The Solid State

General Characteristics of Solid State

- (i) They have definite mass, volume and shape.
- (ii) Intermolecular distances are short.
- (iii) Intermolecular forces are strong.
- (iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
- (v) They are incompressible and rigid.

Amorphous and Crystalline Solids

- Solids can be classified as *crystalline or amorphous on the basis of the* nature of order present in the arrangement of their constituent particles.

- **Crystalline Solids** In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered.

- It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal.

- Sodium chloride and quartz are typical examples of crystalline solids.

An amorphous solid

- An amorphous solid (Greek *amorphos = no form*) *consists of particles* of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only *short range order.*

- *In* case of amorphous quartz glass there is no *long range order.*

- *The structure of* amorphous solids is similar to that of liquids.

- Glass, rubber and plastics are typical examples of amorphous solids.

# Two dimensional structure of (a) quartz and (b) quartz glass
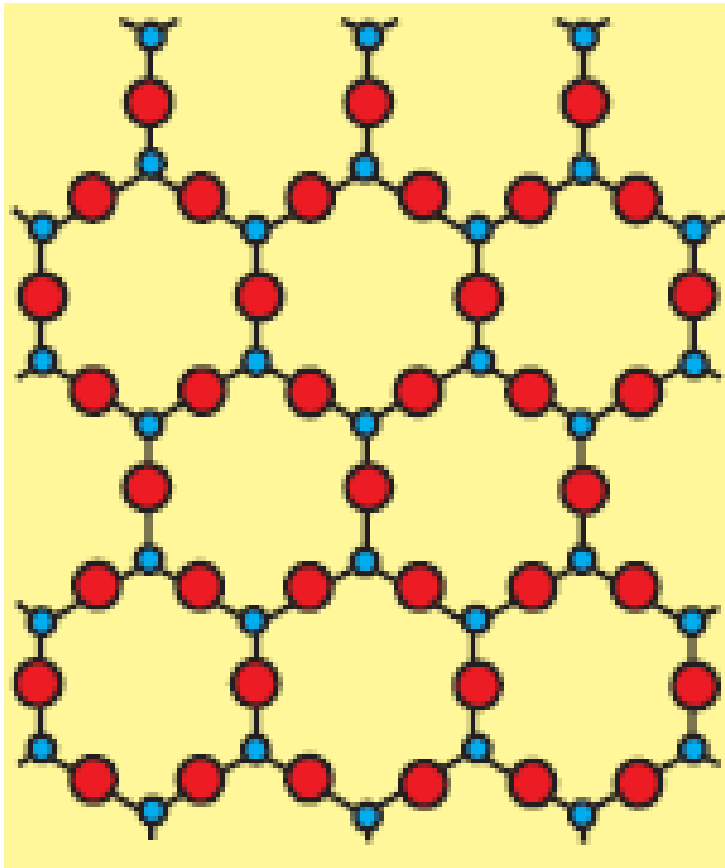
(a)
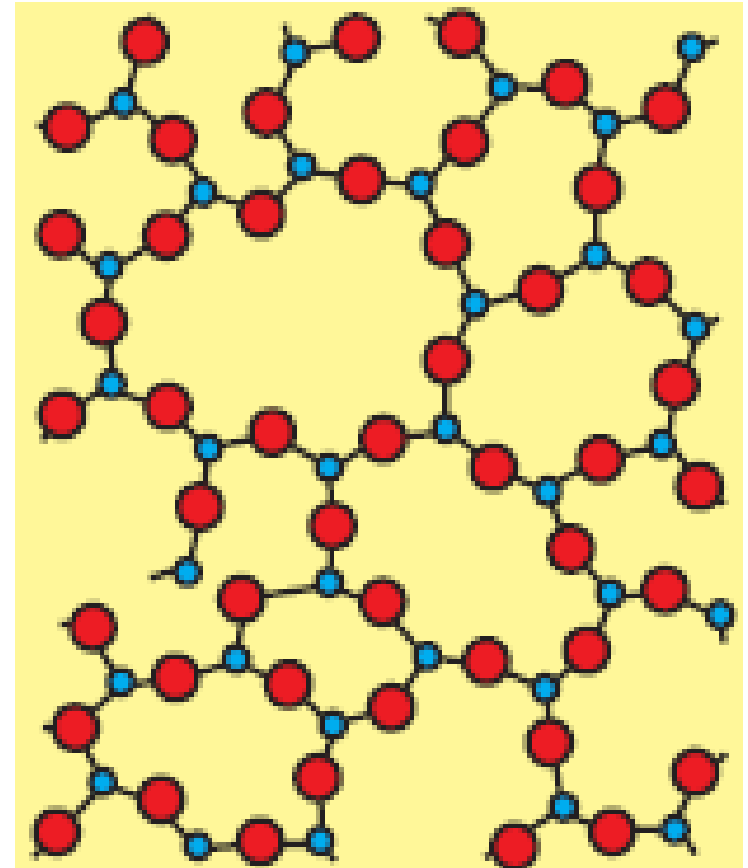
(b)

- Crystalline solids have a sharp melting point.
- On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes.
- On heating they become crystalline at some temperature.
- Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called *pseudo solids or super cooled liquids.*

Anisotropy

- Crystalline solids are *anisotropic in nature, that* is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals.
- This arises from different arrangement of particles in different directions.
- Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction.

Anisotropy
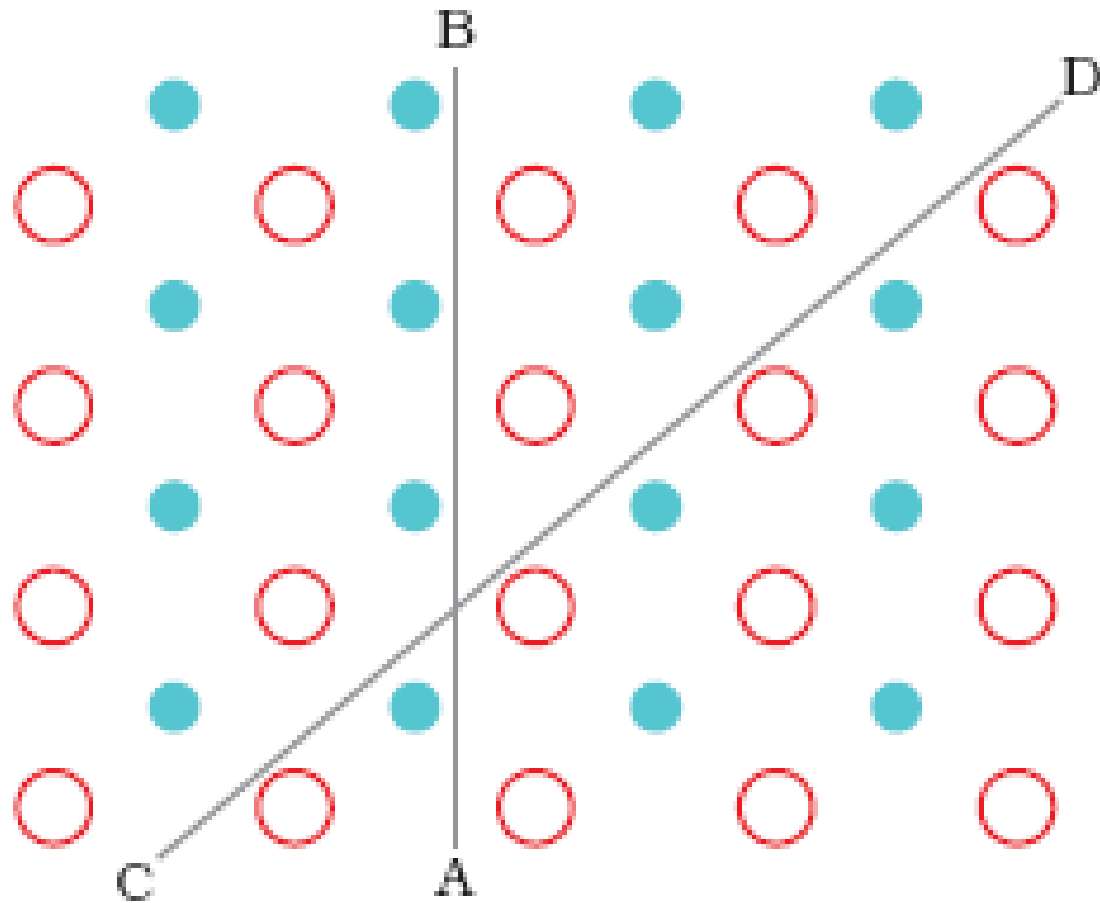
isotropic

- Amorphous solids on the other hand are *isotropic* in nature.
- It is because there is no *long range order in them and* arrangement is irregular along all the directions.
- Therefore, value of any physical property would be same along any direction.

summary

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Classification of Crystalline Solids

- Crystalline solids can be classified on the basis of nature of intermolecular forces operating in them into four categories viz.,

❑molecular,

❑ ionic,

❑ metallic and

❑covalent solids.

Molecular Solids

- These are further sub divided into the following categories:

❖ (i) *Non polar Molecular Solids:*

❖ (ii) *Polar Molecular Solids:*

❖ (iii) *Hydrogen Bonded Molecular Solids:*

(i) *Non polar Molecular Solids:*

- *They comprise of either atoms, for* example, argon and helium or the molecules formed by non polar covalent bonds for example H2, Cl2 and I2.
- In these solids, the atoms or molecules are held by weak dispersion forces or London forces
- These solids are soft and non-conductors of electricity.
- They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) *Polar Molecular Solids:*

- *The molecules of substances like HCl, SO2, etc. are formed by polar covalent bonds.*
- *The molecules in such* solids are held together by relatively stronger dipole-dipole interactions.
- These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room emperature and pressure.
- Solid SO2 and solid NH3 are some examples of such solids.

(iii) *Hydrogen Bonded Molecular Solids:*

- *The molecules of such solids* contain polar covalent bonds between H and F, O or N atoms.

- Strong hydrogen bonding binds molecules of such solids like H_2O (ice).

- They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

Ionic Solids

- Ions are the constituent particles of ionic solids.
- Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces.
- These solids are hard and brittle in nature.
- They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state.
- However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

Metallic Solids

- Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons.

- These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons.

- These free and mobile electrons are responsible for high electrical and thermal conductivity of metals.

Metallic Solids

- When an electric field is applied, these electrons flow through the network of positive ions.

- Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons.

- Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them.

- Metals are highly malleable and ductile.

Covalent or Network Solids

- A wide variety of crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal.

- They are also called **giant molecules.**

- Diamond and silicon carbide are typical examples of such solids.

- Graphite is soft and a conductor of electricity.

structures

141.5 pm

340 pm
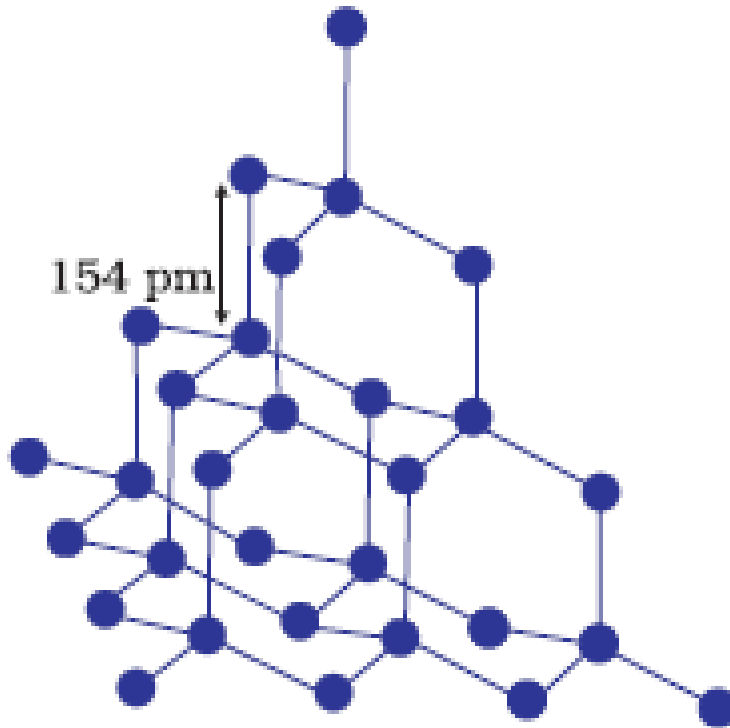
Fig. 1.3: Network structure
of diamond

154 pm
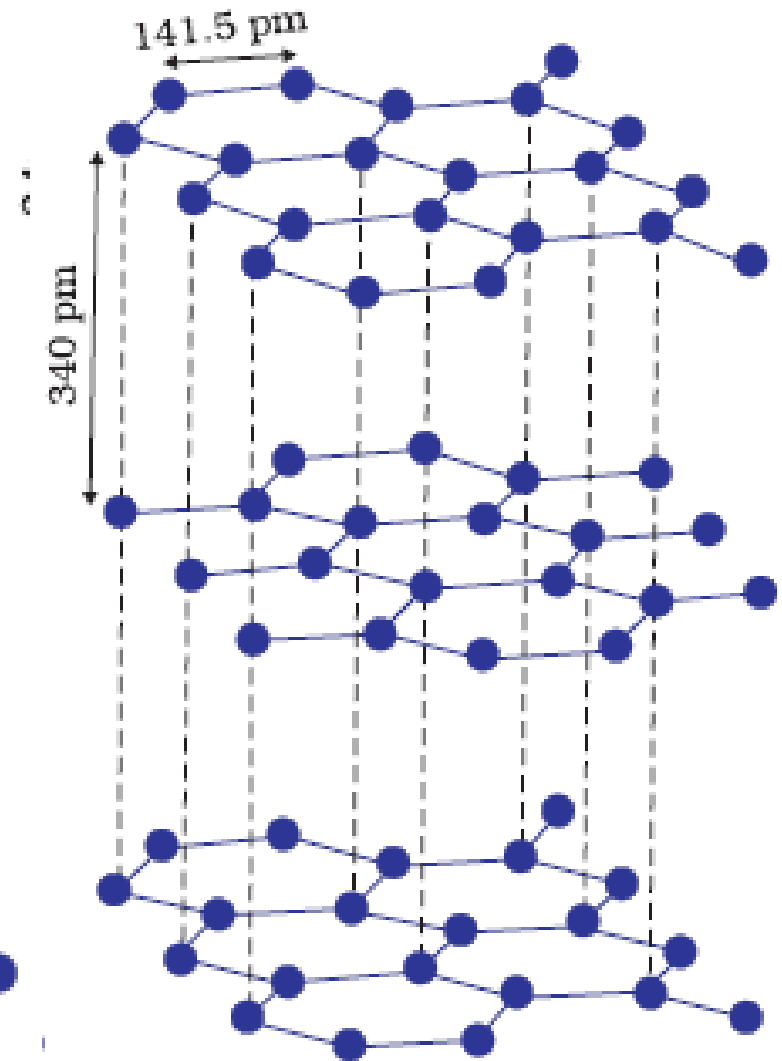
Fig. 1.4: Structure of graphite

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conduc-tivity	Melting Point
(1) Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	$NaCl$, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$	Hard Soft	Insulators Conductor (exception)	Very high

Crystal Lattices and Unit Cells

- A regular three dimensional arrangement of points in space is called a **crystal lattice.**
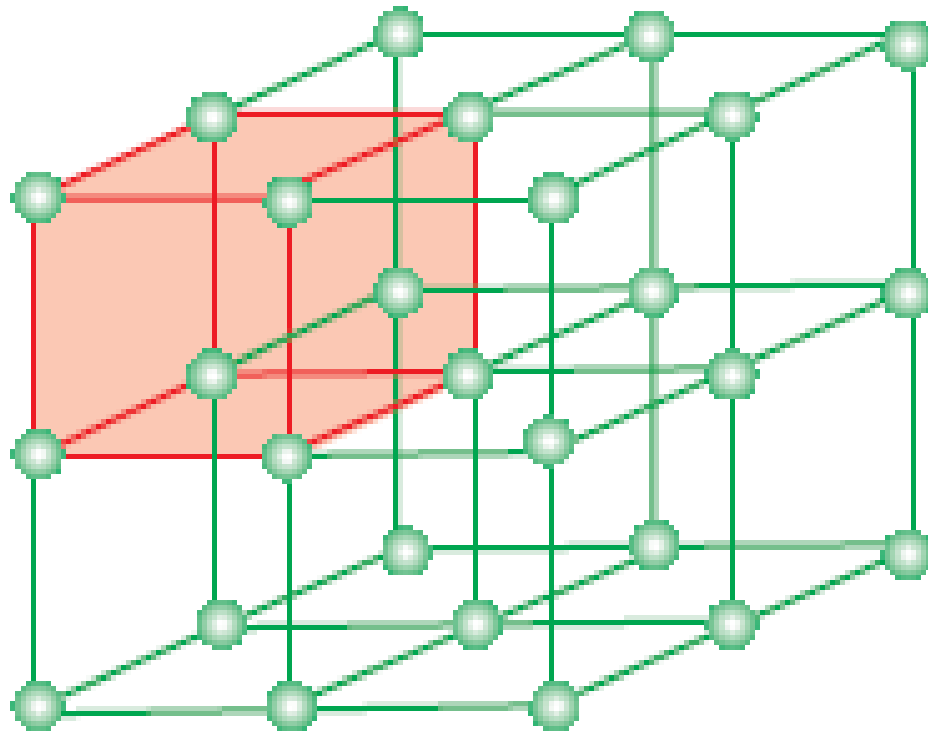
- There are only 14 possible three dimensional lattices.
- These are called **Bravais Lattices**
- The following are the characteristics of a crystal lattice:
- (a) Each point in a lattice is called lattice point or lattice site.
- (b) Each point in a crystal lattice represents one constituent particle 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.

