tetrahedral are called Tetrahedral Voids.

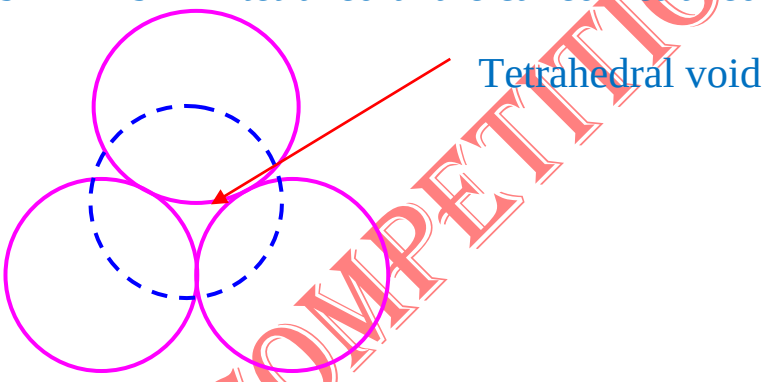


Fig.-Tetrahedral Voids

Tetrahedral Voids may or not may be tetrahedral in shape but arrangement of constituent particles around these voids is always tetrahedral.

Locating Tetrahedral Voids

If a unit cell of *ccp* or *fcc* lattice is divided into eight small cubes by bisecting through the opposing faces then, each small cube has 4 atoms at alternate corners. When these are joined to each other, a regular tetrahedron is formed. The centre of these small cubes represent a tetrahedral void.

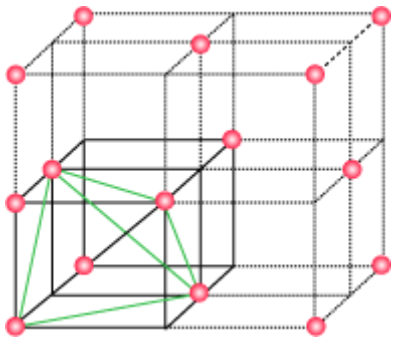


Fig.- Locations of tetrahedral voids

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Thus, a total of eight tetrahedral voids are present per unit cell in *hcp* or *ccp* structures. Since there are 4 atoms per unit cell in *ccp* structures, the number of tetrahedral voids is twice to the number of atoms in the unit cell.

(2)Octahedral Voids- Such voids around which the arrangement of constituent particles is octahedral are called Octahedral Voids.

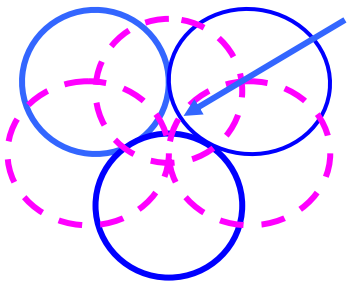


Fig. Octahedral Void

Octahedral Voids may or not may be octahedral in shape but arrangement of constituent particles around these voids is always octahedral.

Locating Octahedral Voids

If six atoms of the face centres are joined, an octahedron is formed. Hence, body centre represents the position of octahedral void in unit cell.

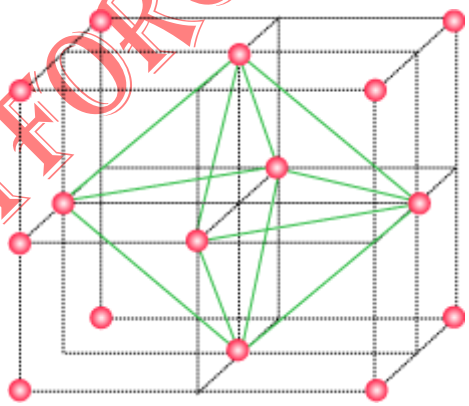


Fig.- Locations of octahedral voids

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. However, only $1/4^{th}$ of each of these voids belongs to the one unit cell.

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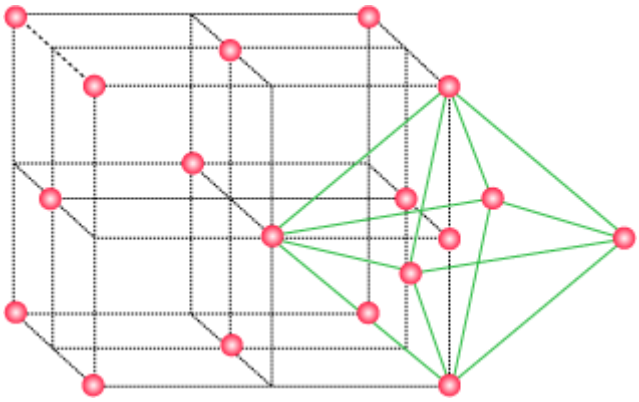


Fig .- Locations of octahedral voids

Hence, the total number of octahedral voids in a cubic loose-packed structures-

$$N = 1(\text{at body centre}) + \tfrac{1}{4} \times 12 \ (\text{at edges})$$
$$= 1 + 3$$
$$= 4$$

Thus, there are in all four octahedral voids per unit cell in cubic close-packed structures.

This means that, in *ccp* structures, the number of octahedral voids is equal to the number of atoms in each unit cell.

Coordination number-

"The number of nearest neighbours of a constituent particle in a solid crystal is called coordination number of respective constituent particle."

For example, Coordination number in both hcp and ccp structures is 12. Here, 6 spheres of same layer and 3 each of immediate upper and lower layers are in direct contact of a sphere.

