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Syllabus

CENTRAL BOARD OF SECONDARY EDUCATION,
NEW DELHI

CHEMISTRY (Theory)

CLASS-XII

Total Periods (Theory 160+ Practical 60)

One paper

Time: 3 hours

70 marks

Unit	Title	No. of Periods	Marks
I	Solid State	10	} 10
II	Solutions	10	
III	Electrochemistry	12	(23)
IV	Chemical Kinetics	10	
V	Surface Chemistry	08	
VI	General Principles and Processes of Isolation of Elements	08	} 34
VII	<i>p</i> -Block Elements	12	(19)
VIII	<i>d</i> - and <i>f</i> -Block Elements	12	
IX	Coordination Compounds	12	
X	Haloalkanes and Haloarenes	10	
XI	Alcohols, Phenols and Ethers	10	
XII	Aldehydes, Ketones and Carboxylic Acids	10	
XIII	Organic Compounds containing Nitrogen	10	} 28
XIV	Biomolecules	12	
XV	Polymers	08	
XVI	Chemistry in Everyday Life	06	} 16
Total		160	70

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THE SOLID STATE

BASIC CONCEPTS



The particles in solid are closely packed and held together by strong intermolecular forces. The building constituents have fixed positions and can only oscillate about their mean positions. They have definite shape and definite volume. The density of solids is high and they have low compressibility.

1. Classes of Solids: Two types of solids are known:

(i) Amorphous solids, (ii) Crystalline solids.

(i) **Amorphous solids:** In amorphous solids, the arrangement of building constituents is not regular but haphazard. They may have a short range order. Their melting points are not sharp. They are isotropic in nature i.e., their properties such as mechanical strength, electrical conductivity, etc. are same in all directions. Examples: rubber, quartz glass, etc.

(ii) **Crystalline solids:** In crystalline solids, the arrangement of building constituents is regular throughout the entire three-dimensional network. A crystalline solid has sharp melting point and is anisotropic in nature i.e., some of their physical properties such as electrical resistance or refractive index show different values when measured along different directions in the same crystal. It has a definite geometrical shape with flat faces and sharp edges. Examples: sodium chloride, quartz, etc.

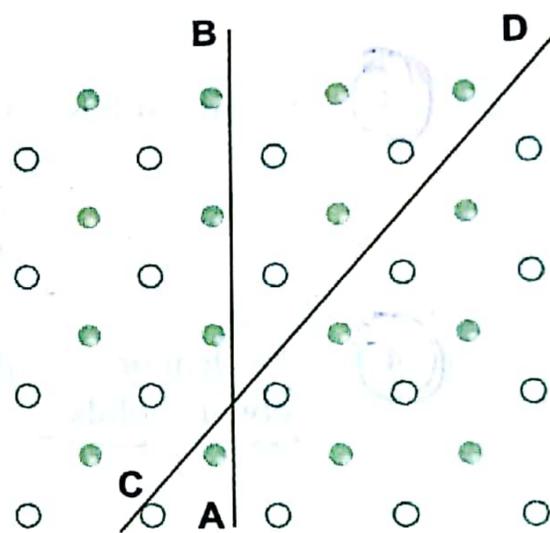


Fig. 1.1: Anisotropic behaviour of crystal

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline Solids	Amorphous Solids
Shape	Definite characteristics and 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 a definite heat of fusion.
Isotropy	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.

Table 1.2. Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	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
		Dipole-dipole interactions	HCl, SO ₂	Soft	Insulator	Low
		Hydrogen bonding	H ₂ O (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,	Hard	Insulators	Very high
			C (graphite)	Soft	Conductor (exception)	

2. Space Lattice and Unit Cell

Space Lattice: It is the three-dimensional arrangement of identical points in the space which represent how the constituent particles (atoms, ions, molecules) are arranged in a crystal. Each particle is depicted as a point.

Unit Cell: A unit cell is the smallest portion of a space lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by six parameters, i.e., axial angles α , β and γ and axial lengths a , b and c . Thus, unit cell of a crystal possesses all the structural properties of a given crystal.

3. Crystal Systems: On the basis of the axial distances and the axial angles between the edges, the various crystals can be divided into seven systems. These are listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu, KCl, Diamond
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO ₂ , TiO ₂ , CaSO ₄

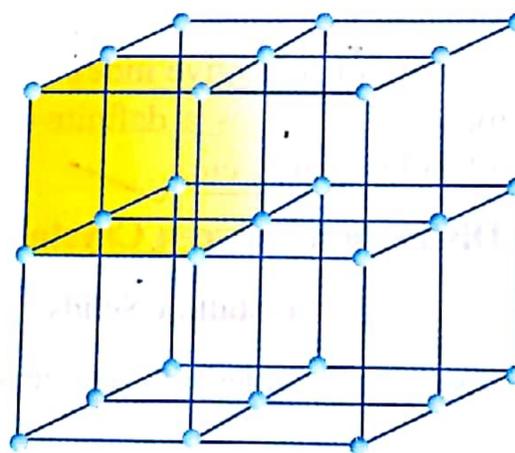


Fig. 1.2: A portion of a three dimensional cubic lattice and its unit cell

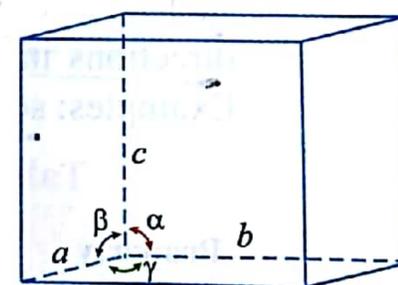
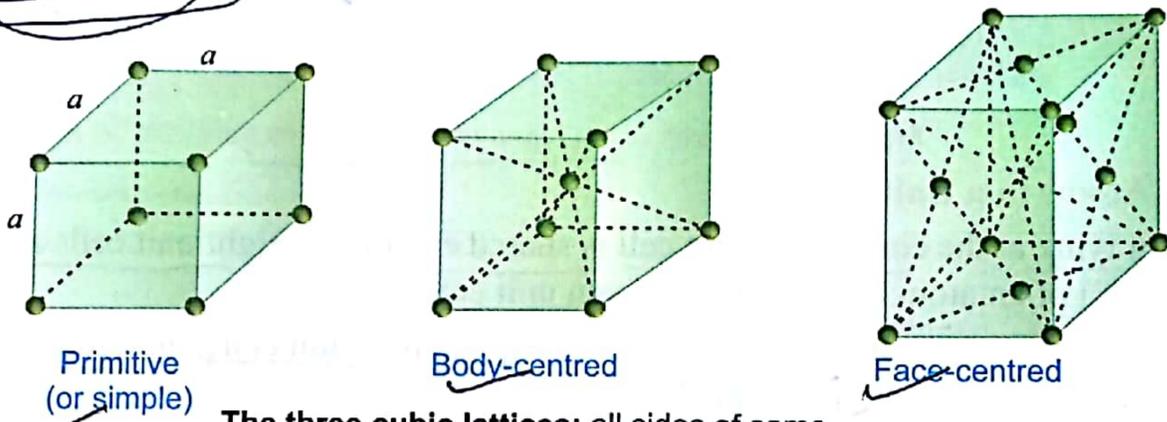