Unit cell

- Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

- A unit cell is characterised by:

- (i) its dimensions along the three edges, *a, b and c.*

- *These* edges may or may not be mutually perpendicular.

- (ii) angles 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 six parameters, *a, b, c, α, β and γ.*

- These parameters of a typical unit cell are shownbelow

Unit cell
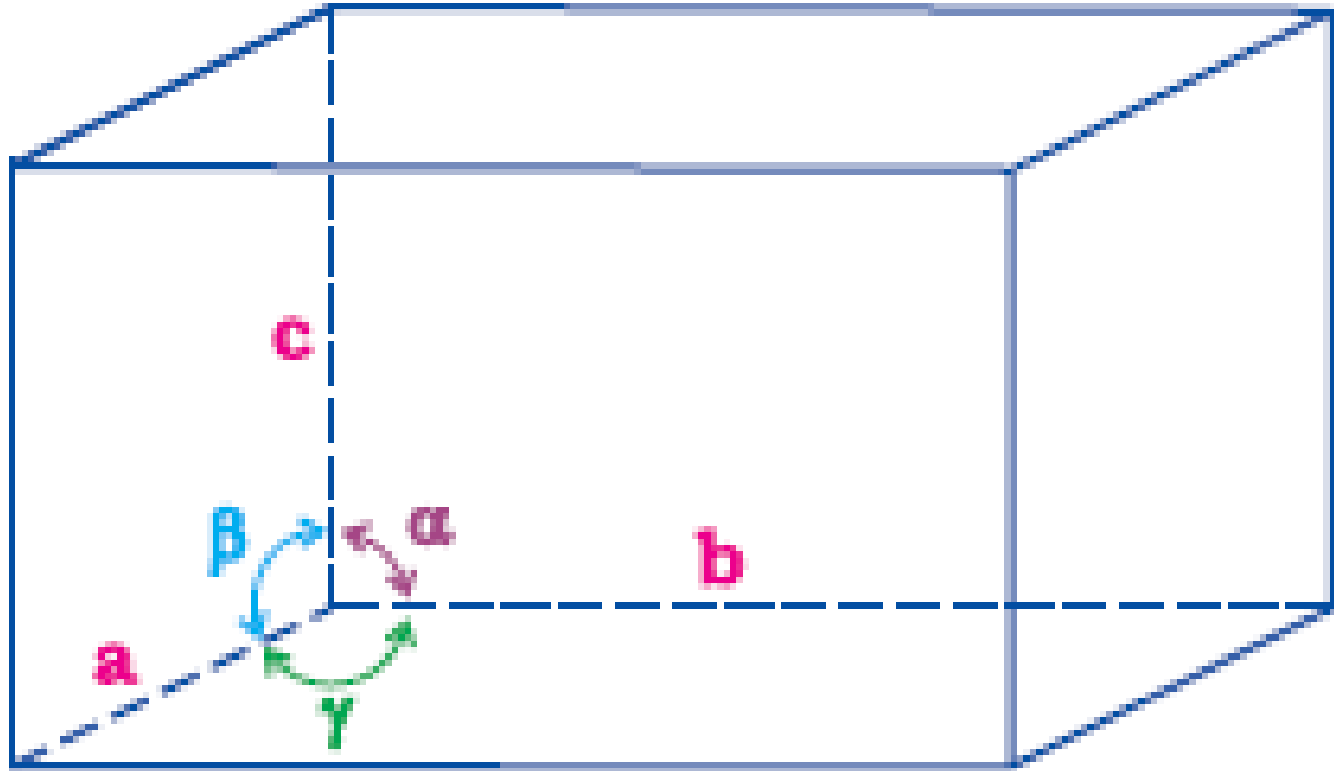
Primitive and Centred Unit Cells

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

(a) Primitive Unit Cells

- When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell.**

(b) Centred Unit Cells

- When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a **centred unit cell.**

Centred unit cells are of three types:

Centred unit cells

- (i) *Body-Centred Unit Cells:*
- *Such a unit cell contains one constituent* particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
- (ii) *Face-Centred Unit Cells: Such a unit cell contains one constituent* particle present at the centre of each face, besides the ones that are at its corners.
- (iii) *End-Centred Unit Cells: In such a unit cell, one constituent particle* is present at the centre of any two opposite faces besides the ones present at its corners.

Seven types of primitive unit cells
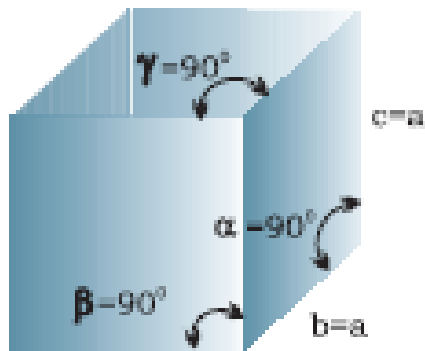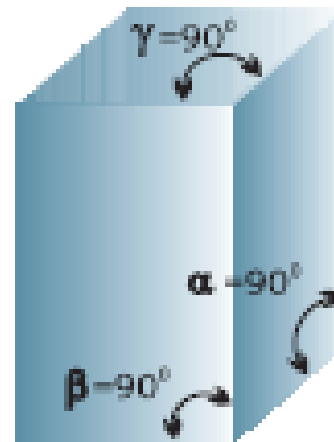
Cubic

Tetragonal
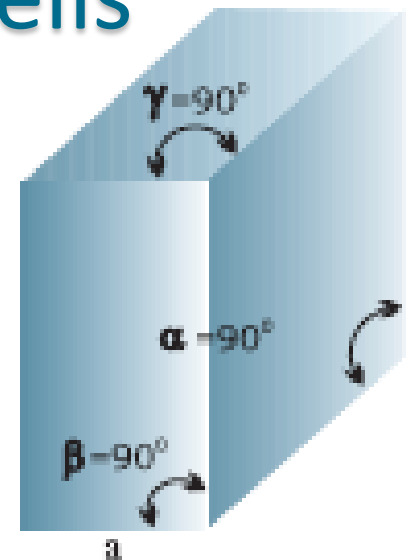
Orthorhombic
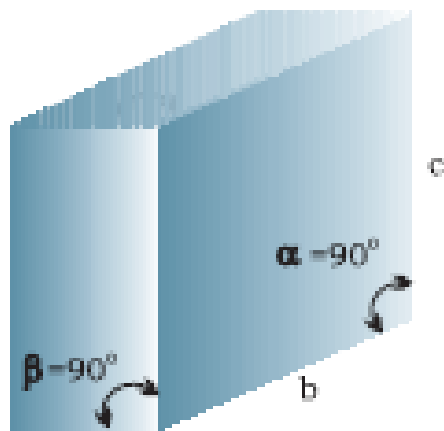
Monoclinic
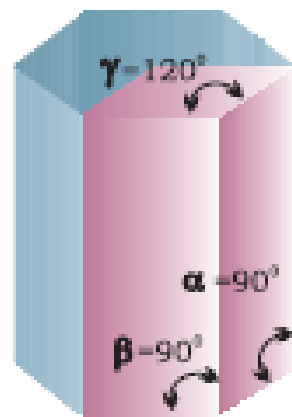
Hexagonal
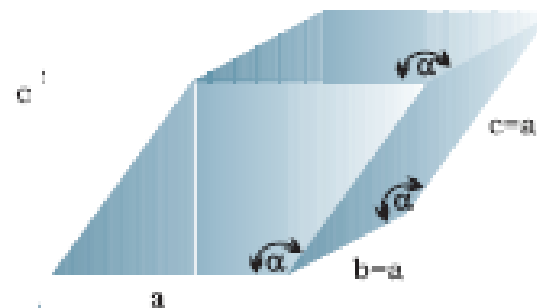
Rhombohedral
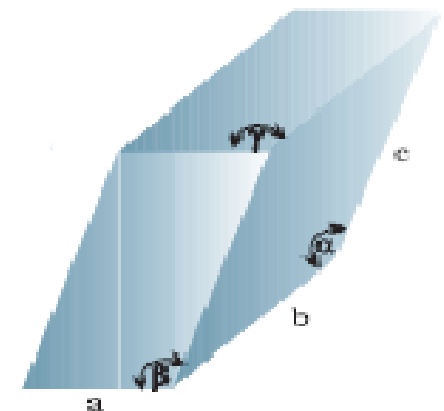
Triclinic

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)

cubic lattices

Primitive (or simple)   Body-centred   Face-centred
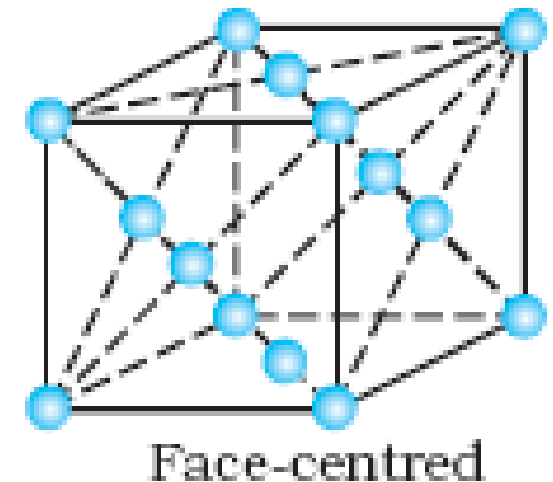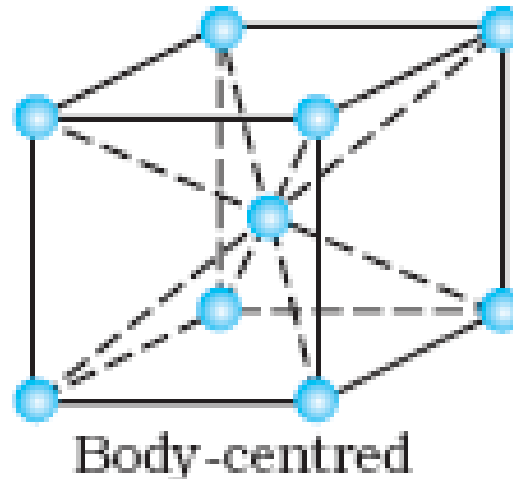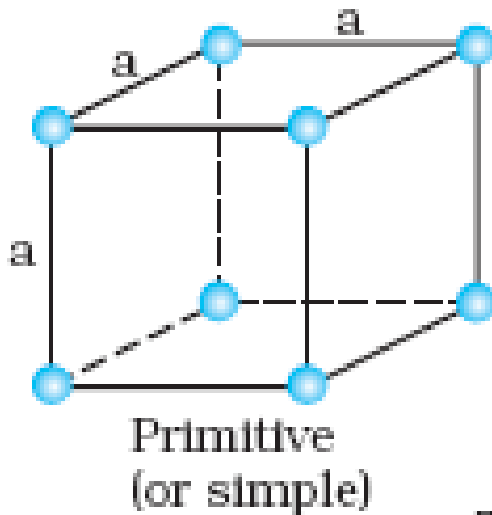
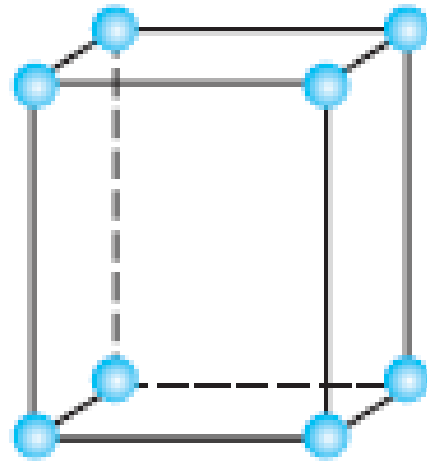- The three cubic lattices: all sides of same length, angles between faces all 90°
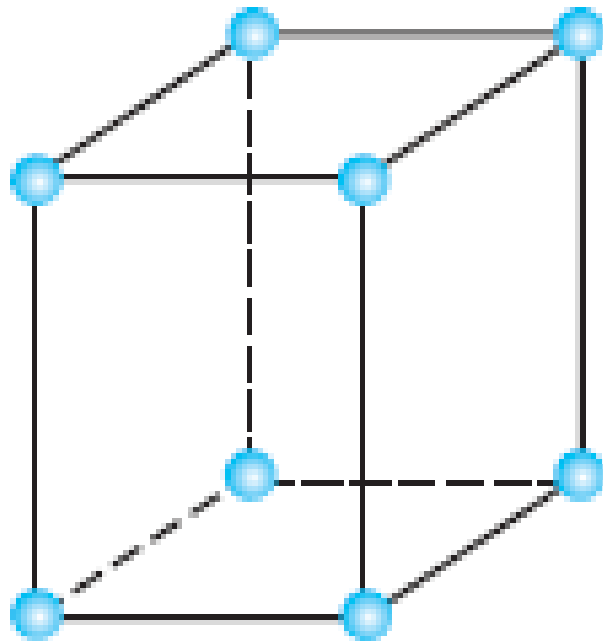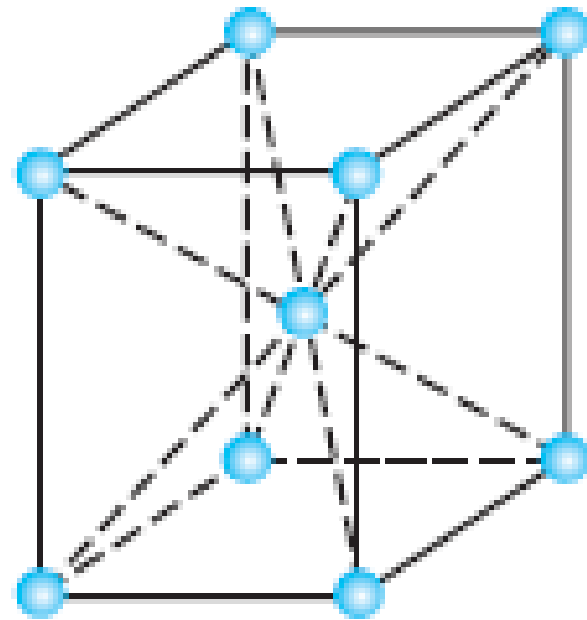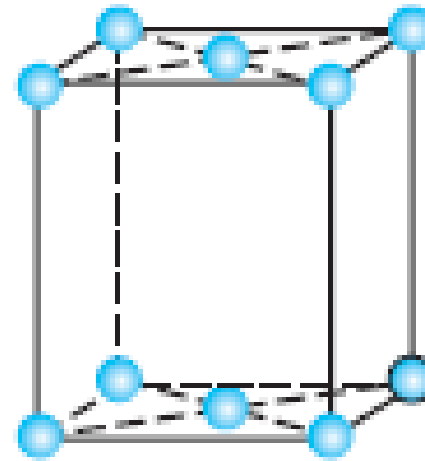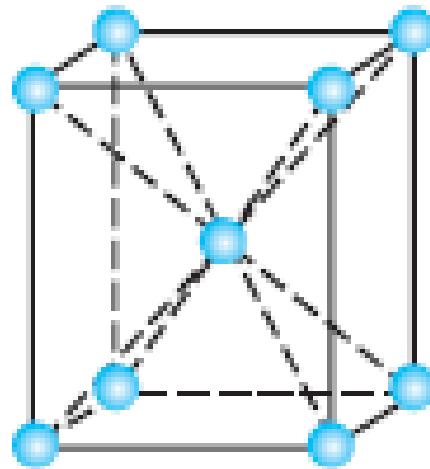
Primitive   Body-centred