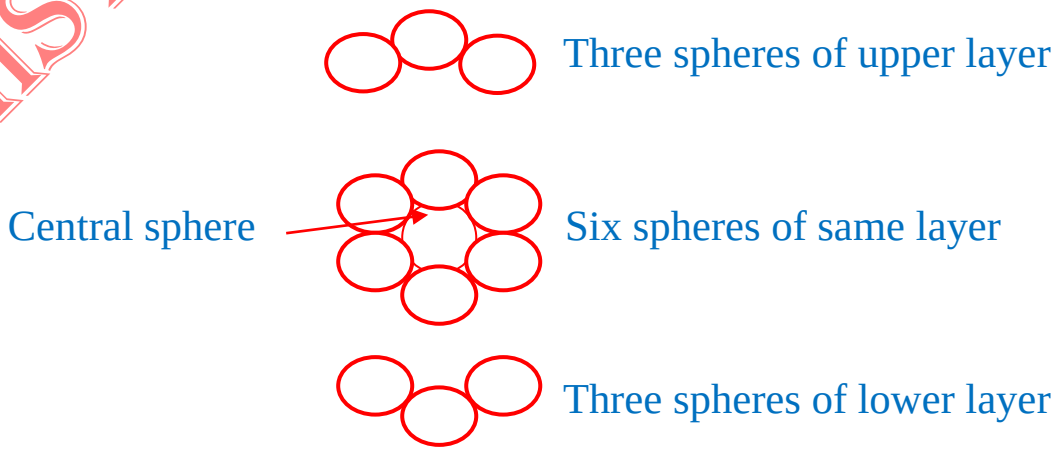


Fig.- Co-ordination number in Closed Packed Structures

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Q.1. A compound is formed by two elements X and Y. The atoms of element X form hcp lattice and those of element Y occupy $1/4^{th}$ of the tetrahedral voids. What is the formula of the compound formed?

Solution-

Let, the total number of the atoms of element packed is n.

Then, the number of tetrahedral voids formed = 2n

Hence, the number of tetrahedral voids occupied by the atoms of element Y $= 1/4 \times 2n$

Therefore, ratio of the number of atoms of X and Y = $n : 1/4 \times 2n$

$= 2 : 1$

Hence, the formula of the compound formed is X_2Y.

Q.2. A cubic solid is made of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound?

Solution- Since, the atom at the body centre give their entire contribution to the same unit cell, while that present at the corner is equally shared by 8 cubes and give only their 1/8th contribution to the unit cell.

Thus,

The number of atoms of element Y per unit cell = 1/8 × 8 (atoms at corners)

= 1

Number of atoms of element X per unit cell = 1 (atoms at body centre)

= 1

Thus, the ratio of the number of atoms of X and Y = 1 : 1

Hence, the formula of the given compound will be XY.

Packing Efficiency

The percentage of total available space filled by the constituent particles in a unit cell is called Packing efficiency of the solid crystal.

Mathematically,

$$\text{Packing Efficiency} = \frac{\text{Volume Occupied by the Constituent Particle}}{\textit{Total Volume of the Unit cell}} \times 100$$

(1) Packing Efficiency of Simple cubic lattice

In simple cubic structures, the constituent particles are present only at all the corners of the cube touching each other along the edge.

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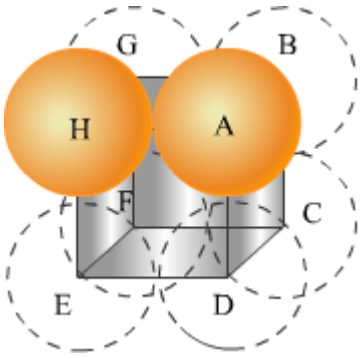


Fig.-Simple cubic Unit cell

Let the edge length of the cube is 'a' and the radius of constituent particle is ***r.***

Then,

$$a = 2r$$

Here, the volume of the cubic unit cell = a^3

$$= (2r)^3$$

$$= 8r^3$$

The number of particles per unit cell in simple cubic structures is 1.

Hence,

$$\text{Packing Efficiency} = \frac{\text{Volume Occupied by the Constituent Particle}}{Total\ Volume\ of\ the\ Unit\ cell} \times 100$$

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

$$= \frac{1}{6}\pi \times 100\ \%$$

$$= \frac{1}{6} \times \frac{22}{7} \times 100\ \%$$

$$= 52.4\ \%$$

Thus, packing efficiency of simple cubic structures is only 52.4 %.

(2) Packing Efficiency of hcp or ccp Structures

Both **hcp and ccp** structures have same packing efficiency. Here, the constituent particles remain present at all the corners as well as at all the faces of the cube.

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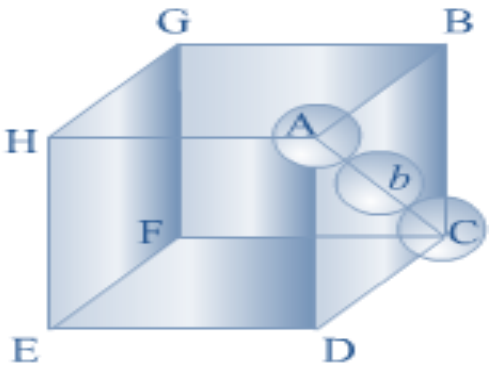


Fig.- ccp unit cells

Let the edge length of the unit cell is '*a*' and the length of the face diagonal AC is b, then

In ΔABC,

$$AC^2 = BC^2 + AB^2$$

or $b^2 = a^2 + a^2$

or $b^2 = 2a^2$

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

If the radius of the atom is r, then it is clear that,

$$b = 4r$$

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

or $a = 2\sqrt{2}\ r$

Since, there are 4 constituent particles per unit cell in hcp or ccp structures. Hence,

$$\text{So, volume of the occupied unit cell} = 4 \times \frac{4}{3}\pi r^3$$

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

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

$$= \frac{\frac{16}{3}\pi r^3}{16\sqrt{2}r^3} \times 100\ \%$$

$$= 74\%$$

Thus, packing efficiency of a **hcp and ccp** structures is the highest and it is 74 %.

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(3) Packing Efficiency of Body-centred cubic Structures

In bcc structures, the constituent particles are present at all the corners as well as at body centre of the cube. Here, the atom present at the centre is in contact with the other two atoms arranged diagonally.

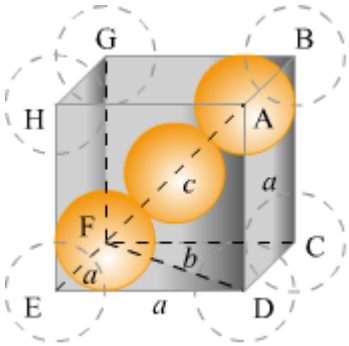


Fig.- bcc Unit Cell

In ΔFED,

$$b^2 = a^2 + a^2$$
$$\Rightarrow b^2 = 2a^2$$
$$\Rightarrow b = \sqrt{2}a$$

In ΔAFD,

$$c^2 = a^2 + b^2$$
$$\Rightarrow c^2 = a^2 + 2a^2 \qquad (\text{Since } b^2 = 2a^2)$$
$$\Rightarrow c^2 = 3a^2$$
$$\Rightarrow c = \sqrt{3}a$$

Let the radius of the atom is *r*.
Then, the length of the body diagonal, $c = 4r$

$$\Rightarrow \sqrt{3}a = 4r$$
$$\Rightarrow a = \frac{4r}{\sqrt{3}}$$

or,
$$r = \frac{\sqrt{3}a}{4}$$

Thus, Volume of the cube,

$$a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

A body-centred cubic structure contains in all 2 atoms per unit cell.