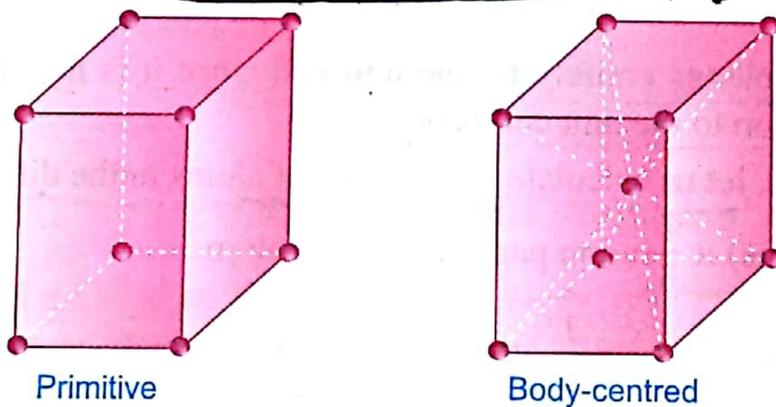
Fig. 1.3: Illustration of parameters of a unit cell

Orthorhombic or Rhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Graphite, ZnO , CdS , Mg , Zn
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3) HgS (cinnabar), ICl , As , Sb , Bi
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Monoclinic sulphur, PbCrO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3

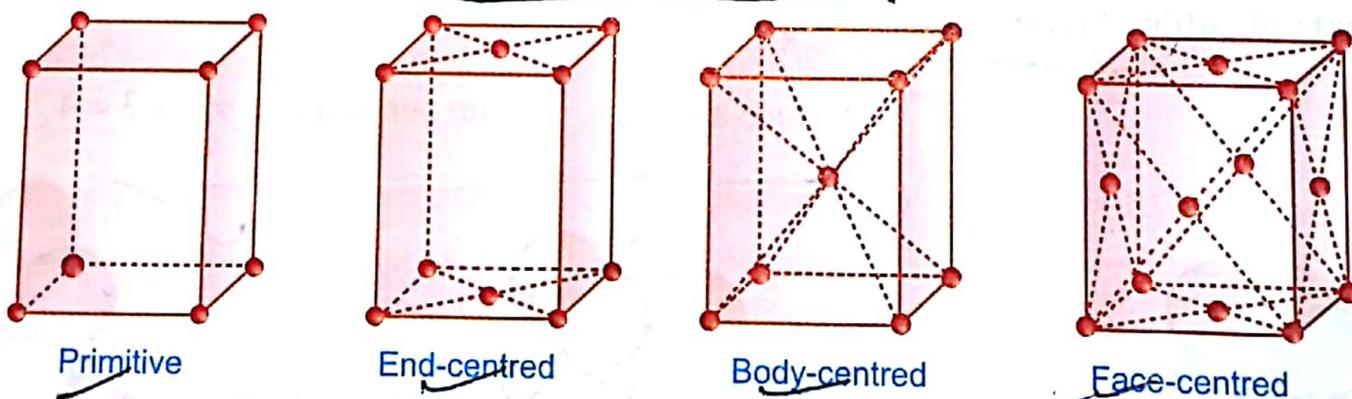
There can be 14 different ways in which similar points can be arranged in a three-dimensional space. These are called Bravais lattices.



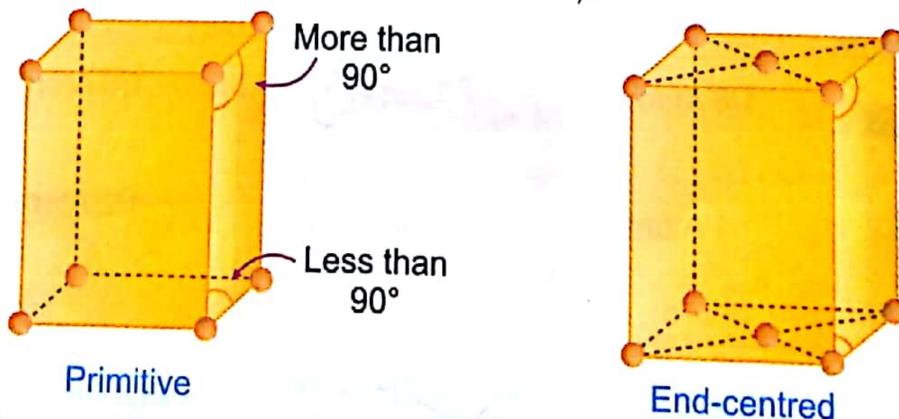
The three cubic lattices: all sides of same length, angles between faces all 90°