- The two tetragonal: one side different in length to the other, two angles between faces all 90°
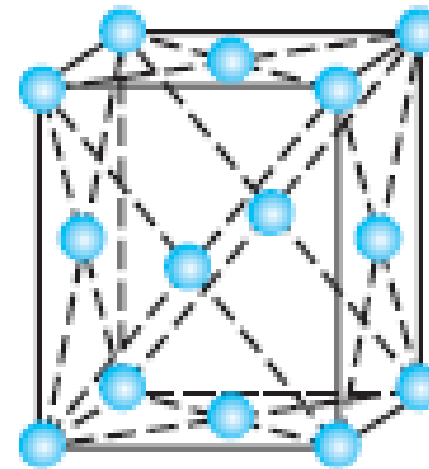
Primitive

End-centred

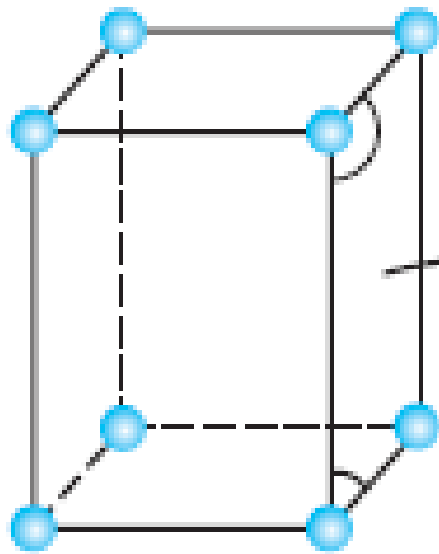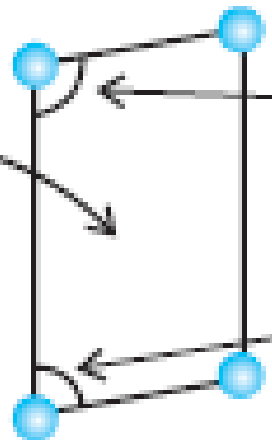Body-centred

Face-centred

- The four orthorhombic lattices: unequal sides, angles between faces all 90°

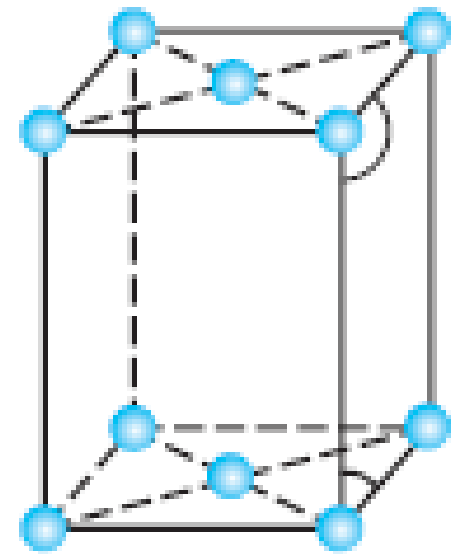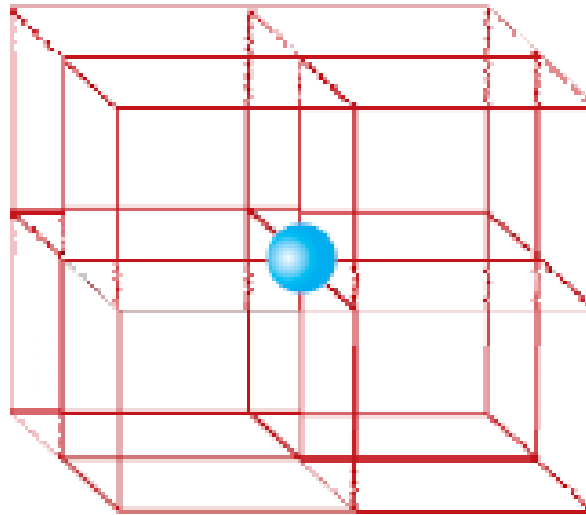Primitive · · · · More than 90° · · · Less than 90° · · · End-centred

- The two monoclinic lattices: unequal sides, two faces have angles different to 90°
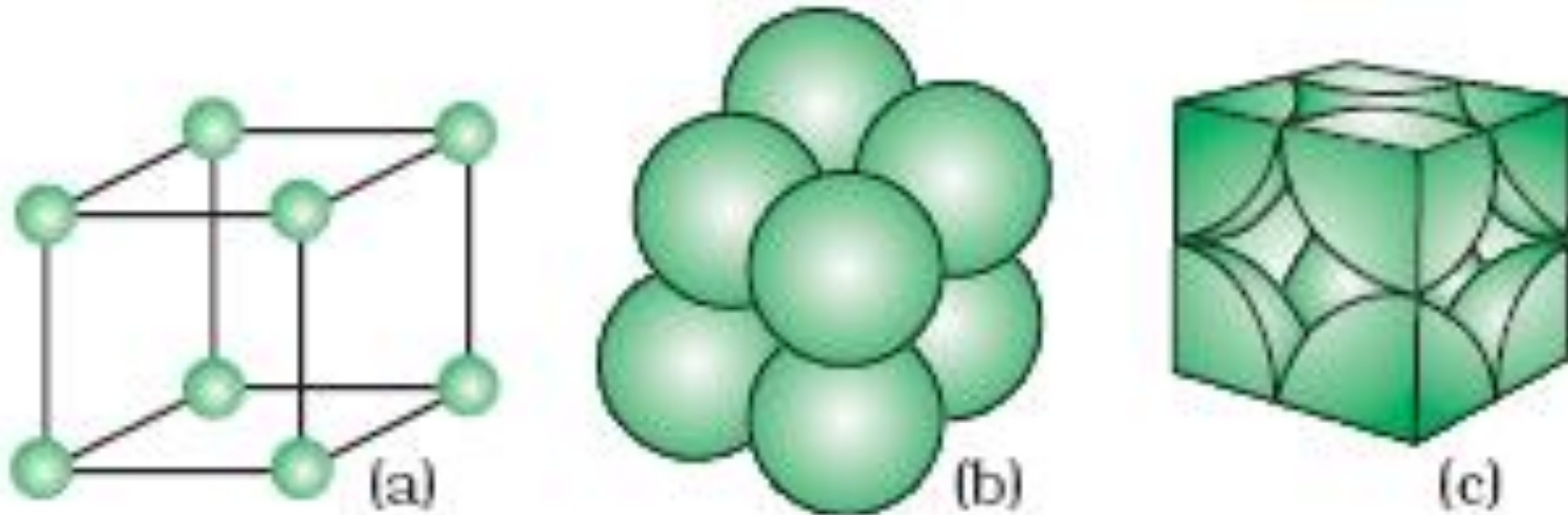
Number of Atoms in a Unit Cell

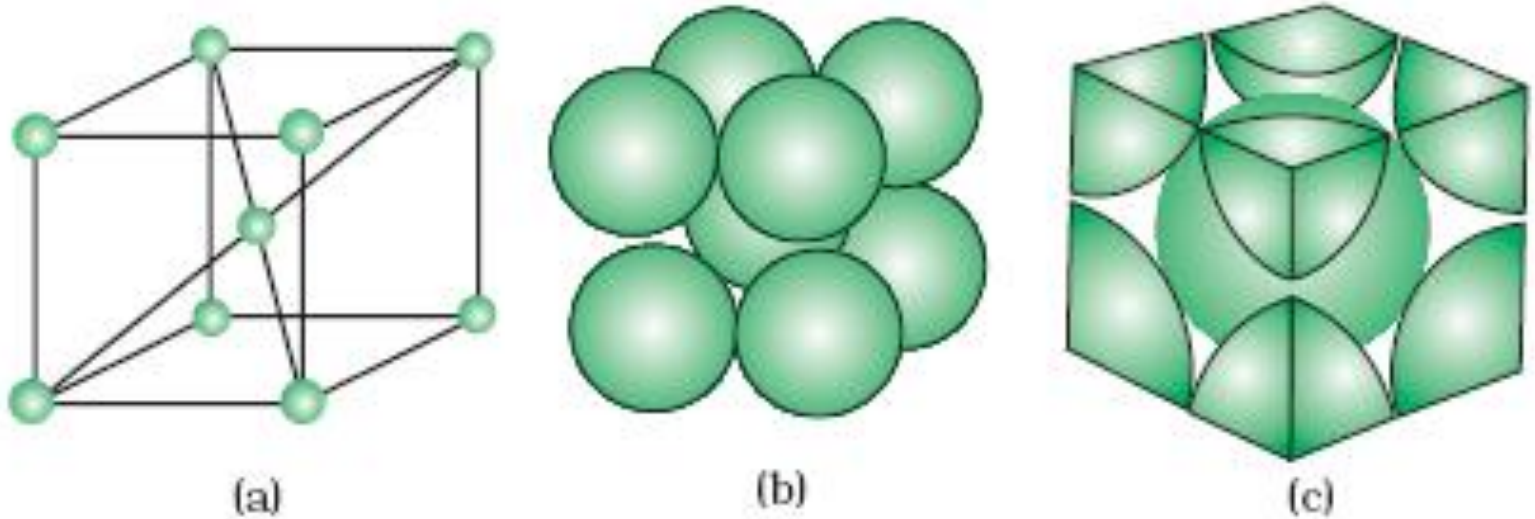- **Primitive Cubic Unit Cell**

In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is

=8 x   I/8 = I atom.

Primitive Cubic Unit Cell

The total number of atoms in one unit cell is
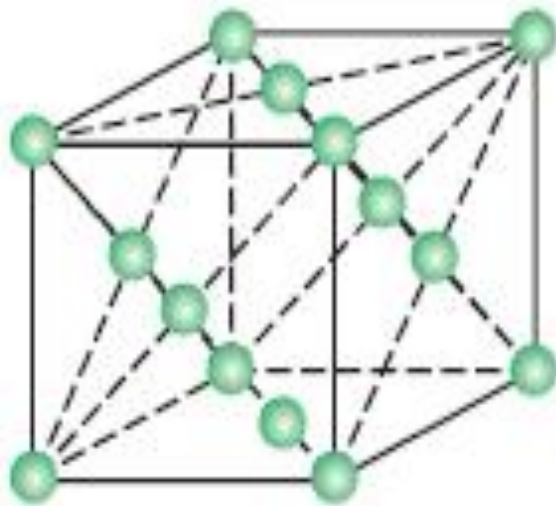=8 x   I/8 = I atom.

Body- Centred Cubic Unit Cell

(a)   (b)   (c)

Thus in a body-centered cubic (bcc) unit cell:

(i) 8 corners $\times \dfrac{1}{8}$ per corner atom $= 8 \times \dfrac{1}{8}$ = 1 atom

(ii) 1 body centre atom = 1 × 1   = 1 atom

$\therefore$ Total number of atoms per unit cell   = 2 atoms

Face- Centred Cubic Unit Cell
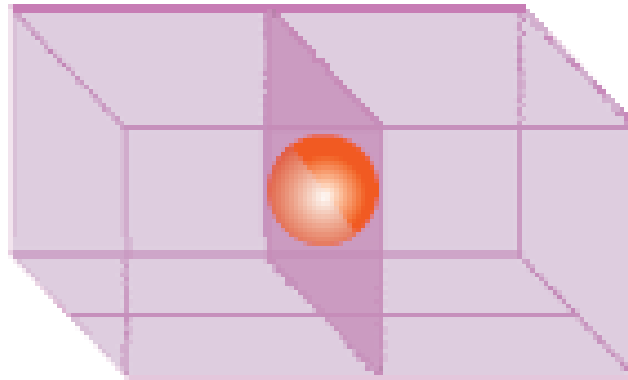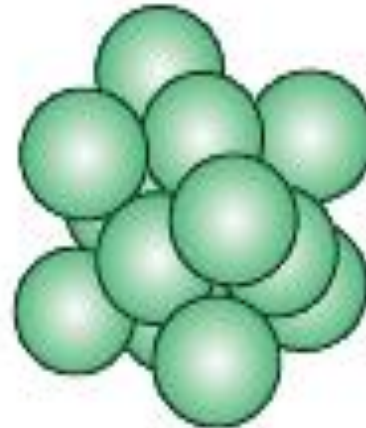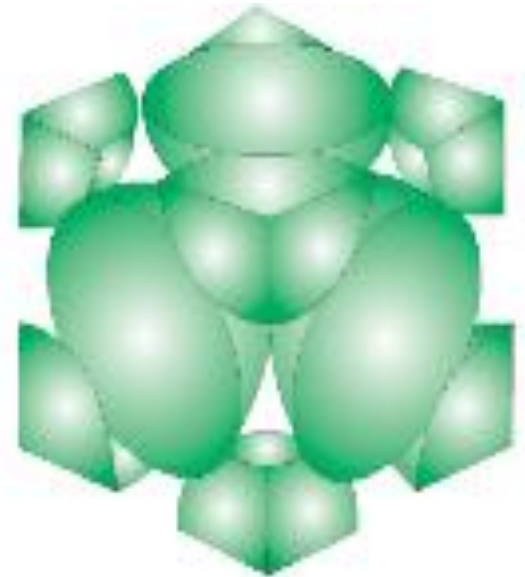

(a) (b) (c)

Face- Centred Cubic Unit Cell

- A face-centred cubic (*fcc) unit cell contains atoms at all the corners and* at the centre of all the faces of the cube.
- It can be seen in Fig that each atom located at the face-centre is shared between two adjacent unit cells and only
- Half of each atom belongs to a unit cell
- Thus, in a face-centred cubic (*fcc) unit cell:*