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$$\text{So, volume of the occupied cubic lattice} = 2\times\frac{4}{3}\pi r^3$$

$$= \frac{8}{3}\pi r^3$$

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

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

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} \times 100\ \%$$

$$= 68\ \%$$

Crystal Density

The density of unit cell corresponds to the density of the respective solid crystal.

Let in a cubic crystal, edge length of the unit cell is a. then,

volume of the unit cell = a^3

If z is the number of atoms per unit cell and m is the mass of each atom, then-

Mass of the unit cell = Number of atoms per unit cell × Mass of one atom

$= \boldsymbol{z \times m}$

Thus, the density of the solid substance,

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

$$= \frac{z\,.\,m}{a^3}$$

If molar mass of the substance is M, then, mass of one atom,

$$m = \frac{M}{N_A}$$ Where, N_A is Avogadro's Number

or $$d = \frac{z\,.\,M}{a^3\,.\,N_A}$$

If other parameters are known then the density of a solid crystal can be calculated using this expression.

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Numericals

Ques. Iron has a body-centred cubic unit cell with a cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number. (At. Mass of Fe = 56 g mol^{-1}).

Sol: In a body-centred cubic unit cell, number of atoms present = 2

Atomic mass of iron = 56 g mol^{-1}

Density of iron = 7.87 g cm^{-3}

Mass of iron = 7.87 × Volume

Volume in BCC = $(a)^3$

$= (286.65)^3$ pm

$= 2.34 \times 10^{-23}$ cm

Mass = $7.87 \times 2.34 \times 10^{-23}$ g

$$\text{Avogadro's number} = \frac{\text{No.of atoms} \times \text{Molar mass}}{\text{Given mass}}$$

$$= \frac{2 \times 56}{7.87 \times 2.34 \times 10^{-23}}$$

$$= 6.022 \times 10^{23}$$

Ques. An element has a body-centred cubic structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3} Calculate the number of atoms presents in 208 g of the element.

Sol: Cell edge (a) = 288 pm

Volume of unit cell = a^3

$= (288 \text{ pm})^3$

$= (288 \times 10^{-10} \text{ cm})^3$

$= 2.389 \times 10^{-23}$ cm^3

Volume of 208 g of the element = $\frac{Mass}{Density}$

$$= \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}}$$

$= 28.89$ cm^3

Number of unit cells = $\frac{Total\ volume}{Volume\ of\ one\ unit\ cell}$

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$$= \frac{28.89\ \text{cm}^3}{2.389 \times 10^{-23}\ \text{cm}^3}$$

$$= 12.09 \times 10^{23}$$

$\because$ In a bcc structure, the number of atoms per unit cell = 2

$\therefore$ number of atoms in 208 g of the given element $= 2 \times 12.09 \times 10^{23}$

$= 24.18 \times 10^{23}$

Ques. Aluminium metal forms a cubic close-packed crystal structure. Its atomic radius is 125 x 10^{-12} m.
(a) Calculate the length of the side of the unit cell.
(b) How many such unit cells are there in 1.00 m^3 of aluminium ?

Soln-
(a) For a cubic close-packed crystal structure,
Radius of an atom,

$$r = \frac{a}{2\sqrt{2}}$$

Where, a = Edge length

$$= 2\sqrt{2}r$$

$$= 2\sqrt{2} \times 125 \times 10^{-12}$$

$$= 354 \times 10^{-12}\ \text{m}$$

Hence, the length of the side of the unit cell is 354×10^{-12} m.

(b) Volume of the unit cell = a^3

$$= (354 \times 10^{-12}\ \text{m})^3$$

$$= 4.436 \times 10^{-29}\ \text{m}^3$$

$$\text{Therefore, the number of unit cells in 1.00 m}^3 \text{ of aluminium} = \frac{1}{4.436 \times 10^{-29}\ \text{m}^3}$$

$$= 2.25 \times 10^{28}$$

Ques. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom is 127.8 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure? (Given: At. Mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23}\ mol^{-1}$).

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Sol: Given that, $M = 63.54 \text{ g mol}^{-1}$

$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

$r = 127.8 \times 10^{-10} \text{ cm}$

Since. density,

$$d = \frac{z \times M}{a^3 \times N_A}$$

For SCC- $z = 1$ and $a = 2r$

For BCC- $z = 2$ and

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

For FCC- $z = 4$ and

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

Substituting the values of z and a in equation (i) we get,

$$\text{so } d = \frac{z \times 63.54}{a^3 \times 6.02 \times 10^{23}} = \frac{z \times 10.55 \times 10^{-23}}{a^3}$$

$$\text{For SCC: } d = \frac{(1) \times 10.55 \times 10^{-23}}{(2 \times 127.8 \times 10^{-10})^3}$$

$$= \frac{10.55}{1.67} = 6.31 \text{ g/cm}^3$$

$$\text{For BCC: } d = \frac{(2) \times 10.55 \times 10^{-23}}{\left(\frac{4}{\sqrt{3}} \times 127.8 \times 10^{-10}\right)^3}$$

$$= \frac{21.10}{2.57} = 8.2 \text{ g/cm}^3$$

$$\text{For FCC: } d = \frac{4 \times 10.55 \times 10^{-23}}{\left(\frac{4}{\sqrt{2}} \times 127.8 \times 10^{-10}\right)^3}$$

$$= \frac{42.2}{4.73} = 8.92 \text{ g/cm}^3$$

The given value of density is 8.95 g/cm^3. Hence, it can be concluded that the copper unit cell is face centred cubic or fcc.

Ques. Calculate the density of silver which crystallizes in the face-centred cubic structure. The distance between the nearest silver atoms in this structure is 287 pm.