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



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



The two monoclinic lattices: unequal sides, two faces have angles other than 90°



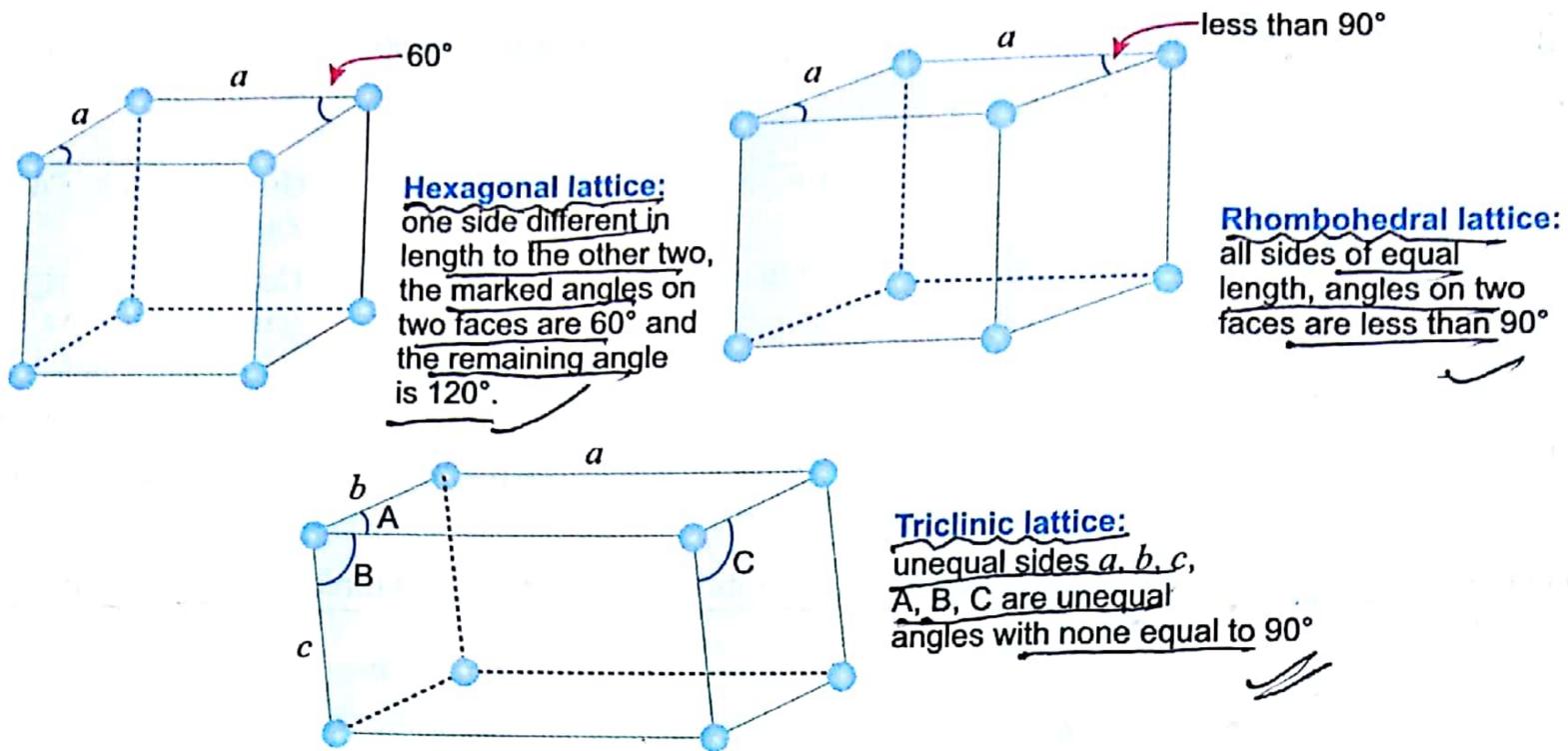


Fig. 1.4: Unit Cells of 14 Types of Bravais Lattices

4. Number of Atoms in a Unit Cell

- (i) An atom lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only one-eighth ($1/8$) of an atom belongs to the given unit cell.
- (ii) An atom present on an edge is distributed among the four unit cells, therefore only one-fourth ($1/4$) of an atom belongs to the given unit cell.
- (iii) A face-centred atom is shared between two adjacent unit cells. Therefore, one-half ($1/2$) of an atom lies in each unit cell.
- (iv) A body-centred atom belongs entirely to one unit cell since it is not shared by any other unit cell. Therefore, its contribution to the unit cell is one.

Applying above stated points, let us calculate the number of atoms in the different cubic unit cells.

Simple cubic: 8 (corner atoms) $\times \frac{1}{8}$ atom per unit cell = 1 atom

Body-centred cubic: 8 (corner atoms) $\times \frac{1}{8}$ atom per unit cell + 1 (body centre atom) $\times 1$ atom per unit cell
 $= 1 + 1 = 2$

Face-centred cubic: 8 (corner atoms) $\times \frac{1}{8}$ atom per unit cell
 $+ 6$ (face atoms) $\times \frac{1}{2}$ atom per unit cell = $1 + 3 = 4$

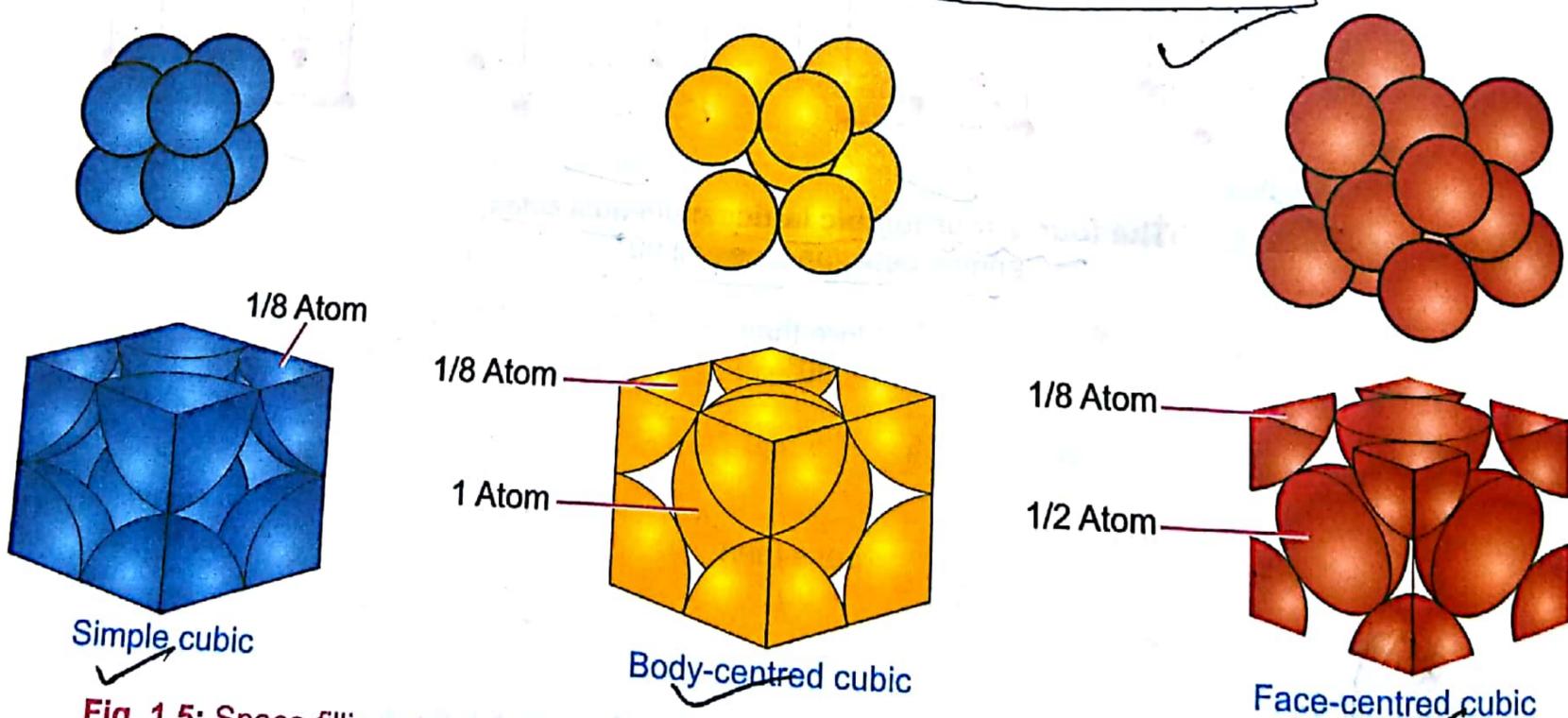


Fig. 1.5: Space-filling structures and actual portions of atoms belonging to one unit cell

Table 1.4: Number of Atoms per Unit Cell

Type of cell	Number of atoms at corners	Number of atoms in faces	Number of atoms in the body of cube	Total
Simple or primitive cubic	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic (bcc)	$8 \times \frac{1}{8} = 1$	0	$1 \times 1 = 1$	2
Face-centred cubic (fcc)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