Face- Centred Cubic Unit Cell

- Thus, in a face-centred cubic (*fcc) unit cell:*
- Total number of atoms per unit cell is as follows

(i) 8 corners atoms $\times \dfrac{1}{8}$ atom per unit cell $= 8 \times \dfrac{1}{8}$ $= 1$ atom

(ii) 6 face-centred atoms $\times \dfrac{1}{2}$ atom per unit cell $= 6 \times \dfrac{1}{2} = 3$ atoms

$\therefore$ Total number of atoms per unit cell $= 4$ atoms

Close Packed Structures

(a) Close Packing in One Dimension

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each Other.
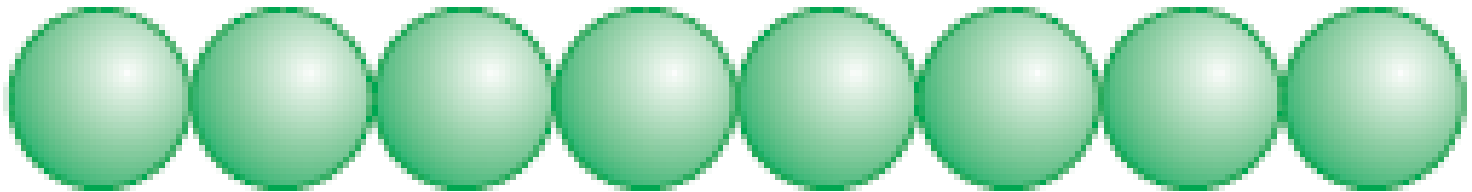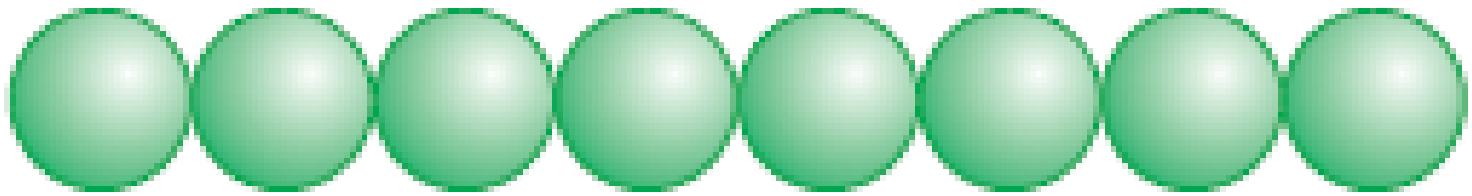
❑In this arrangement, each sphere is in contact with two of its neighbours.

❑The number of nearest neighbours of a particle is called its **coordination number.**

❑ **Thus, in one dimensional close packed** arrangement, the coordination number is **2**.

Close Packing in Two Dimensions

- *Square close packing of spheres in two dimensions*
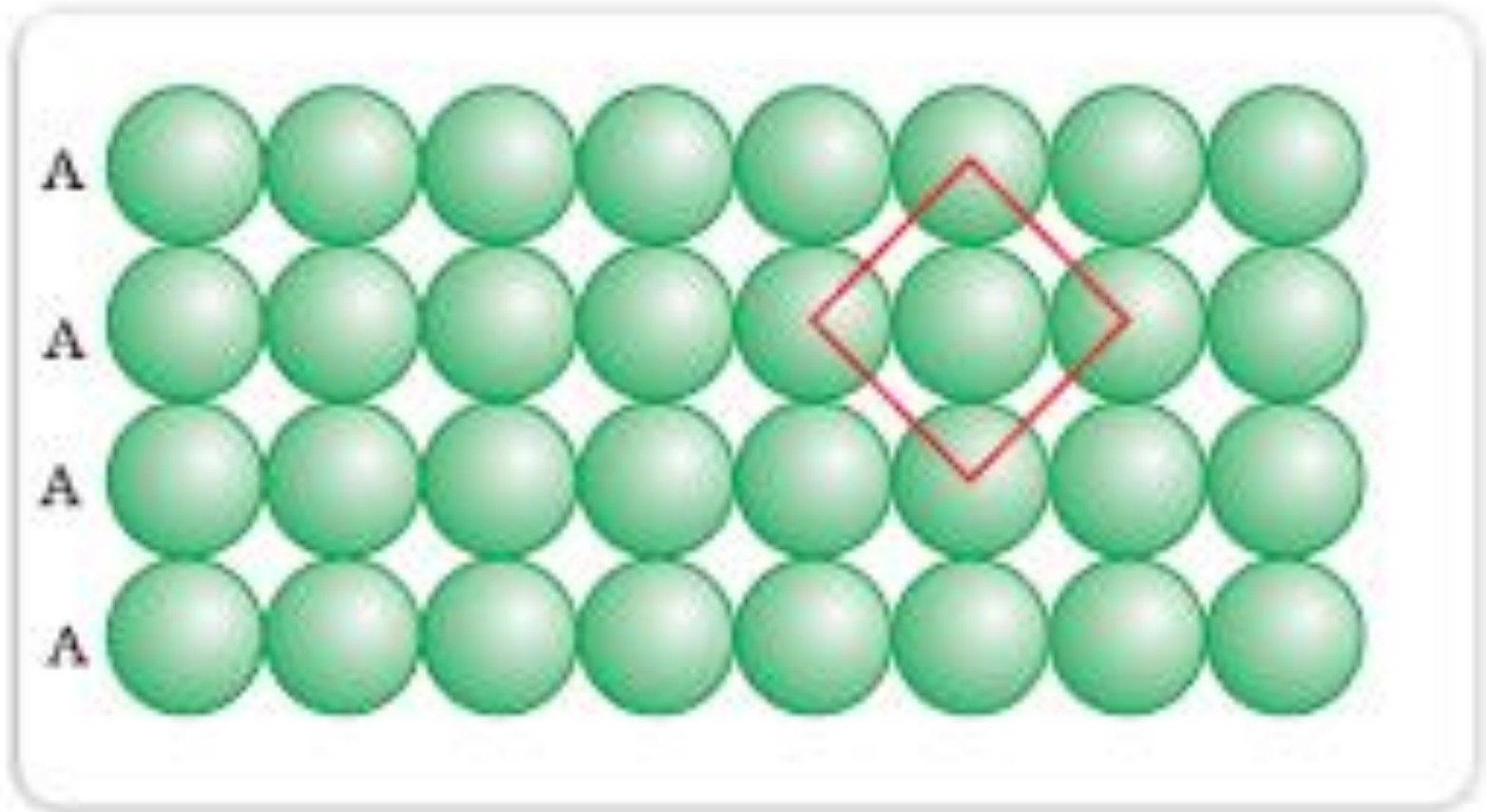
Close Packing in Two Dimensions

- *hexagonal close packing of spheres in two dimensions*
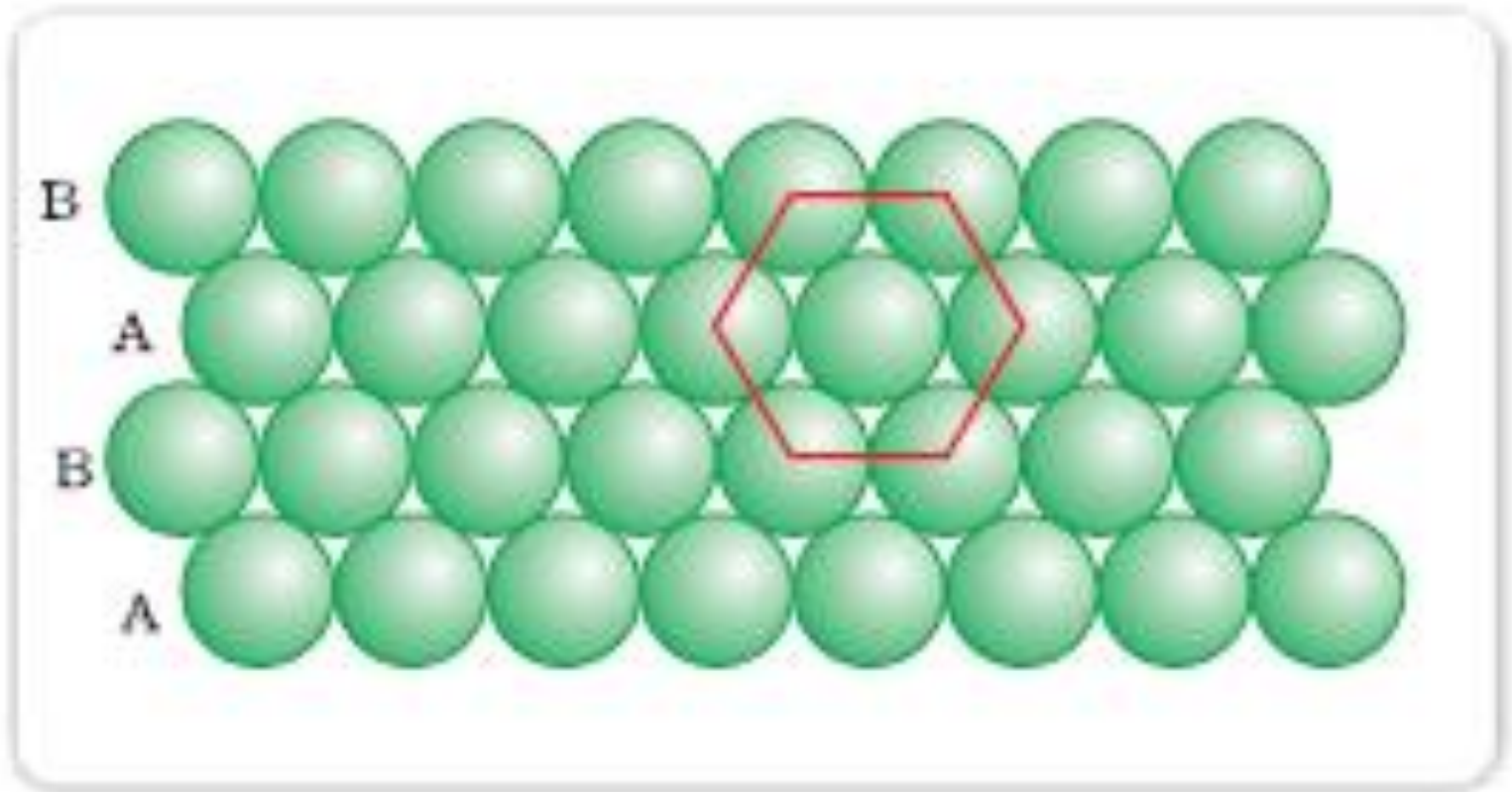
Close Packing in Three Dimensions

- *Three dimensional close packing from two dimensional square close-packed layers*
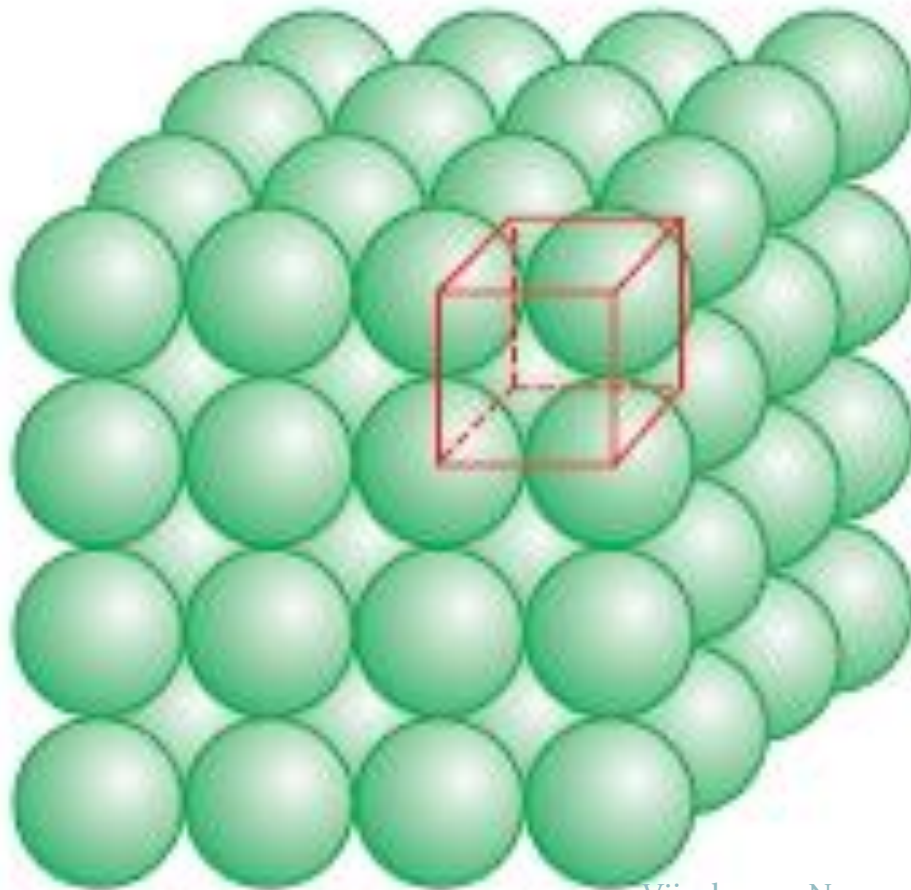
- *Three dimensional close packing from two dimensional hexagonal close packed layers:*
- Three dimensional close packed structure can be generated by placing layers one over the other.
- *(a) Placing second layer over the first layer*
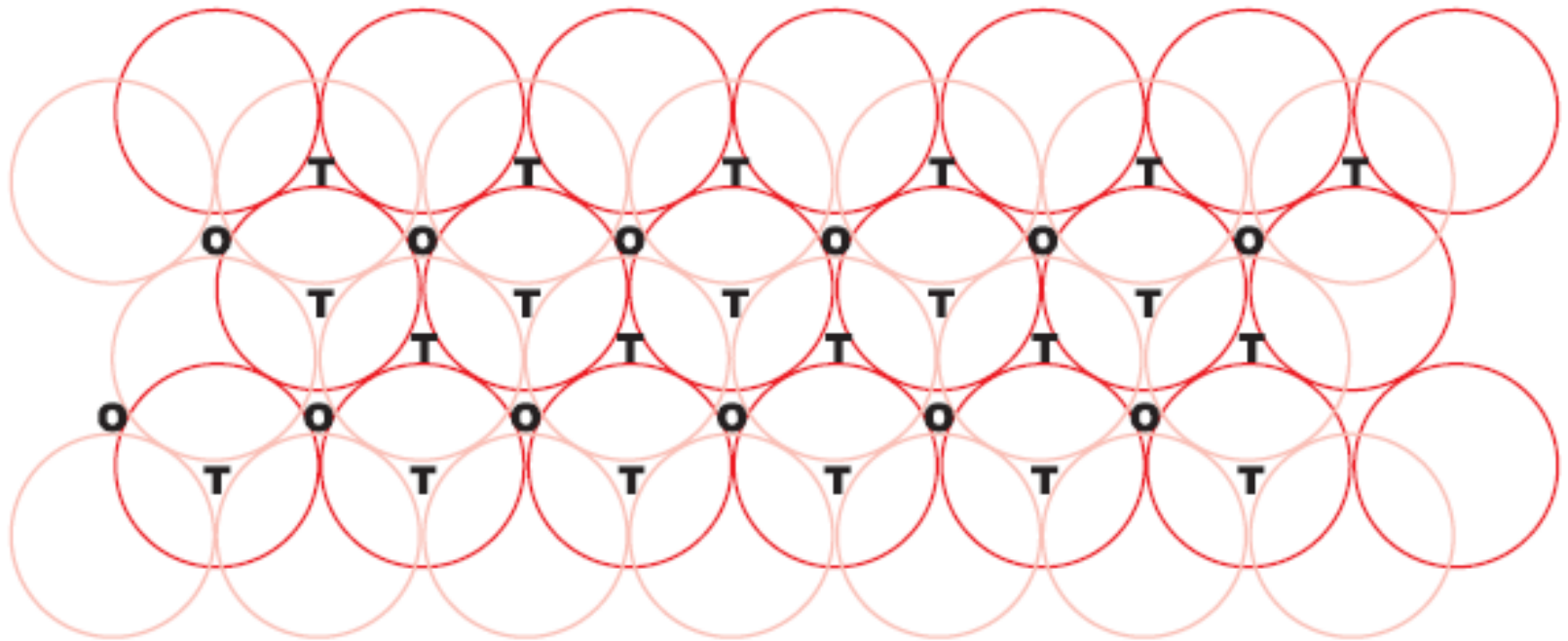
Tetrahedral voids

- Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called **tetrahedral voids because a *tetrahedron*** is formed when the centres of these four spheres are joined. They have been marked as 'T'

Tetrahedral hole

Tetrahedral hole

Tetrahedron
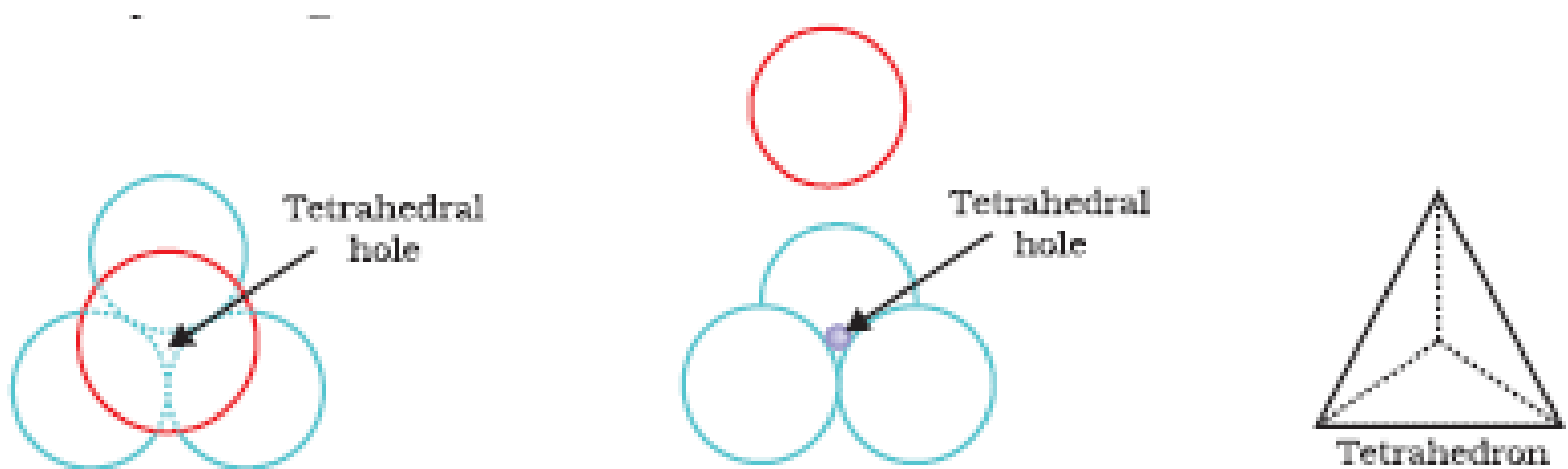
Octahedral voids

- At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards.

- These voids have been marked as 'O'

- Such voids are surrounded by six spheres and are called **octahedral voids.**

Octahedral voids

Octahedral hole

(a)
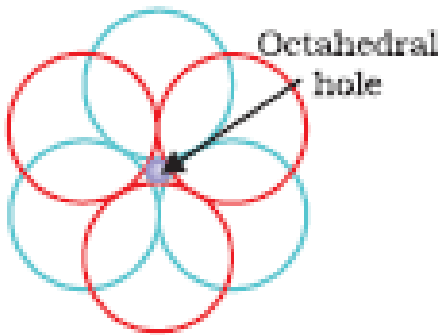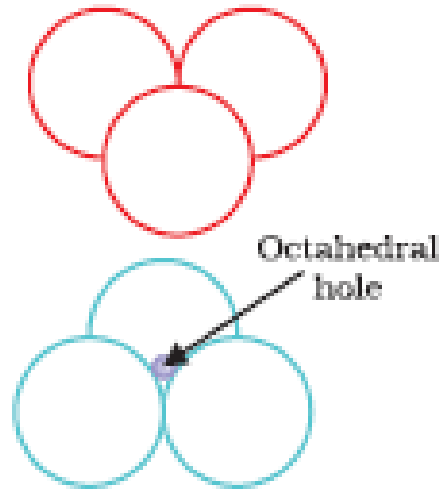
Octahedral hole

(b)
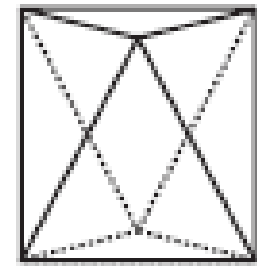
Octahedron

(c)

The number of two types of voids

- The number of these two types of voids depend upon the number of close packed spheres.

- Let the number of close packed spheres be *N, then:*

- The number of octahedral voids generated = *N*

- The number of tetrahedral voids generated = *2N*

(b) *Placing third layer over the second layer*

- When third layer is placed over the second, there are two possibilities.
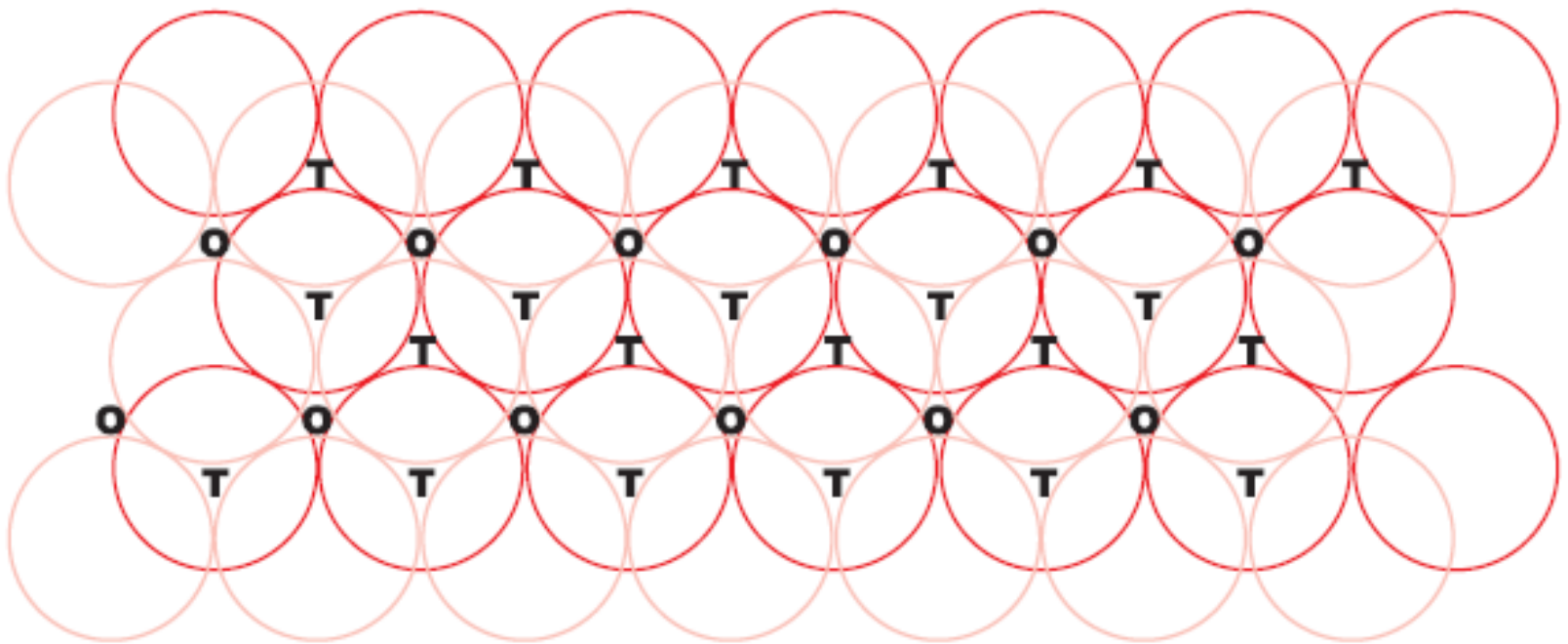
(i) *Covering Tetrahedral Voids: &* (ii) *Covering Octahedral Voids:*

(i) *Covering Tetrahedral Voids:*

- Tetrahedral voids of the second layer may be covered by the spheres of the third layer.

- In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers.

- This pattern is often written as ABAB ……. pattern.

- This structure is called hexagonal close packed (*hcp) structure*

- *This* sort of arrangement of atoms is found in many metals like magnesium and zinc.

Hexagonal close packed (*hcp) structure*
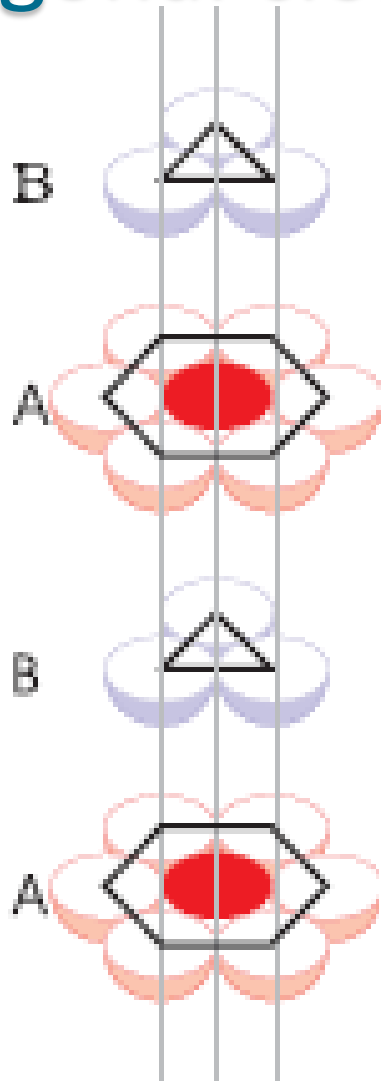
Hexagonal packing
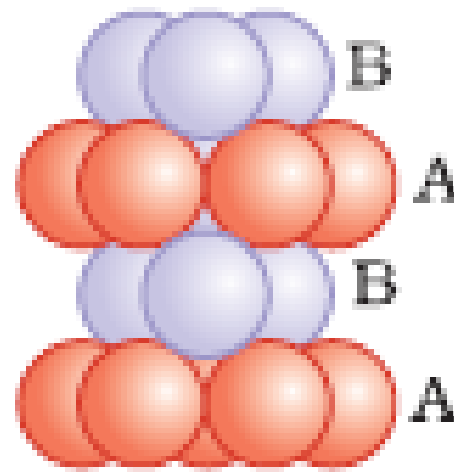
Hexagonal
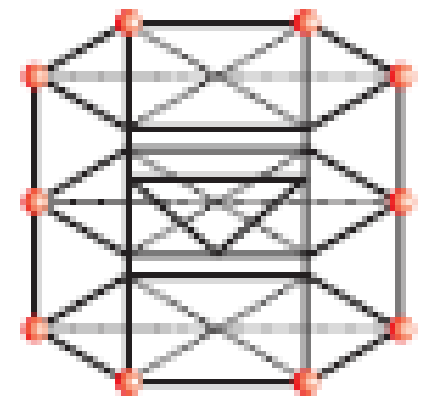
hcp

(ii) *Covering Octahedral Voids:*

- The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer.

- This arrangement is called "C' type. Only when fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs.

- This pattern of layers is often written as **ABCABC** ....

- This structure is called cubic close packed (*ccp)* or *face-centred cubic (fcc) structure*.

- *Metals* such as copper and silver crystallise in this structure.