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Soln- Given that, molar mass of Ag, $M = 107.87\ g\ mol^{-1}$

$N_A = 6.02 \times 10^{23}\ mol^{-1}$

For fcc lattice, number of atoms per unit cell, $z = 4$

Distance between two nearest Ag atoms = 287 pm

$$\Rightarrow \frac{\text{Face diagonal}}{2} = 287\ \text{pm}$$

$$\Rightarrow \frac{\sqrt{2}a}{2} = 287\ \text{pm}$$

$$\Rightarrow a = 287 \times \sqrt{2}\ \text{pm}$$

$$\Rightarrow a = 287 \times 1.414\ \text{pm}$$

$$\Rightarrow a = 405.818\ \text{pm}$$

Thus, edge length = 406 pm (approx)

$= 406 \times 10^{-12}$ m

Therefore, density of silver,

$$d = \frac{z.M}{a^3.N_A}$$

$$= \frac{4 \times 107.87\ g\ mol^{-1}}{(406 \times 10^{-12}\ m)^3 \times (6.02 \times 10^{23}\ mol^{-1})}$$

$$= 1.07 \times 10^{7}\ g\ m^{-3}$$

$$= 1.07 \times 10^{4}\ kg\ m^{-3}$$

Formula of a Compound and Number of Voids Filled

- Number of octahedral voids formed = Number of particles packed in HCP and CCP
- Number of tetrahedral voids = 2 × Number of particles packed in HCP and CCP
- In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.
- If the latter ion is small enough, then it occupies the tetrahedral void, and if bigger, then it occupies the octahedral void.
- Not all the voids are occupied. Only a fraction of the octahedral or tetrahedral voids are occupied.

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- The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Some Important Competitive Tips

- In NaCl, the Na^+ ions occupy all the octahedral voids.
- In ZnS, Zn^{2+} are in alternate tetrahedral voids.
- In CaF_2, F^- ions occupy all the tetrahedral voids.
- In Fe_3O_4, if Fe^{2+} ions are replaced by divalent cations such as Mg^{2+} and Zn^{2+}, then the compounds obtained are called ferrites.

Imperfections in Solids

The irregularities or deviations observed in ideal arrangement of constituent particles in a solid crystal are called imperfections or defects in solids.

It may be of following two types-

(A)Point defects- Irregularities in the arrangement of constituent particles around a point or constituent particle in a crystalline substance is called point defect.

(B)Line defects- Irregularities in the arrangement of constituent particles in entire rows of lattice points is called line defect.

Types of Point Defects-

Point defects may be of following three types-

(1) Stoichiometric defects

(2) Non-stoichiometric defects

(3) Impurity defect

(1) Stoichiometric Defects-

In this type of point defect stoichiometry of the solid remains unchanged. It is also called intrinsic or thermodynamic defect and may be of following two types-

(i) Vacancy defect-

It is specially shown by non-ionic solids. Here, some of the lattice sites remain vacant during packing of constituent particles.

Such defects are produced on heating the solid crystal and results in the decrease of density of the crystal.

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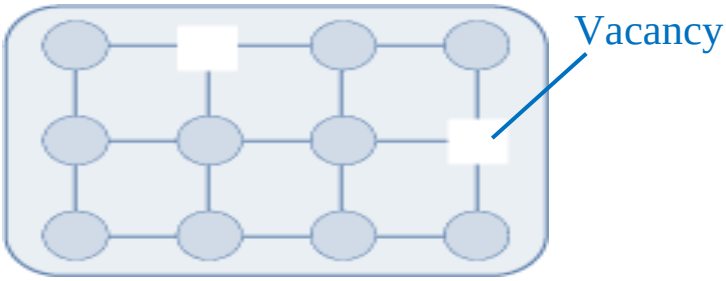


Fig.- Vacancy Defect

In ionic solids this defect is called **Schottky** defect.

(ii) Interstitial defect

It is also shown by non-ionic solids, where some of the constituent particles (atoms or molecules) get dislocalised and occupy an interstitial site of the crystal.

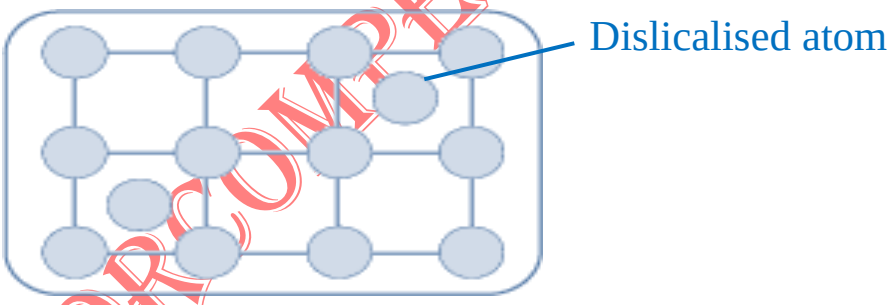


Fig.- Interstitial Defect

I

In ionic solids this defect is called **Frenkel** defect.

Schottky defect-

It is basically a vacancy defect shown by ionic solids, where equal number of cations and anions are completelly missing from the crystal lattice. Thus,

"Such stoichiometric point defect in which equal number of cations and anions are completelly missing from the crystal lattice is called **Schottky** defect."

In **Schottky** defect, due to formation of vacancies, the density of the crystal gets decreased and electrical conductance gets increased but electrical neutrality remains unchanged.

Significant number of Schottky defect is present in ionic solids such as NaCl, KCl CsCl, AgBr etc. For example, in NaCl, there are approximately 10^6 Schottky pairs per cm^3, at room temperature.

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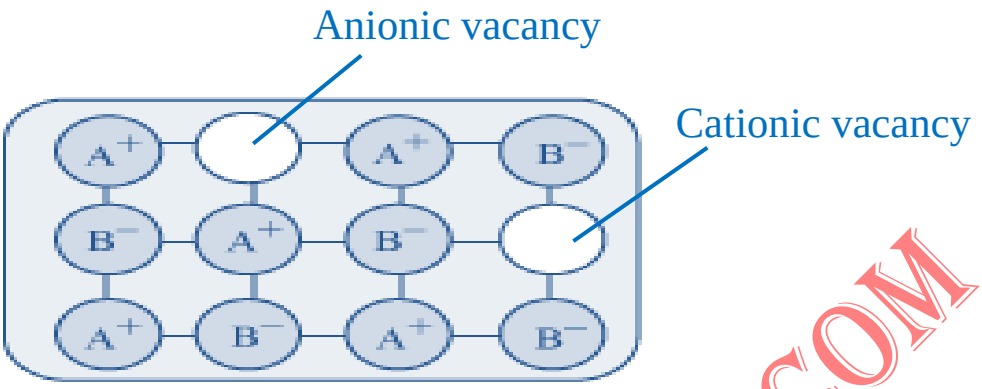


Fig.- Schottky defect

Conditions for showing Schottky Defect-

(1) The ionic size of cation and anion should be comparable.
(2) The coordination number of cation should be high.