5. **Density of Unit Cell:** Suppose edge of a unit cell of a cubic crystal is a , d is the density of the substance and M is the molar mass, then in case of cubic crystal,

$$\text{Mass of unit cell} = \text{Number of atoms in unit cell} \times \text{Mass of each atom}$$

$$= z \times m$$

$$\text{Mass of each atom } (m) = \frac{\text{Molar mass}}{\text{Avogadro number}}$$

$$m = \frac{M}{N_A}$$

$$\text{Mass of unit cell} = \frac{z \times M}{N_A}$$

$$\text{Volume of a unit cell} = a^3$$

Therefore, density of the unit cell,

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

$$d = \frac{z \times M}{a^3 \times N_A}, \text{ where } d \text{ is in g/cm}^3 \text{ and } a \text{ is in cm.}$$

6. Other Parameters of a Cubic System

(a) **Atomic radius:** It is defined as half of the distance between nearest neighbouring atom in a crystal. It is expressed in terms of length of the edge (a) of unit cell of the crystal.

(i) **Simple cubic structure (sc):** Radius of atom ' r ' = $\frac{a}{2}$, as atoms touch each other along the edges.

(ii) **Body-centred cubic structure (bcc):** Radius of atom ' r ' = $\frac{\sqrt{3}a}{4}$, as the atoms touch each other along the cross diagonal of the cube.

(iii) **Face-centred cubic structure (fcc):** Radius of atom ' r ' = $\frac{a}{2\sqrt{2}}$, as the atoms touch each other along the face diagonal of the cube.

(b) **Coordination number:** It is defined as the number of nearest neighbours that a particle has in a unit cell. It depends upon the structure of unit cell of the crystal.

(i) **Simple cubic structure (sc):** Coordination number (C.N.) = 6

(ii) **Body-centred cubic structure (bcc):** C.N. = 8

(iii) **Face-centred cubic structure (fcc):** C.N. = 12

7. Packing Efficiency

Packing efficiency is the percentage of total space filled by the particles.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms in unit cell } (v)}{\text{Total volume of the unit cell } (V)} \times 100$$

(a) **Packing efficiency in simple cubic structures:**

Let ' a ' be the cube edge and ' r ' the atomic radius.

As the particles touch each other along the edge, therefore $a = 2r$

Volume of the unit cell $= a^3$

Since one atom is present in a unit cell, its volume

$$v = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\therefore \text{Packing efficiency} = \frac{v}{V} \times 100 = \frac{\pi a^3/6}{a^3} \times 100$$

$$= \frac{\pi}{6} \times 100 = \frac{3.14}{6} \times 100$$

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

Therefore, 52.4% of unit cell is occupied by atoms and the rest 47.6% is empty space.

(b) **Packing efficiency in ccp and hcp structures:** The efficiencies of both types of packing, *ccp* and *hcp*, are equally good since in both, atom spheres occupy equal fraction (74%) of the available volume. We shall now calculate the efficiency of packing in *ccp* structure. Let the unit cell length be 'a' and face diagonal be 'b' (represented as AC in Fig. 1.7). In this figure other sides are not shown for the sake of clarity.

In triangle ABC, $\angle ABC$ is 90° , therefore,

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

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

If r is the radius of the sphere, we find

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

or

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r \quad \text{or,} \quad r = \frac{a}{2\sqrt{2}}$$

As *ccp* structure has 4 atoms per unit cell, therefore the total volume of 4 spheres (v) is $= 4 \times \frac{4}{3}\pi r^3$

Total volume of the unit cell (V) $= a^3 = (2\sqrt{2}r)^3$

$$\text{Packing efficiency} = \frac{v}{V} \times 100$$

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

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

Therefore, 74% of unit cell is occupied by atoms and the rest 26% is empty space.

(c) **Efficiency of packing in bcc structures:** In this case the atom at the centre is in touch with other two atoms which are diagonally arranged (see Fig. 1.8). The spheres along the body diagonal are shown with solid boundaries.

In $\triangle EFD$,

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

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

In $\triangle AFD$,

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

\therefore

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

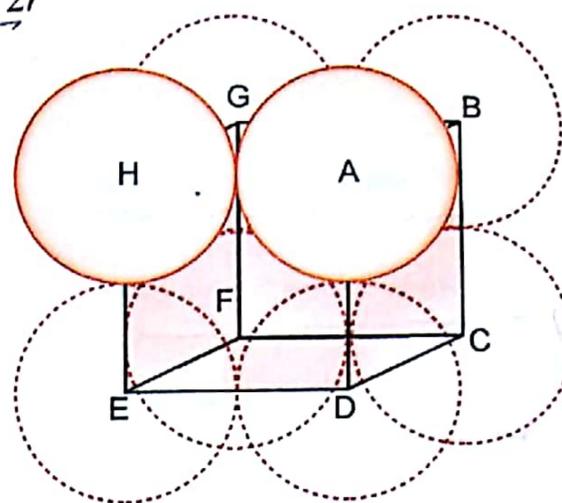


Fig. 1.6: Simple cubic unit cell. The spheres are in contact with each other along the edge of the cube.

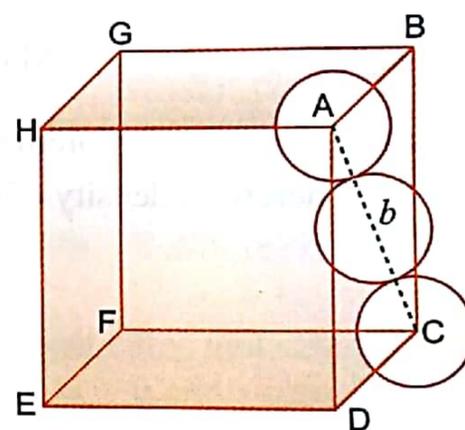


Fig. 1.7: Cubic close packing

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

Therefore,

$$c = 4r$$

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

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

As already calculated, the total number of atoms associated with a bcc unit cell is 2, the volume (v) is, therefore,

$$2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$$

$$\text{Volume of the unit cell (V)} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{Packing efficiency} = \frac{v}{V} \times 100 = \frac{(8/3)\pi r^3}{(64/3\sqrt{3}) \times r^3} \times 100 = \frac{\sqrt{3}}{8}\pi \times 100 = 68\%$$

Therefore, 68% of unit cell is occupied by atoms and the rest 32% is empty space.

8. Close Packing of Constituents

(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 one-dimensional close packed arrangement, the coordination number is 2.



Fig. 1.9: Close packing of spheres in one dimension

(b) Close packing in two dimensions

Two-dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways as shown in Figs. 1.10(a) and (b).