cubic close packed (*ccp*) or *face-centred cubic (fcc) structure.*

Cubic close packing

cubic

fcc
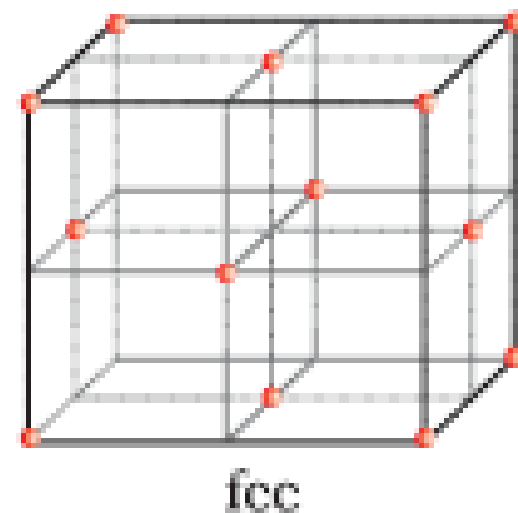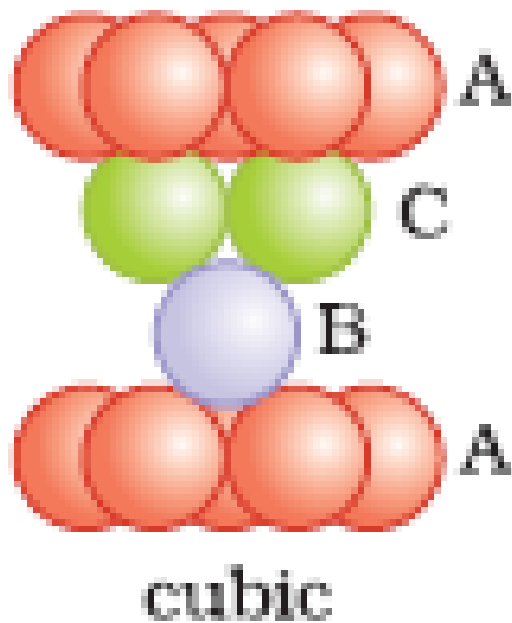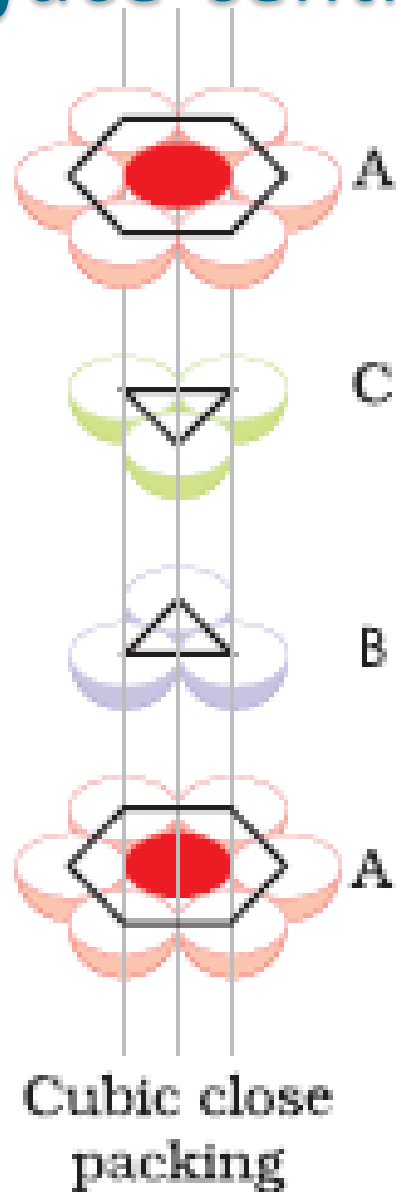
cubic close packed (*ccp*) or face-centred cubic *(fcc)* structure.
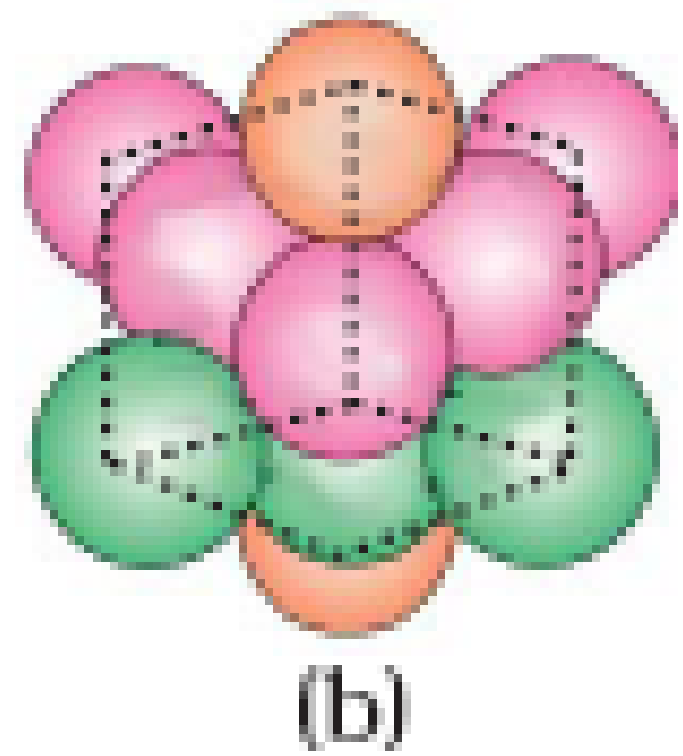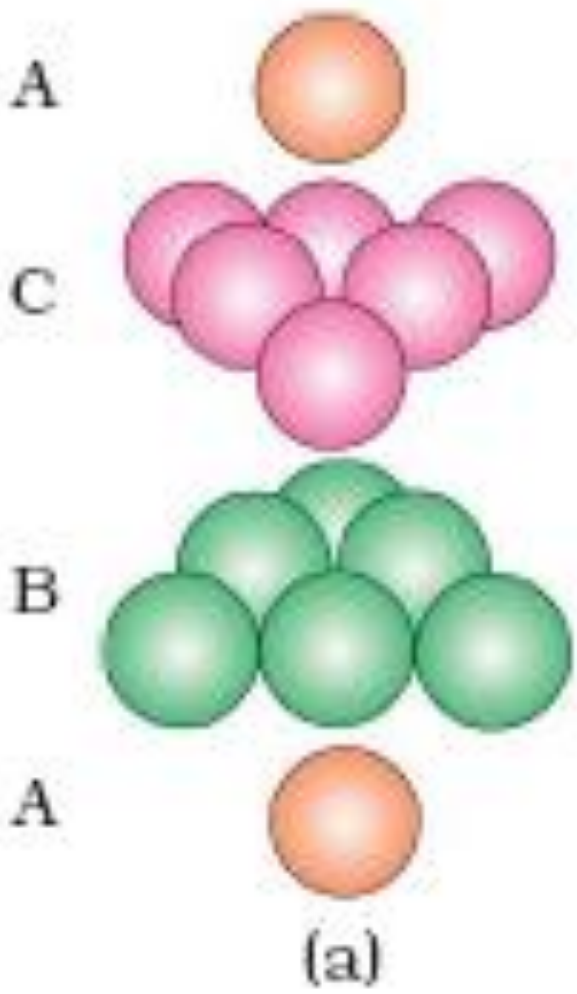
(hcp) & (ccp) or (fcc) structure.

- Both these types of close packing are highly efficient and 74% space in the crystal is filled.

- In either of them, each sphere is in contact with twelve spheres.

- Thus, the coordination number is 12 in either of these two structures.

Formula of a Compound and Number of Voids Filled

Packing Efficiency

- **Packing Efficiency in *hcp and ccp* Structures**

  let the unit cell edge length be 'a' and face diagonal
  AC = b.
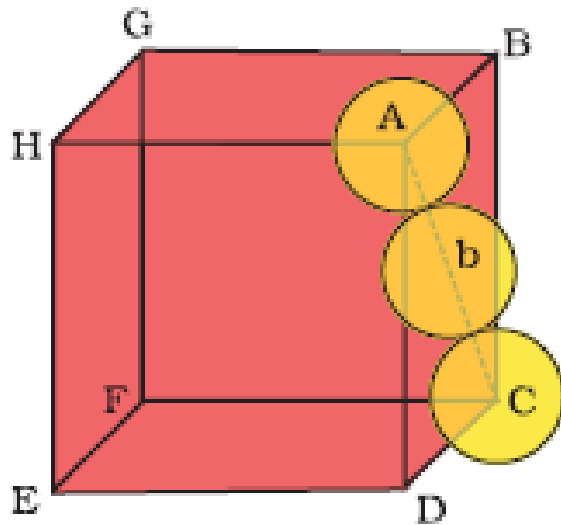
In $\triangle$ ABC

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

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

$b = \sqrt{2}a$

If r is the radius of the sphere, we find

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

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

(we can also write, $r = \dfrac{a}{2\sqrt{2}}$)

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $\left(2\sqrt{2}r\right)^3$.

Therefore,

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

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

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

Therefore Packing Efficiency in *hcp and ccp* Structures= 74%

- **Efficiency of Packing in Body- Centred Cubic Structures**

Therefore Packing Efficiency in Body- Centred Cubic Structures **= 68%**

From Fig. 1.21, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

In Δ EFD,

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

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

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

Therefore, $\sqrt{3}a = 4r$

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

Also we can write, $r = \dfrac{\sqrt{3}}{4}a$
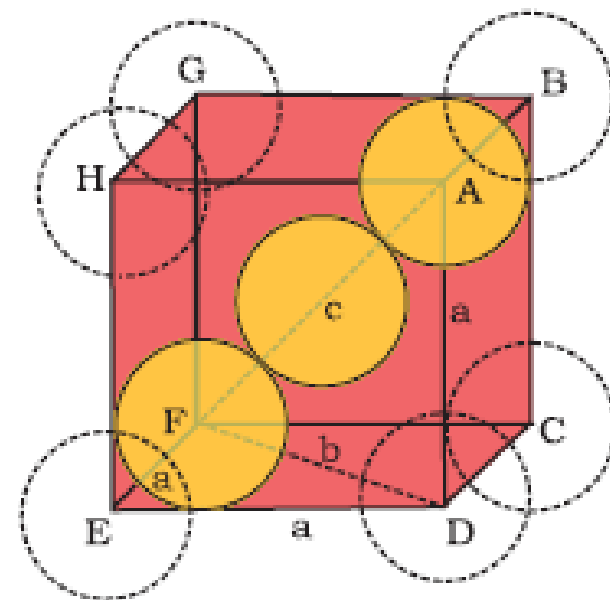
In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\dfrac{4}{3}\right)\pi r^3$.

Volume of the cube, a^3 will be equal to $\left(\dfrac{4}{\sqrt{3}}r\right)^3$ or $a^3 = \left(\dfrac{4}{\sqrt{3}}r\right)^3$.
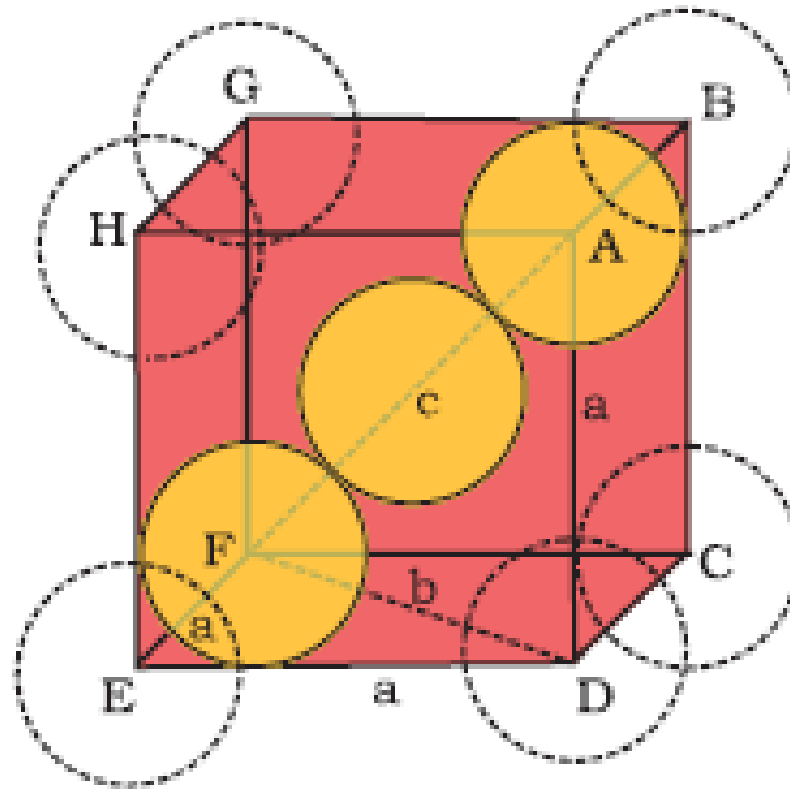
Therefore,

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

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

$$= \frac{(8/3)\pi r^3 \times 100}{64/(3\sqrt{3})r^3}\% = 68\%$$
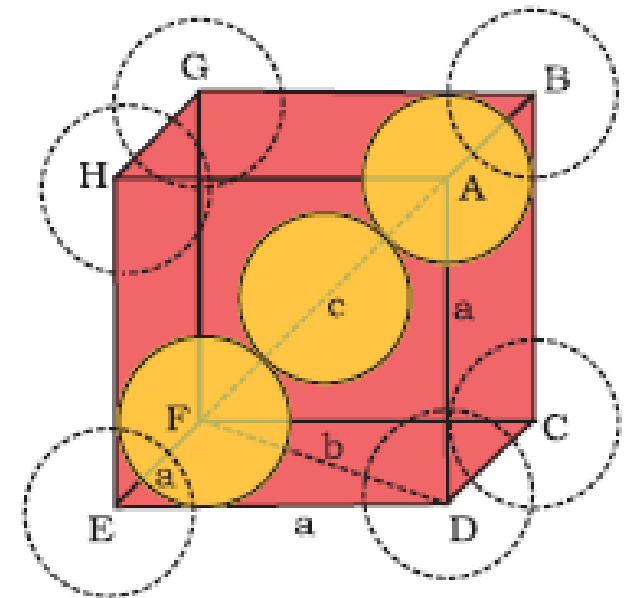
Packing Efficiency in Simple Cubic Lattice
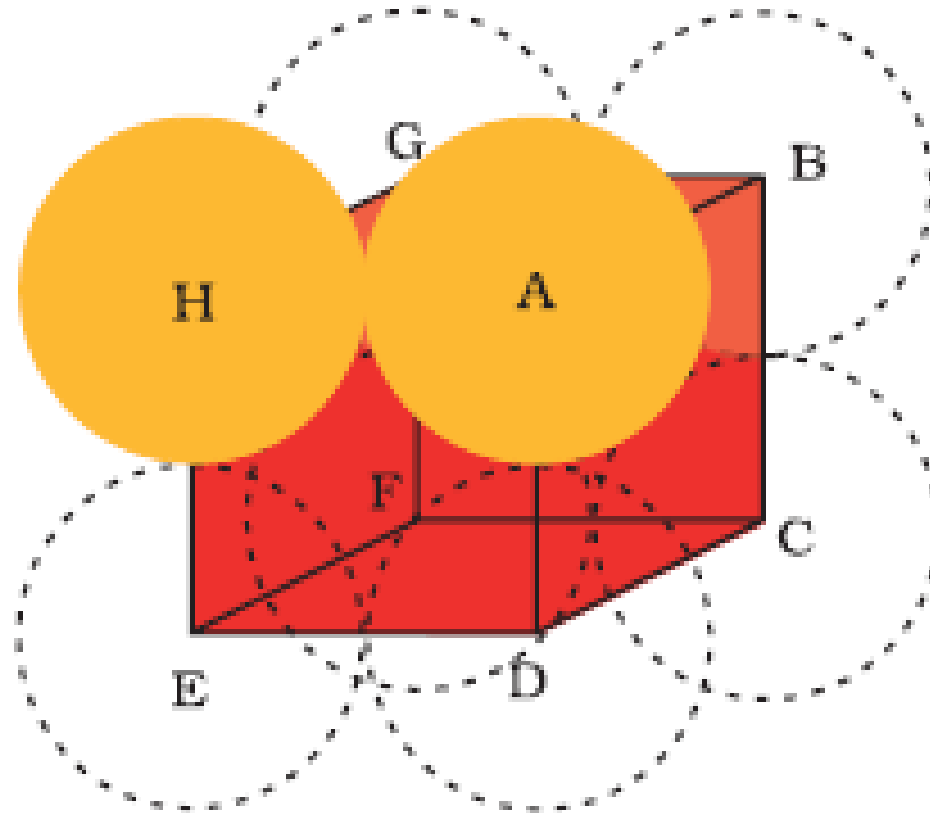
• **Packing Efficiency in Simple Cubic Lattice**

In a simple cubic lattice the atoms are located only on the corners of the cube.

The particles touch each other along the edge.

Thus, the edge length or side of the cube '**a**', and the

radius of each particle, **r** are related as

$$a = 2r$$

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

Since a simple cubic unit cell contains only 1 atom

The volume of the occupied space $= \dfrac{4}{3}\pi r^3$

$\therefore$ Packing efficiency

$$= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% = 52.4\%$$

Thus, we may conclude that *ccp* and *hcp* structures have maximum packing efficiency.

Therefore Packing Efficiency in Simple Cubic Structures = 52.4%

Calculations Involving Unit Cell Dimensions

- From the unit cell dimensions, it is possible to calculate the volume of the unit cell.

- Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell.

- The determination of the mass of a single atom gives an accurate method of determination of Avogadro constant. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is *a, d the density of the solid substance and M the* molar mass. In case of cubic crystal:

Volume of a unit cell = a^3

Mass of the unit cell

= number of atoms in unit cell × mass of each atom = $z \times m$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \text{ (M is molar mass)}$$

Therefore, density of the unit cell

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

$$= \frac{z.m}{a^3} = \frac{z.M}{a^3.N_A} \quad or \quad d = \frac{zM}{a^3 N_A}$$

The density of the solid can always be determined by other methods.
Out of the five parameters **(d, z M, a and NA),** *if any* four are known, we can determine the fifth.

Imperfections in Solids or defects

- The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, *point defects and line defects.*

- ***Point defects*** *are the irregularities or* deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the ***line defects*** *are the irregularities or* deviations from ideal arrangement in entire rows of lattice points.

- These irregularities are called ***crystal defects***.

Types of Point Defects

Point defects can be classified into three types :

- (i) stoichiometric defects
- (ii) impurity defects and
- (iii) non-stoichiometric defects.

Stoichiometric Defects

- These are the point defects that do not disturb the stoichiometry of the solid.

- They are also called *intrinsic or* ***thermodynamic defects.***

- Basically these are of two types,

- **vacancy defects** and

- **interstitial defects**.

(i) *Vacancy Defect:*

- When some of the lattice sites are vacant, the crystal is said to have **vacancy defect** .