Frenkel defect-

It is shown by ionic solids containing very large sized anions as compared to cations. Here, small sized cations get dislocalised from their normal site to the interstitial sites. Hence, it is also called dislocation defect. Thus,

"Such stoichiometric point defect in which one or more cations get dislocalised from their normal site and occupy the interstitial sites is called **Frenkel** defect."

It creates both vacancy as well as interstitial defects and is most common in ionic solids such as AgCl, AgBr, AgI, ZnS etc.

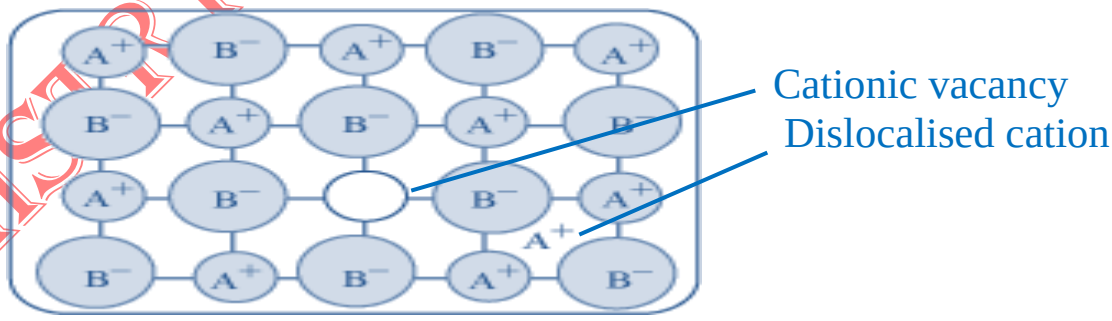


Fig.-Frenkel Defect

In **Frenkel** defect, the density and electrical neutrality of the crystal remains unchanged but electrical conductance gets increased.

Conditions for showing Frenkel Defect

(3) The ionic size of anion should be much more larger than that of cation.
(4) The coordination number of cation should be low.

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(2) Non-Stoichiometric Defects

In this type of point defect, the stoichiometry of the solid gets changed. It may be of following two types:

(i) Metal excess defect

(ii) Metal deficiency defect

(i) Metal excess defect-

(a) Metal excess defect due to anionic vacancies

Alkali metals like NaCl and KCl show this type of defect.

When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl. During this process, the Na atoms on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic sites, creating F-centres.

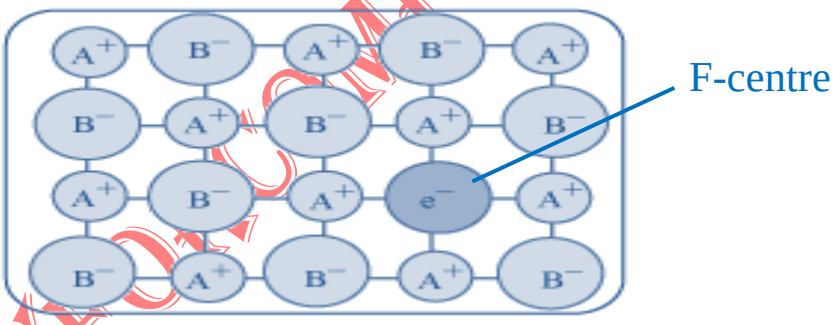


Fig.- Metal excess defect due to anionic vacancies

(b)Metal excess defect due to the presence of extra cations at interstitial sites-

When white coloured zinc oxide is heated, it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\Delta} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Thus, zinc becomes excess in the crystal, leading the formula of the oxide to $Zn_{1+x}O$. The excess Zn^{2+} ions move to the interstitial sites, and the electrons occupy the neighbouring interstitial sites.

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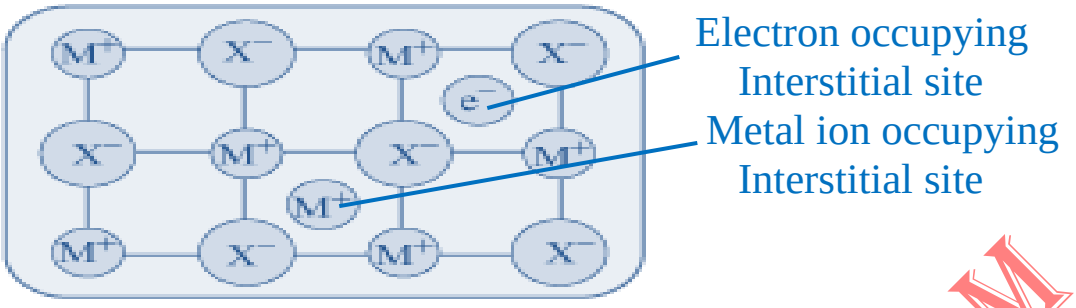


Fig.- Metal excess defect due to the presence of extra cations

(ii) Metal deficiency defect

It arises due to presence of lesser number of cations as compared to the stoichiometric proportion in the solid. For example, FeO is mostly found with a composition of $Fe_{0.95}O$. In fact in crystals of FeO, some of the Fe^{2+} ions are missing, and this loss of positive charge is compensated by the presence of the required number of Fe^{3+} ions.

Electrical Properties of Solids

Solids

Conductors	**Semiconductors**	**Insulators**
High conductivity	**Intermediate conductivity**	**Low conductivity**
(Order- 10^{7} $ohm^{-1}m^{-1}$)	(Range- 10^{-6}- 10^{4} $ohm^{-1}m^{-1}$)	(Range-10^{-20}-10^{-10} $ohm^{-1}m^{-1}$)

Conduction of Electricity in Metals

Metals conduct electricity due to flow of electrons. Hence, the conductivity of metals depends upon the number of their valence electrons. The larger the number of valence electrons, more is electrical conductance of respective metal.