(i) Square close packing [Fig. 1.10(a)]

(ii) Hexagonal close packing [Fig. 1.10(b)]

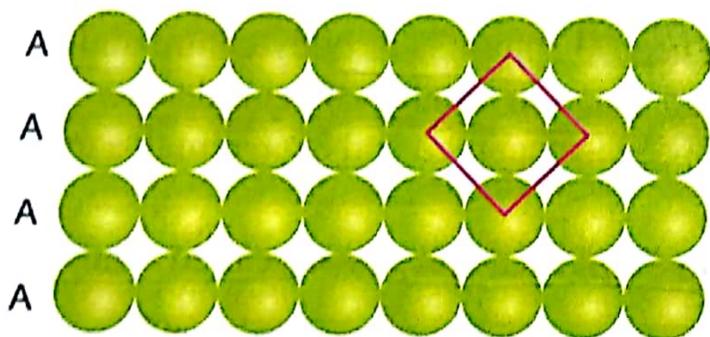


Fig. 1.10(a): AAA type arrangement, C.N. = 4, Square close packing in 2-D

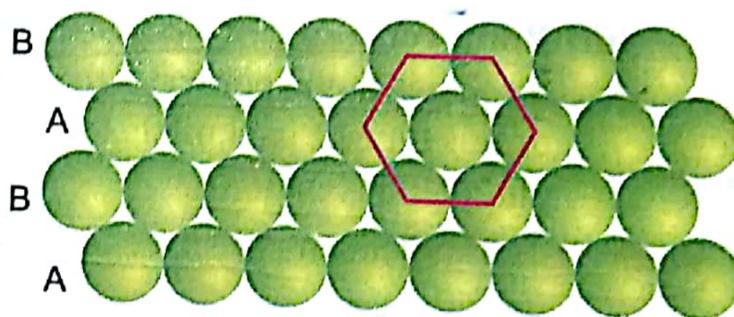


Fig. 1.10(b): ABAB... type arrangement, C.N. = 6, Hexagonal close packing in 2-D

(c) Close packing in three dimensions

(i) **Hexagonal close packing (hcp):** The first layer is formed utilizing maximum space, thus wasting minimum space. In every second row the particles occupy the depressions (also called voids) between the particles of the first row (Fig. 1.11). In the third row, the particles are vertically aligned with those in the first row giving AB AB AB... arrangement. This structure has hexagonal symmetry and is known as hexagonal close packing (hcp). This packing is more efficient and leaves small space which is unoccupied by spheres. In hcp arrangement, the coordination number is 12 and only 26% space is free. A single unit cell has 4 atoms.

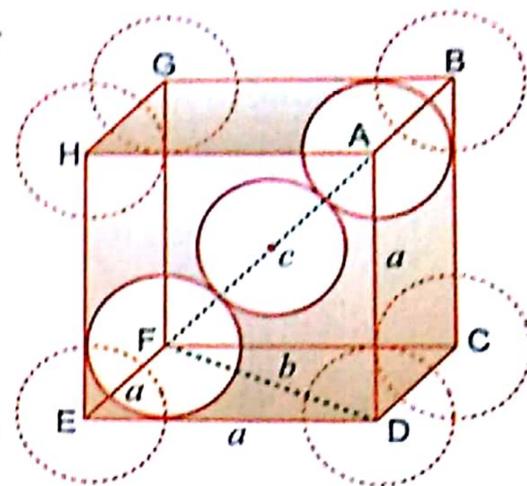


Fig. 1.8: Body-centred cubic unit cell

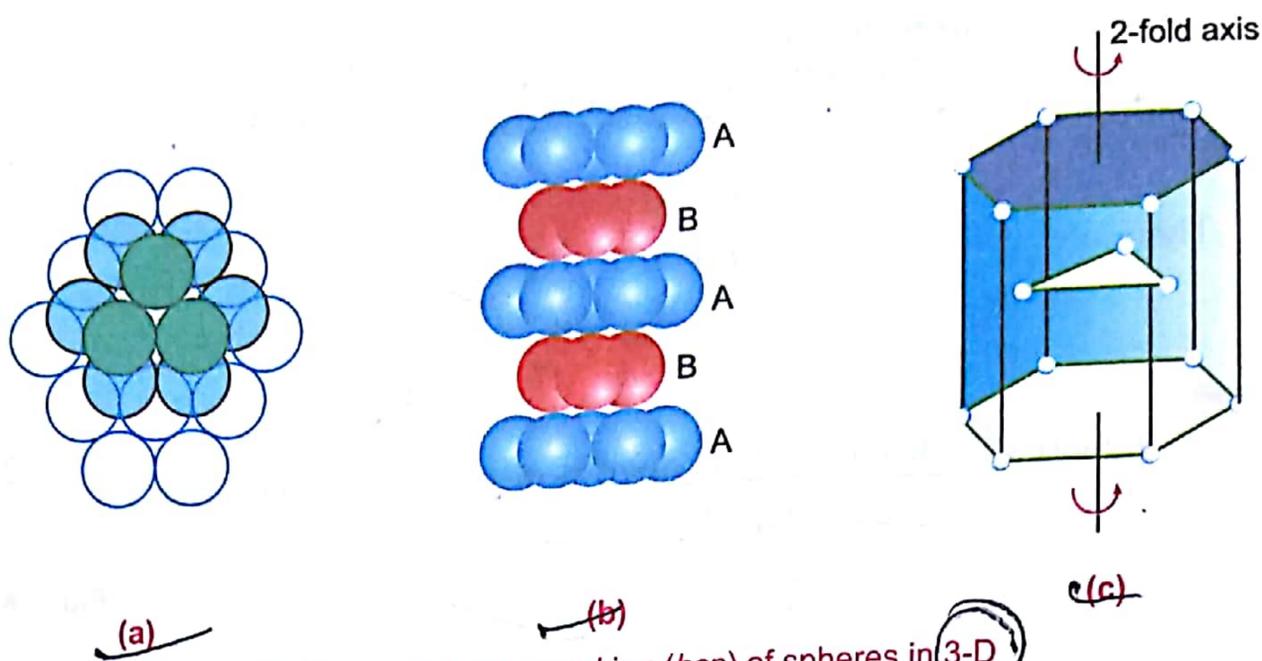


Fig. 1.11: Hexagonal close packing (hcp) of spheres in 3-D

(ii) **Cubic close packing (ccp):** Again, if we start with hexagonal layer of spheres and second layer of spheres is arranged by placing the spheres over the voids of the first layer, half of these holes can be filled by these spheres. Presume that spheres in the third layer are arranged to cover octahedral holes. This arrangement leaves third layer not resembling with either first or second layer, but fourth layer is similar to first, fifth layer to second, sixth to third and so on giving pattern ABCABCABC... . This arrangement has cubic symmetry and is known as cubic closed packed (ccp) arrangement. This is also called face-centred cubic (fcc) arrangement [Fig. 1.12(a) and (b)].