- **This results in** decrease in density of the substance. This defect can also develop when a substance is heated.
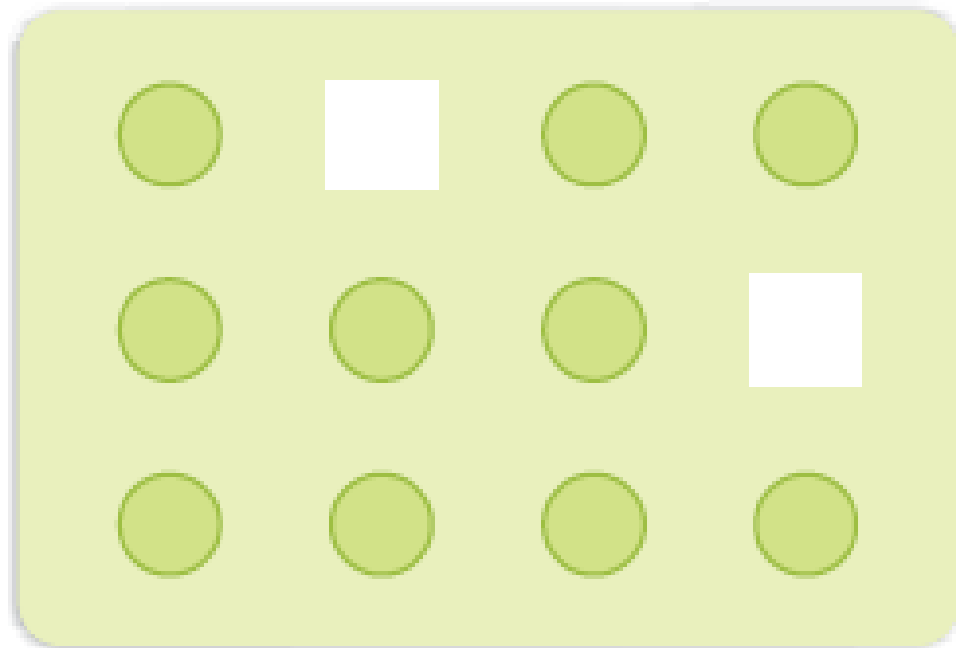
Fig. 1.23: Vacancy defects

(ii) *Interstitial Defect:*

- When some constituent particles (atoms or molecules) occupy an **interstitial site,** the crystal is said to have **interstitial defect**
- This defect increases the density of the substance.
- Vacancy and interstitial defects as explained above can be shown by non-ionic solids.
- Ionic solids must always maintain electrical neutrality.
- Rather than simple vacancy or interstitial defects, they show these defects as
- **Frenkel and Schottky defects.**

(iii) *Frenkel Defect:*
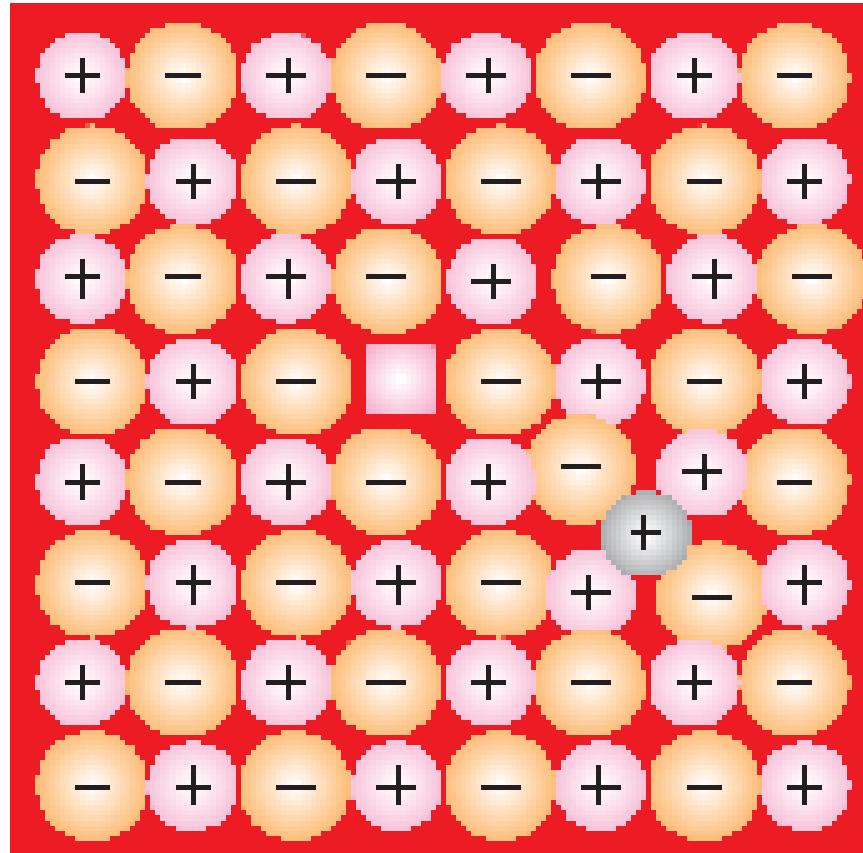
Fig. 1.25: Frenkel defects

(iii) *Frenkel Defect:*

- *This* defect is shown by ionic solids.
- The smaller ion (usually cation) is dislocated from its normal site to an interstitial site.
- It creates a *vacancy defect at its* original site and an **interstitial defect at its** new location. Frenkel defect is also called **dislocation defect.**
- It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.

Schottky Defect:
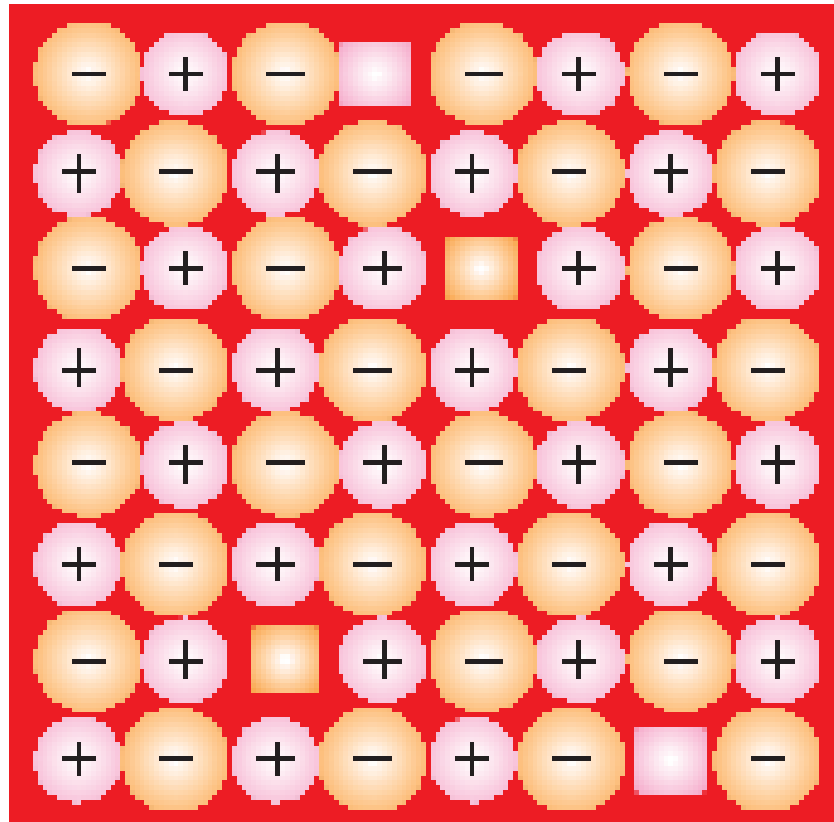
Fig. 1.26: Schottky defects

Schottky Defect:

- It is basically a vacancy defect in ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal (Like simple vacancy defect, Schottky defect also decreases the density of the substance).
- Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm³ at room temperature. In 1 cm³ there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions.
- Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr.
- It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

(b) Impurity Defects
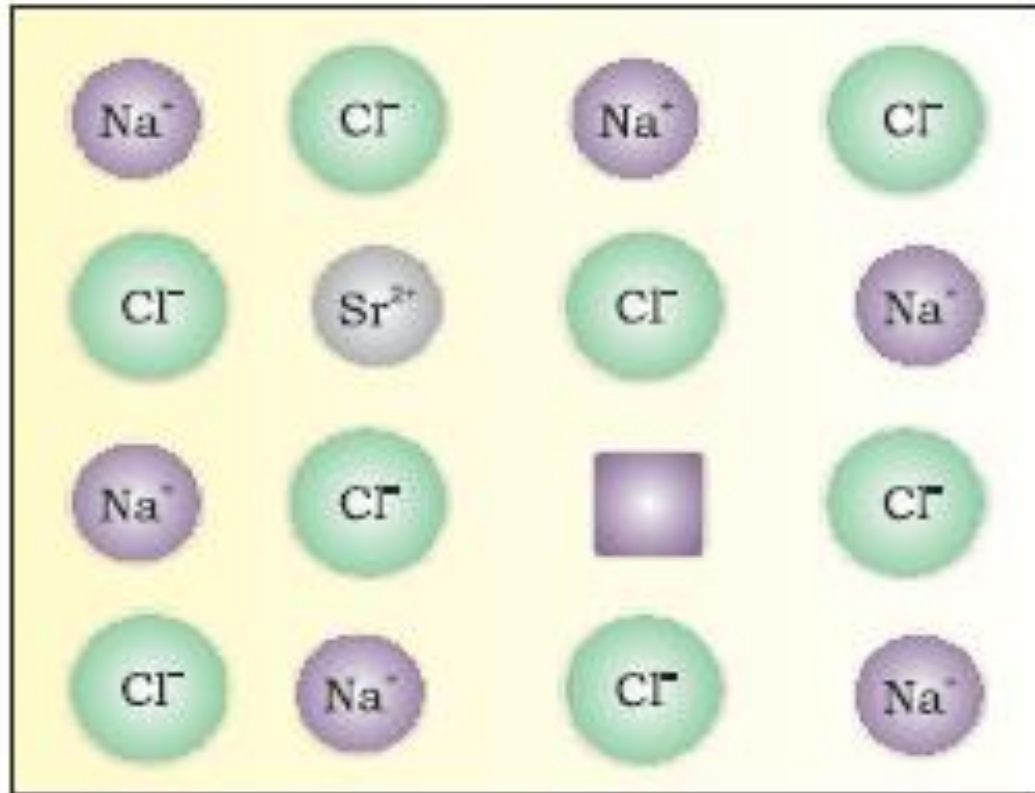
Fig. 1.27: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

- 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 in number to that of Sr^{2+} ions.

- Another similar example is the solid solution of $CdCl_2$ and $AgCl$.

(c) Non-Stoichiometric Defects

These defects are of two types:

 (i) metal excess defect and

 (ii) metal deficiency defect.

- **(i) *Metal Excess Defect***

- *Metal excess defect due to anionic vacancies*:

- *Alkali halides* like NaCl and KCl show this type of defect.

F-centre
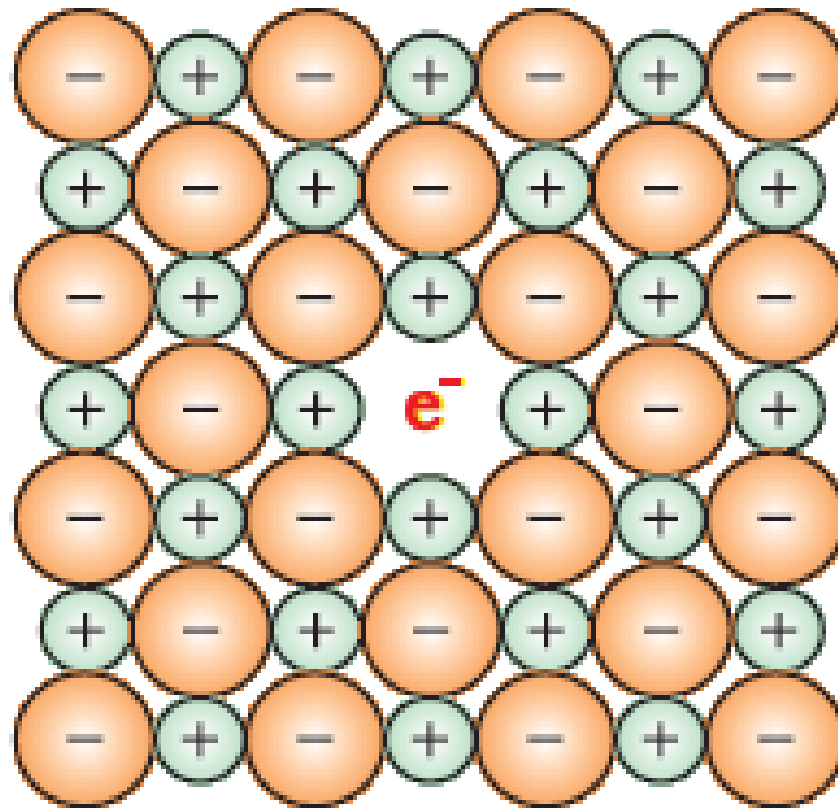
Fig. 1.28: An F-centre in a crystal

- 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 to the surface of the crystal and combine with Na atoms to give NaCl.

- This happens by loss of electron by sodium atoms to form Na+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.28).

- As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres (from the German* word *Farbenzenter for colour centre).*

- *They impart yellow* colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

- Similarly, excess of lithium makes **LiCl** crystals pink and excess of **potassium** makes KCl crystals violet (or lilac).

- *Metal excess defect* *due to the presence of extra cations at interstitial sites*:
- Zinc oxide is white in colour at room temperature.
- On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
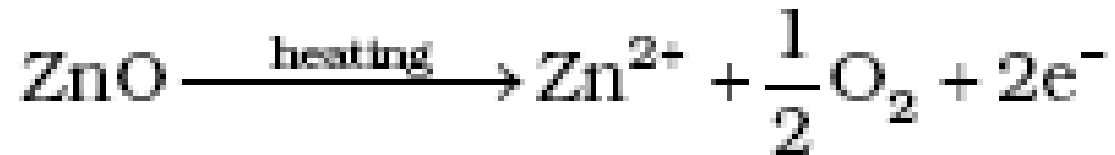
Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) *Metal Deficiency Defect*

- There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion.

- A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$.

- It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO

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

Electrical Properties

- Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}.