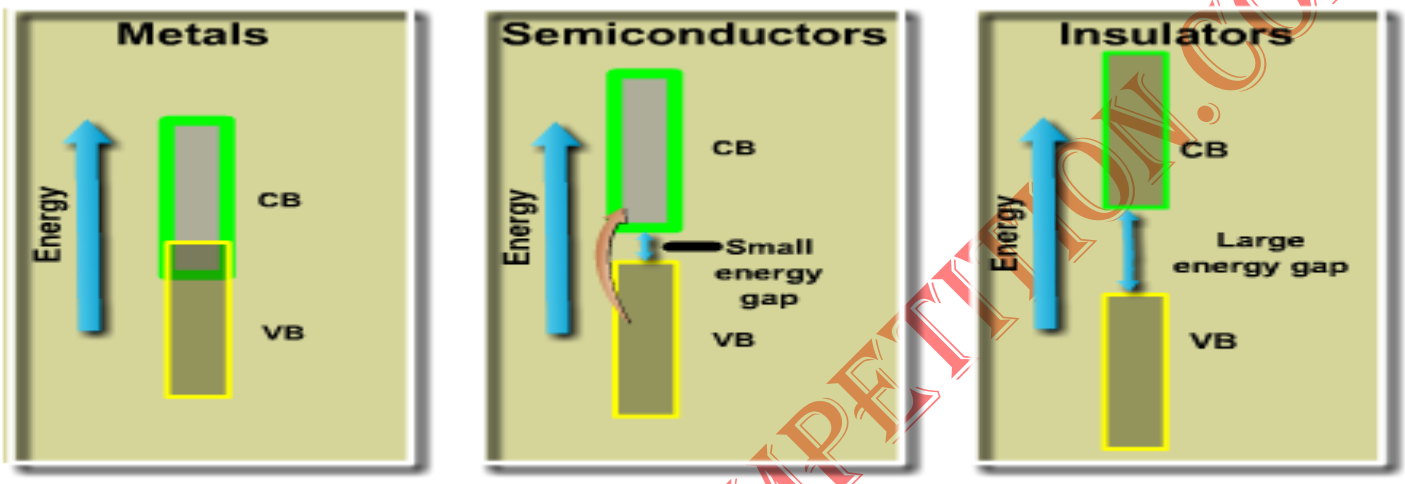
In fact in metals, the valence shell is partially filled and remains overlaped with a higher energy unoccupied conduction band. Hence, the electrons can flow easily through the conduction band under an applied electric field.

In insulators, the gap between filled valence band and the next higher unoccupied conduction band is very large. Hence, the electrons cannot jump from the valence band to the conduction band.

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Conduction of Electricity in Semiconductors

In semiconductors, the gap between the valence band and conduction band is relatively small. Hence, some electrons get jumped to the conduction band and flow under an applied electric field.



CB = Conduction Band, VB = Valance Band

Fig.- Energy difference of valence and conduction bands in metals, semiconductors and insulators

Doping

The conductance of semiconductors is too low and therefore it has no practical use. However, for practical use their conductance is increased by adding some suitable impurities. This process of adding an appropriate amount of suitable impurity to increase conductivity of intrinsic semiconductors is called Doping.

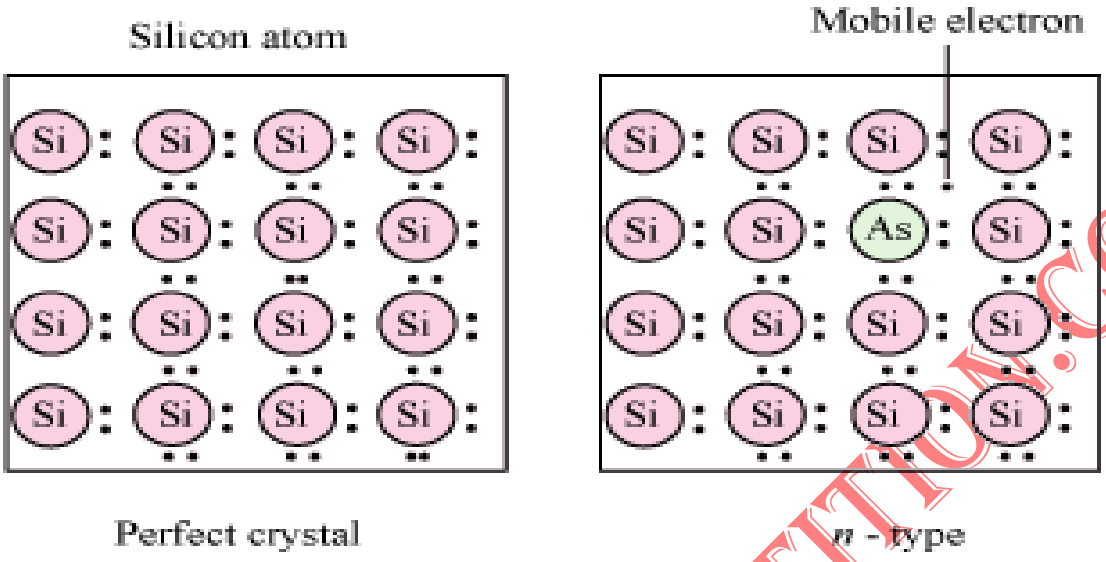
Doping is done with either electron-rich or electron-deficient impurity as compared to the intrinsic semiconductor s i.e. Si or Ge. On this basis there are two types of semiconductors-

n-Type semiconductors

This type of semiconductors are produced by doping of the crystals of Si or Ge, with a group 15 element such as P or As. Here out of the five valence electrons of doped atoms four get involved in bonding with Si or Ge, while the rest one occupies interstitial site and is free to move. Thus, the conductance of the crystal gets increased.

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Since, these crystals contain extra electrons, they are known as *n*-type semiconductors.