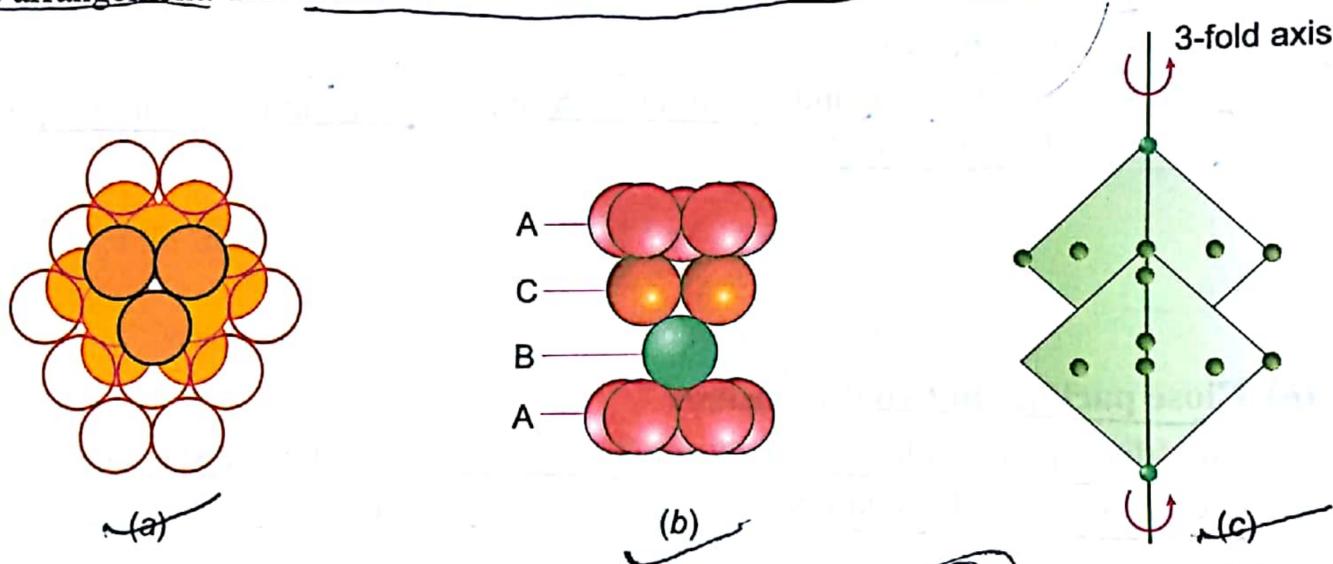


Fig. 1.12: Cubic close packing (ccp) of spheres in 3-D

The free space available in this packing is 26% and coordination number is 12.

(iii) **Body-centred close packing (bcc):** The central sphere is at body centre and it is surrounded by 8 spheres at the corner of the cube. The coordination number of central sphere is 8. The efficiency of this type of packing is less, only 68% space is occupied and 32% remains unoccupied. A single unit cell has 2 atoms.

9. **Voids or holes:** The empty spaces left between closed packed spheres are called voids or holes.

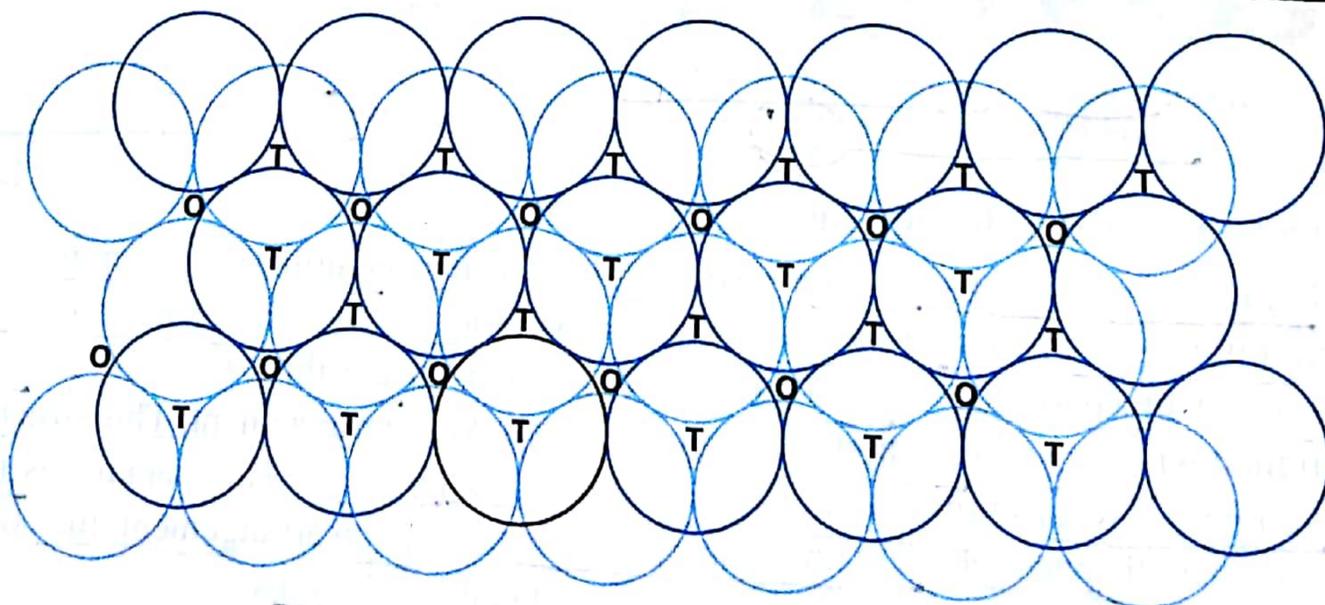


Fig. 1.13: Tetrahedral (T) and octahedral (O) voids

Voids are of three types:

(a) **Octahedral voids:** This void is surrounded by six spheres and formed by a combination of two triangular voids of the first and second layer. There is one octahedral void per atom in a crystal. The radius ratio $\left(\frac{r_{\text{void}}}{r_{\text{sphere}}}\right)$ is 0.414.