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

- (i) *Conductors: The solids with conductivities ranging between 10^4 to 10^7 ohm^{-1}m^{-1} are called conductors. Metals have conductivities in the order of 10^7 ohm^{-1}m^{-1} are good conductors.*

- (ii) *Insulators : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.*

- (iii) *Semiconductors : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm^{-1}m^{-1}.*

Conduction of Electricity in Metals
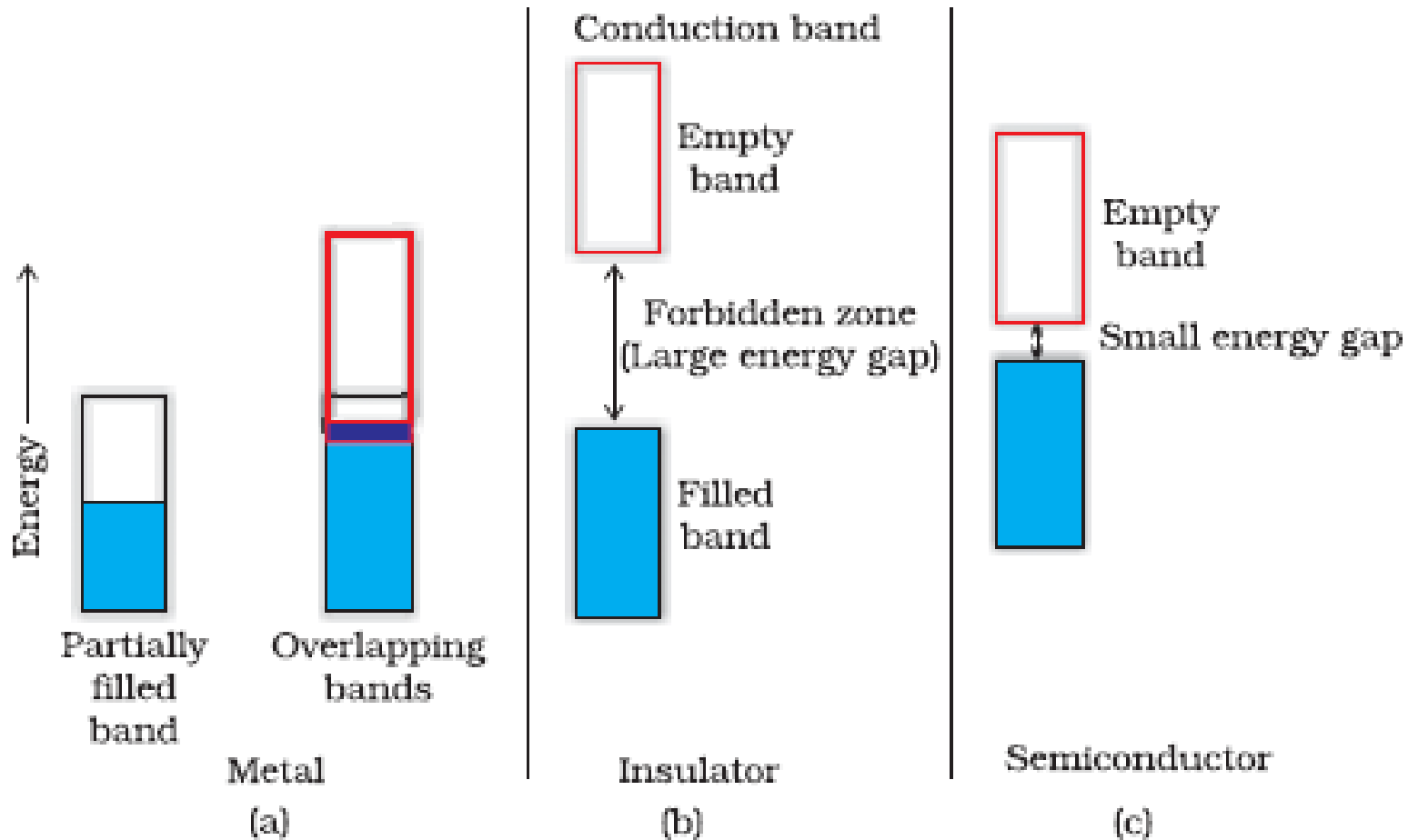
Conduction of Electricity in Metals

- A conductor may conduct electricity through movement of electrons or ions.
- Metallic conductors belong to the former category and electrolytes to the latter.
- Metals conduct electricity in solid as well as molten state.
- The conductivity of metals depend upon the number of valence electrons available per atom.

Conduction of Electricity in Metals

- The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band.**

- If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows **conductivity**

- If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an **insulator.**

Semiconductors

- In case of semiconductors, the gap between the valence band and conduction band is small.
- Therefore, some electrons may jump to conduction band and show some conductivity.
- Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.
- Substances like silicon and germanium show this type of behaviour and are called *intrinsic semiconductors.*

Doping

- The conductivity of these intrinsic semiconductors is too low to be of practical use.
- Their conductivity is increased by adding an appropriate amount of suitable impurity.
- This process is called *doping*.
- *Doping can be done with an impurity which is electron rich* or electron deficient as compared to the intrinsic semiconductor silicon or germanium.
- Such impurities introduce *electronic defects* in them.

(a) Electron – rich impurities

- Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours

- When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal .Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms.

- The fifth electron is extra and becomes delocalised.

- These delocalised electrons increase the conductivity of doped silicon (or germanium).

- Here the increase in conductivity is due to the *negatively charged electron, hence silicon doped with electron-rich* impurity is called *n-type semiconductor.*

(b) Electron – deficit impurities

- Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called *electron hole or electron vacancy.*

- *An electron from a* neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If ithappens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it.

- Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate.

- This type of semi conductors are called *p-type semiconductors.*
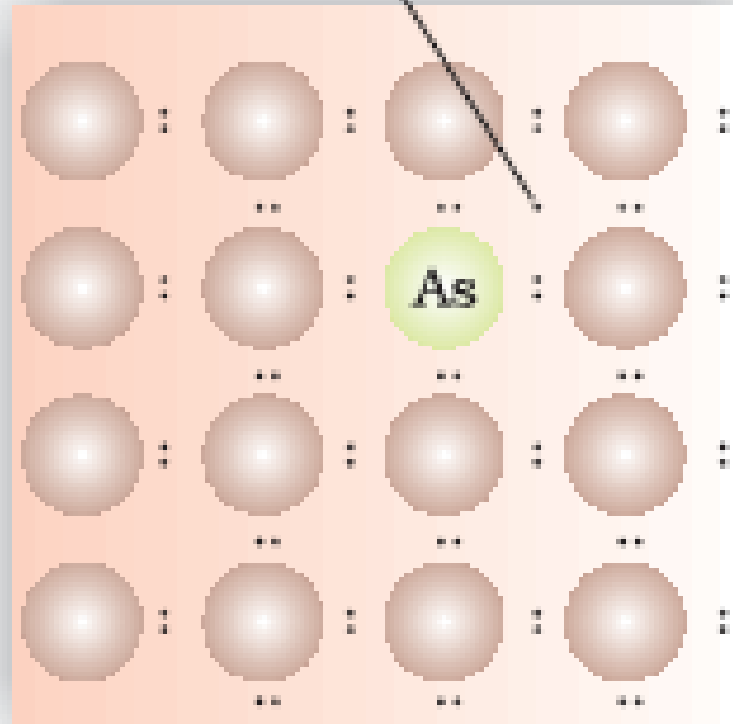
Prfect Crystal
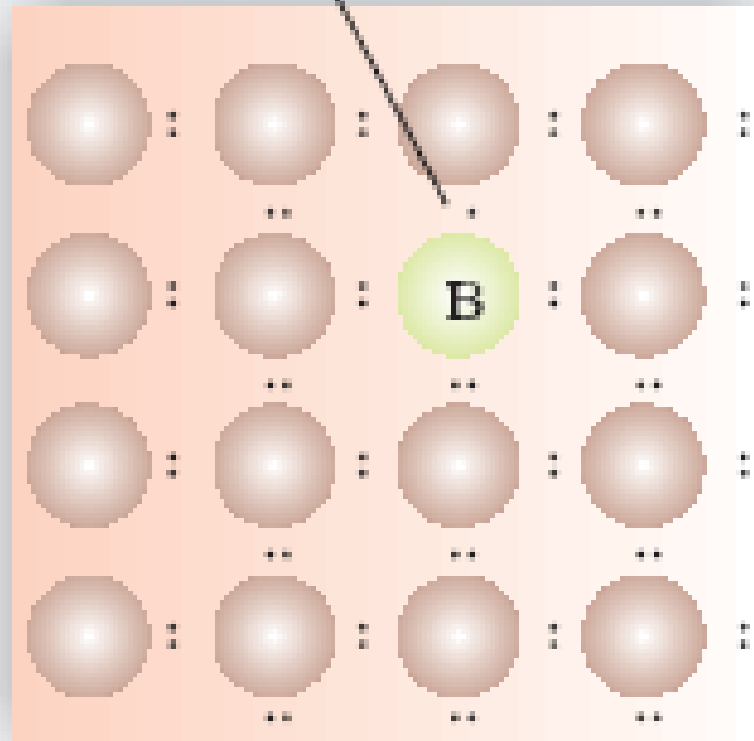
Silicon atom
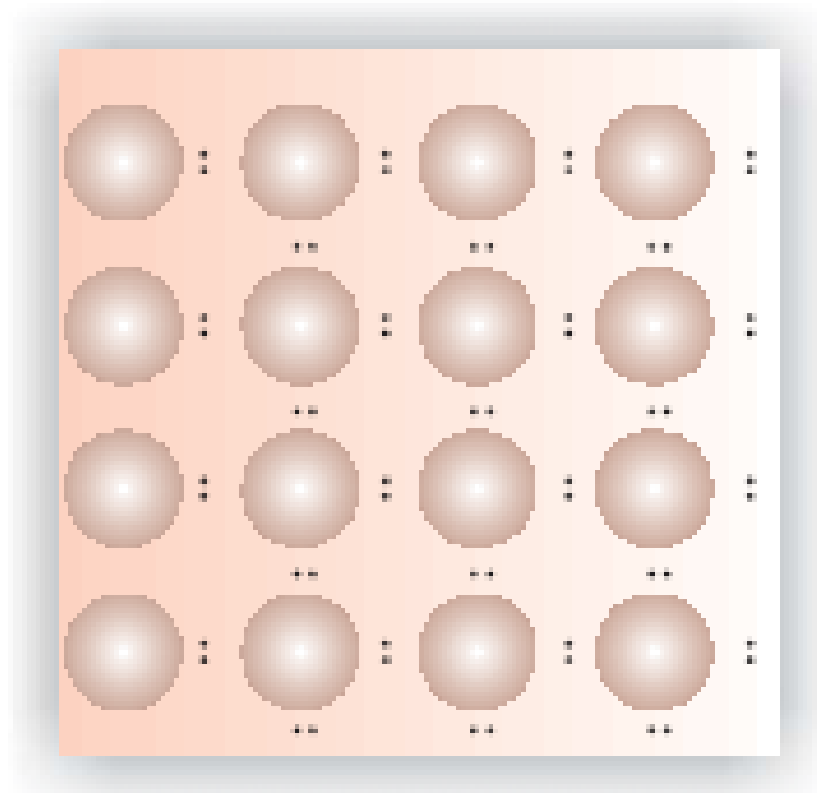
Perfect crystal

n-type semiconductor

Mobile electron

As

n-type

p-type semiconductors.

Positive hole
(no electron)

B

p-type

Applications of *n-type and p-type semiconductors*

- Various combinations of *n-type and p-type semiconductors are used* for making electronic components.

- *Diode* *is a combination of n-type* and *p-type semiconductors and is used as a rectifier.*

- *Transistors* *are* made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor.

- *npn* *and* *pnp* *type of* transistors are used to detect or amplify radio or audio signals.

- The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Magnetic Properties

- Every substance has some magnetic properties associated with it.
- The origin of these properties lies in the electrons.
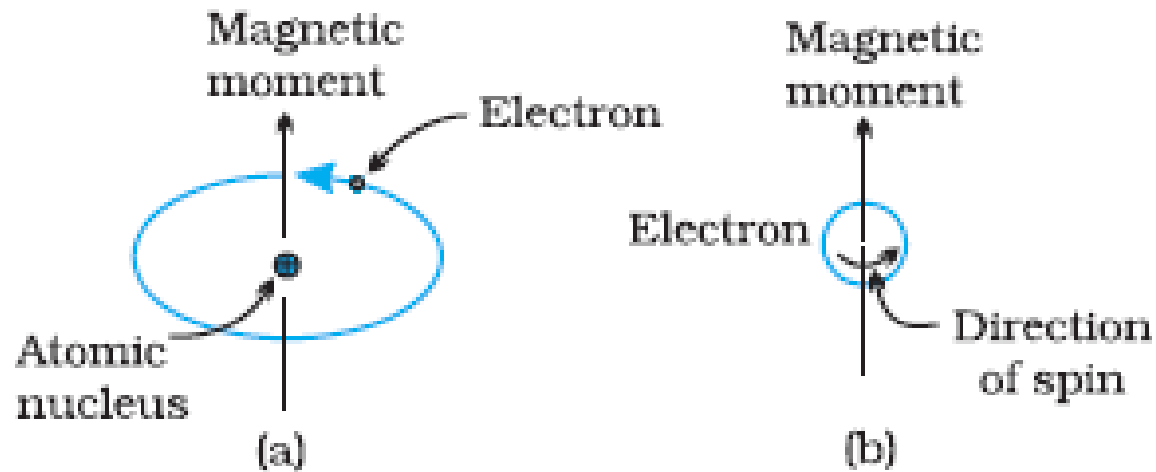- Each electron in an atom behaves like a tiny magnet.

Fig.1.31: Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.

Classification of magnetic properties

On the basis of their magnetic properties, substances can be classified into five categories:

- (i) paramagnetic
- (ii) diamagnetic
- (iii)ferromagnetic
- (iv) antiferromagnetic and
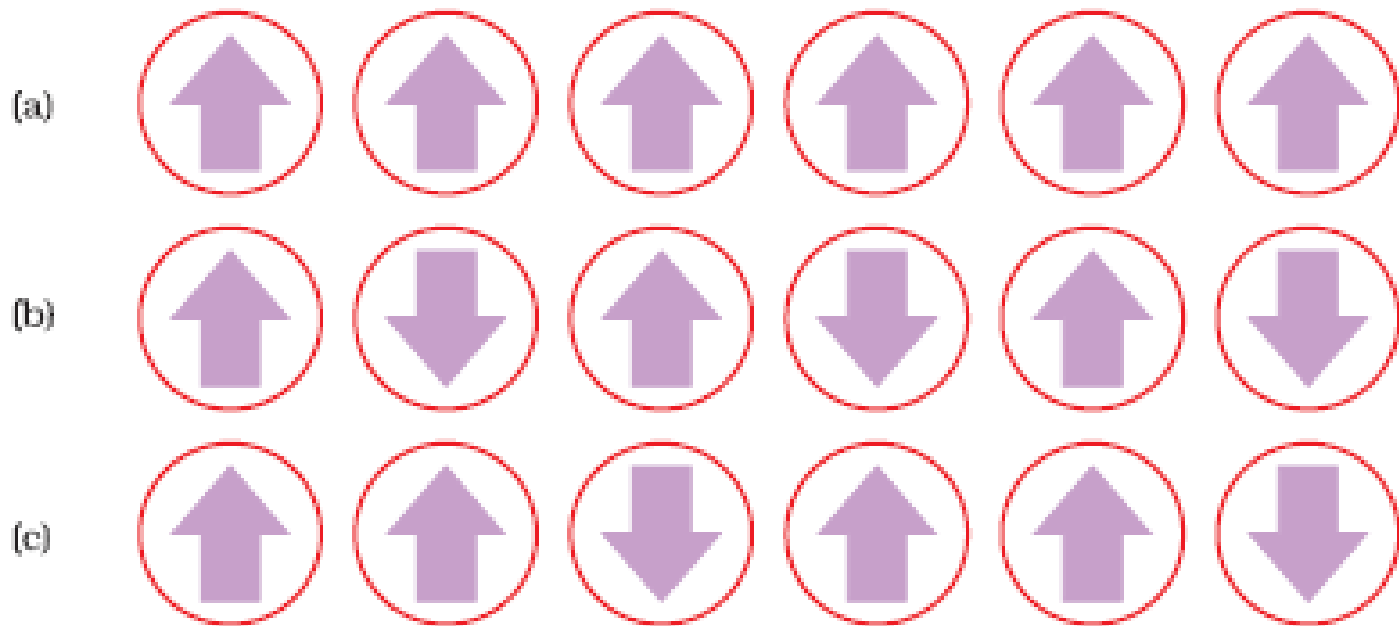- (v) ferrimagnetic.

Magnetic moments

Fig 1.32: Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.

THANK YOU