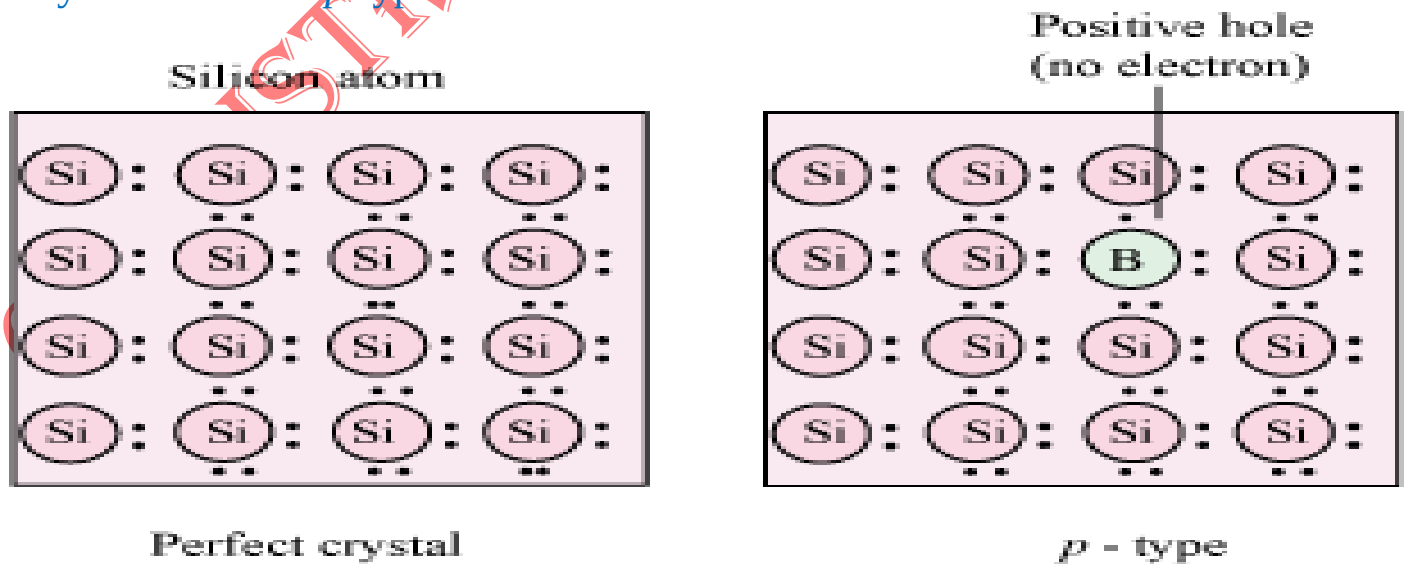


p-Type semiconductor

This type of semiconductors are produced by doping of the crystals of Si or Ge, with a group 13 element such as B, Al or Ga.

Here, three valence electrons of Si or Ge get involved in bonding with three valence electrons of doped atoms, while rest one electron of these atoms remains unpaired and an electron hole is produced at the place where the electron is absent. The neighbouring electrons can move into these holes, thereby creating newer holes.

Thus, due to formation of electron hole the conductance of the crystal gets increased. Since, these crystals contain lesser electrons than un-doped crystals, they are known as *p*-type semiconductors.



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Applications of n-Type and p-Type Semiconductors

(1) In making a diode, which is used as a rectifier.

(2) In making transistors, which are used for detecting or amplifying radio or audio signals.

(3) In making a solar cell, which is a photo diode used for converting light energy into electrical energy.

A large number of compounds (solid) have been prepared by the combination of groups 13 and 15 or 12 and 16 elements to stimulate average valence of four as in Si or Ge. For example,

(1) Compounds prepared by the combination of groups 13 and 15 elements- InSb, AlP, GaAs etc.

(2) Compounds prepared by the combination of groups 14 and 16 elements- ZnS, CdS, CdSe, HgTe etc.

- Some oxides like VO, VO_2, VO_3, TiO_3 etc. show both metallic and insulating properties depending upon temperature.
- Polyacetylene, an organic compound shows conductivity when exposed to iodine vapours.

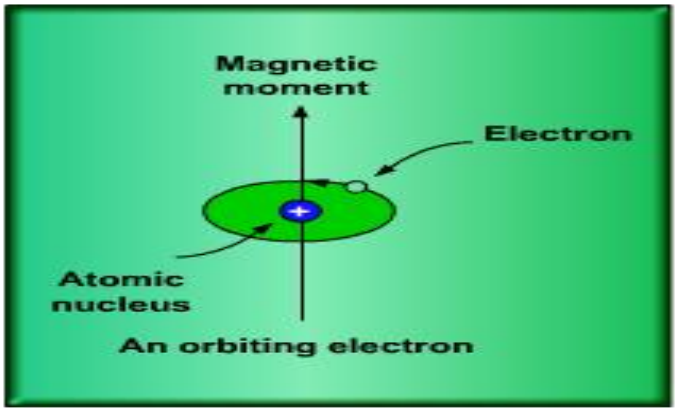
Magnetic Properties of Substances

Each electron in an atom has a definite magnetic moment and behaves like a tiny magnet. The magnetic moment of an electron originates from its two types of motion-

(1) Orbital motion around the nucleus

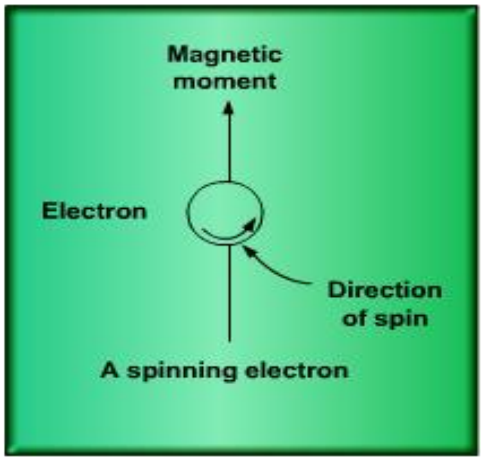
(2) Spin around its own axis

Thus, an electron has a permanent orbital and spin magnetic moment associated with it.



An orbiting electron

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A spinning electron

Fig.- Different types of motion of electrons

Based on magnetic properties, substances are classified into following five categories-

(1) Paramagnetic substances

Those substances which contain one or more unpaired electrons, are attracted in the magnetic field and are called paramagnetic substances and this phenomenon is called paramagnetism.

Some examples of paramagnetic substances are O_2, Cu^{2+}, Fe^{3+} and Cr^{3+} etc.

In magnetic field, Paramagnetic substances get magnetized in the direction of the magnetic field but lose their magnetism when the magnetic field is removed.