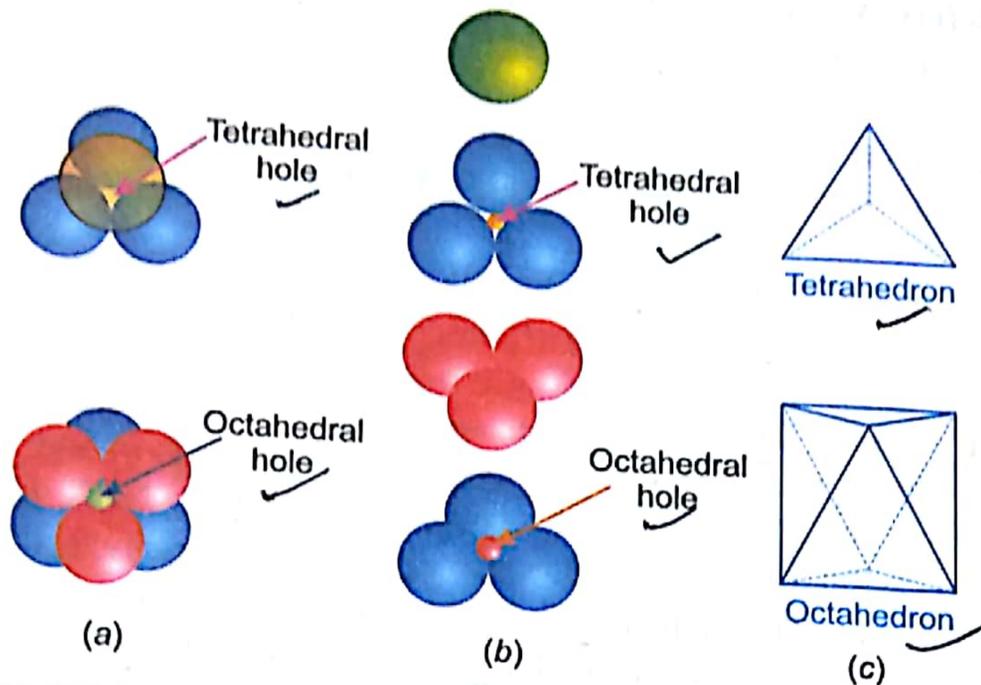


Fig. 1.14: Tetrahedral and octahedral voids (a) top view, (b) exploded side view, and (c) geometrical shape of the void

(b) **Tetrahedral voids:** These voids are surrounded by four spheres which lie at the vertices of a regular tetrahedron. There are 2 tetrahedral voids per atom in a crystal and the radius ratio is 0.225.

(c) **Trigonal voids:** The void, enclosed by three spheres in contact is called a trigonal void. There are 8 trigonal voids per atom in crystal and the radius ratio is 0.155.

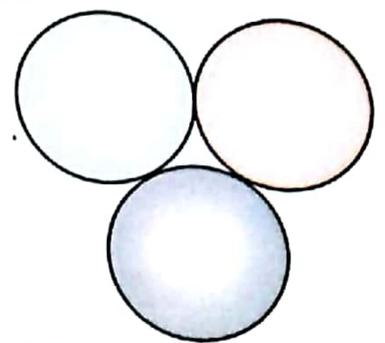


Fig. 1.15: Trigonal void

10. **Locating Tetrahedral and Octahedral Voids:** All closed packed structures have both octahedral and tetrahedral voids. In a ccp pattern, there is one octahedral void at the centre of body and 12 octahedral voids on each of the 12 edges of the cube. Each void on the edge is shared by four other unit cells.

$$\text{Octahedral void at centre of cube} = 1$$

$$\text{Effective number of voids at edges} = 12 \times \frac{1}{4} = 3$$

$$\text{Total number of octahedral voids} = 1 + 3 = 4$$

In ccp structure, there are 8 tetrahedral voids. These are located at the body diagonals, two on each body diagonal at one-fourth of the distance from each end.

11. **Radius Ratio:** For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r^+}{r^-}$$

12. **Crystal Defects:** The defects are basically irregularities in the arrangement of constituent particles. Broadly, crystal 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.

13. **Point Defects**

Interstitials: Atoms or ions which occupy normally voids in a crystal are called interstitials.

Vacancy: When one of the constituent particles is missing from the crystal lattice, this unoccupied position is called vacancy.

Point defects can be classified into three types:

(A) Stoichiometric defects, (B) Impurity defects, and (C) Non-stoichiometric defects.

(A) **Stoichiometric Defects:** The point defects that do not disturb the stoichiometry of the solid are called stoichiometric defects. They are also called intrinsic or thermodynamic defects. These are of two types, vacancy defects and interstitial defects.

(a) **Vacancy defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. It results in decrease in density of the substance. This defect can arise when a substance is heated.

(b) **Interstitial defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. Due to this defect the density of the substance increases.

Vacancy and interstitial defects are generally shown by non-ionic solids because ionic solids must always maintain electrical neutrality. Ionic solids show these defects as Schottky and Frenkel defects as explained below.

(i) **Schottky defect:** This defect arises when equal number of cations and anions are missing from the lattice. It is a common defect in ionic compounds of high coordination number where both cations and anions are of the same size, e.g., KCl, NaCl, KBr, etc. Due to this defect, density of crystal decreases and it begins to conduct electricity to a smaller extent [Fig. 1.16(a)].

(ii) **Frenkel defect:** This defect arises when some of the ions of the lattice occupy interstitial sites leaving lattice sites vacant. This defect is generally found in ionic crystals where anion is much larger in size than the cation, e.g., AgBr, ZnS, etc. Due to this defect density does not change, electrical conductivity increases to a small extent and there is no change in overall chemical composition of the crystal [Fig. 1.16(b)].

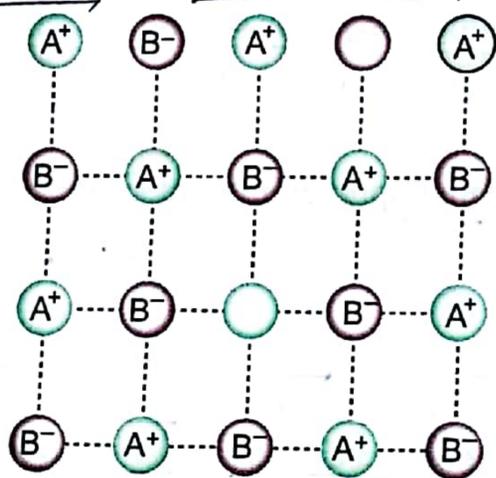


Fig. 1.16(a): Schottky defect

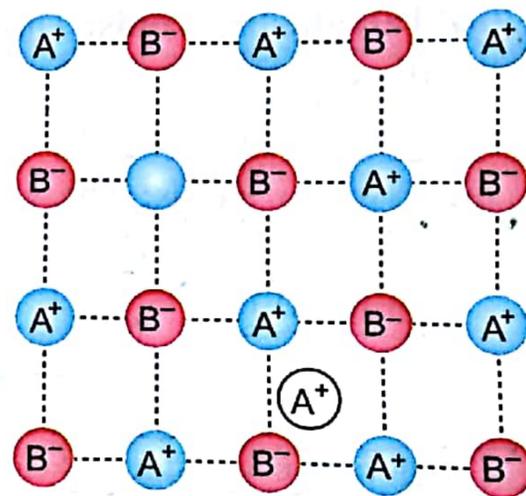


Fig. 1.16(b): Frenkel defect

(B) **Impurity Defects:** These defects arise when foreign atoms or ions are present in the lattice site (substitutional solid solutions) or in the interstitial sites (interstitial solid solutions). For example, when 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.

(C) **Non-stoichiometric Defects:** These defects arise when stoichiometry of a substance is disturbed. These are of two types.

(a) **Metal excess defect:** This may occur in either of the following two ways:

(i) **Metal excess defect due to anion vacancies:** In this defect a negative ion from the crystal lattice may be missing from its lattice site leaving a hole or vacancy which is occupied by the electron originally associated with the anion. In this way crystal remains neutral. Alkali halides like NaCl and KCl show this type of defect.