(2) Diamagnetic substances

The substances which do not contain unpaired electron are not attracted, but weakly repelled in magnetic field are said to be diamagnetic substances and this phenomenon is called diamagnetism.

Some examples of diamagnetic substances are − H_2O, NaCl, C_6H_6 etc.

In magnetic field, Diamagnetic substances get weakly magnetised in direction opposite to magnetic field.

In diamagnetic substances, all the electrons are paired. Hence, the magnetic characters of these substances get lost due to the cancellation of magnetic moments of the electrons.

(3) Ferromagnetic substances

The substances which are strongly attracted in a magnetic field are called ferromagnetic substances and this phenomenon is called ferromagnetism.

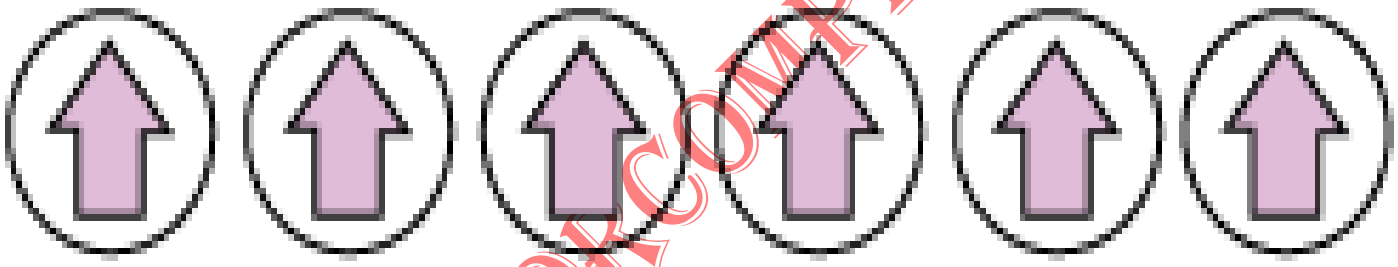
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Ferromagnetic substances get permanently magnetized in magnetic field. They do not lose their magnetic behavior even on the removal of the magnetic field.

Some examples of ferromagnetic substances are iron, cobalt, nickel, gadolinium and CrO_2.

In fact, In solid state, the metal ions of ferromagnetic substances remain grouped together into small regions called domains, and each domain acts as a tiny magnet. In an un-magnetised piece of a ferromagnetic substance, the domains are randomly oriented, so their magnetic moments get cancelled. However, when the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. As a result, a strong magnetic effect is produced. This ordering of domains persists even after the removal of the magnetic field. Thus, the ferromagnetic substance becomes a permanent magnet.

Schematic alignment of magnetic moments of domains in ferromagnetic substances is as follows:



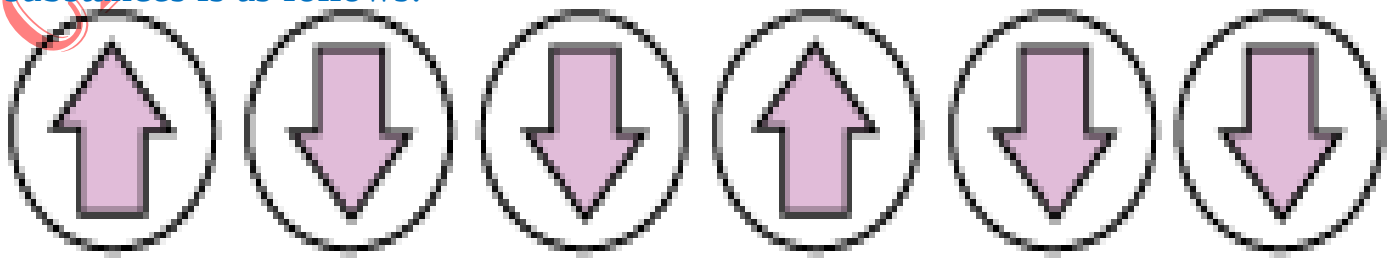
(4) Ferrimagnetic Substances

The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in unequal numbers, are said to have ferrimagnetism. For examples, Fe_3O_4 (magnetite), ferrites such as $MgFe_2O_4$ and $ZnFe_2O_4$.

Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances.

On heating, these substances become paramagnetic.

Schematic alignment of magnetic moments of domains in ferrimagnetic substances is as follows:



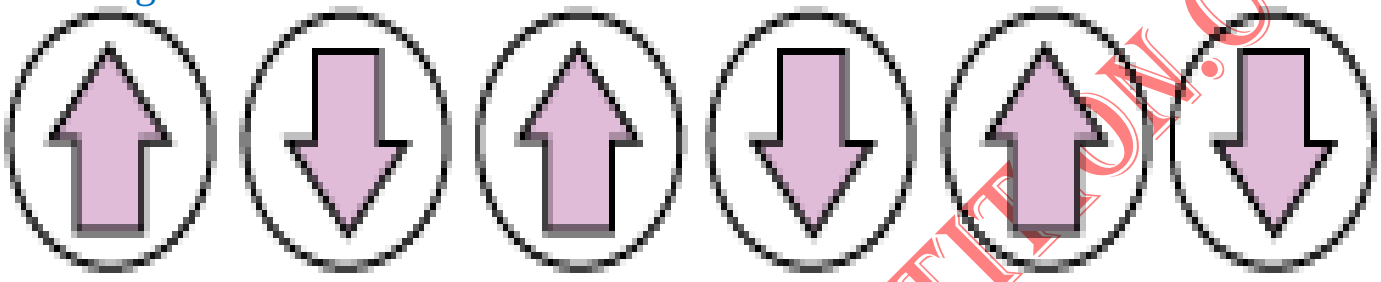
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(5) Anti-ferromagnetic Substances

The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in equal numbers, are said to have anti-ferrimagnetism.

Here, since the domains are oppositely oriented they cancel out the magnetic moments of one another.

Schematic alignment of magnetic moments of domains in anti-ferromagnetic substances is as follows:



Piezoelectric effect-

The production of electricity due to the displacement of ions, on the application of mechanical stress, or the production of mechanical stress and/or strain due to atomic displacement, on the application of an electric field is known as piezoelectric effect. Piezoelectric materials are used in transducers − devices that convert electrical energy into mechanical stress/strain or vice-versa. Some piezoelectric materials are lead-zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), quartz, etc.

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