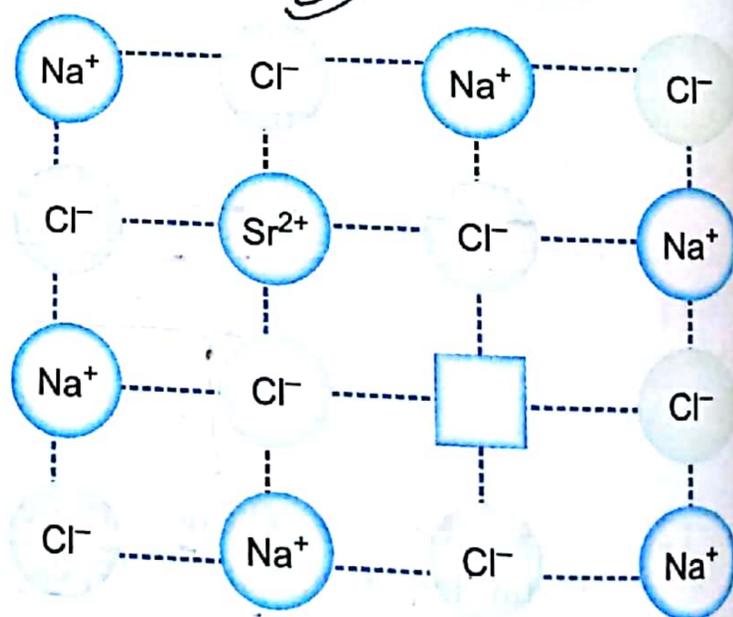
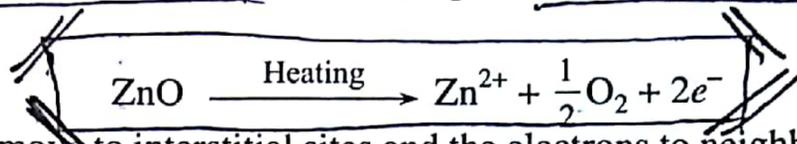


Fig. 1.17: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+} .

→ **F-centres:** These are the anionic sites occupied by unpaired electrons. F-centres impart colour to crystals. They impart yellow colour to NaCl crystals, violet colour to KCl crystals and pink colour to LiCl crystals. The colour results by the excitation of electrons when they absorb energy from the visible light falling on the crystal.

(ii) **Metal excess defect due to interstitial cation:** In this defect an extra positive ion occupies interstitial position in the lattice and the free electron is trapped in the vicinity of this interstitial cation. In this way crystal remains neutral. For example, zinc oxide on heating loses oxygen and turns yellow.



The excess of Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(b) **Metal deficiency defect:** This type of defect generally occurs when metal shows variable valency. The defect arises due to the missing of cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site. For example, Fe_xO , where $x = 0.93$ to 0.96 .

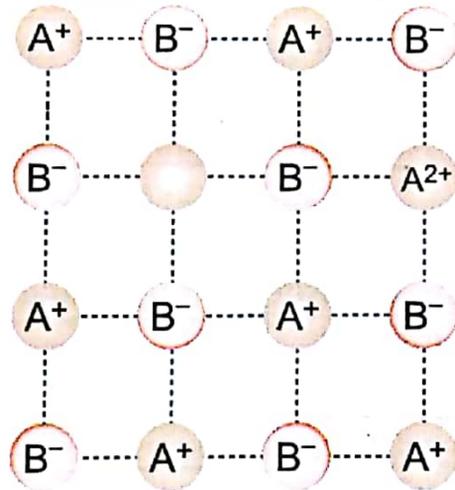


Fig. 1.18: Metal deficiency defect due to missing cations

14. (a) **13-15 Compounds:** When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 13-15 compounds. For example, InSb, AlP, GaAs, etc.

(b) **12-16 Compounds:** Combination of elements of groups 12 and 16 yield some solid compounds which are referred to as 12-16 compounds. For example, ZnS, CdS, CdSe, HgTe, etc. In these compounds, the bonds have ionic character.

15. **Magnetic Moments:** The magnetic properties of substances result from their magnetic moments associated with individual electrons. Each electron has a magnetic moment, origin of which lies in two sources. It is a known fact that an electron shows two types of motions, i.e., it rotates (spins) around its own axis and simultaneously revolves around the nucleus (orbital motion). An electron in motion is just like a small current loop. Two types of motions give rise to two types of magnetic moments—spin and orbital magnetic moments. Spin moment is directed along the spin axis and is shown up or down direction [Fig. 1.19(b)]. Orbital motion also generates a magnetic field and thus gives rise to orbital moment along its axis of rotation [Fig. 1.19(a)]. In this way each electron of the atom behaves like a small bar magnet having permanent orbital and spin magnetic moments. Magnetic moments are measured in Bohr magneton (μ_B) unit (B.M.)

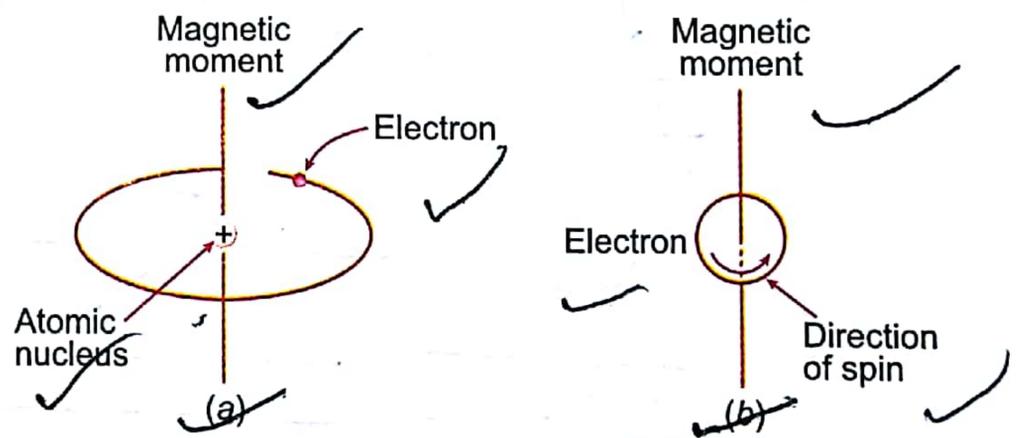


Fig. 1.19: Magnetic moment associated with (a) orbital motion and (b) spin motion of an electron

$$1 \text{ B.M.} = \frac{eh}{4\pi mc} = 9.27 \times 10^{-24} \text{ Am}^2 \text{ or } 9.27 \times 10^{-21} \text{ erg/gauss}$$

where e is charge on electron; h is Planck's constant; m is the mass of electron and c is the velocity of light. Depending upon two spin motions (clockwise and anticlockwise), spin magnetic moment may acquire

two values $\pm M_B$. Contribution of the orbital magnetic moment is equal to $M_L \cdot M_B$, where M_L is magnetic quantum number of electron.

16. Magnetic Properties of Solids: On the basis of their magnetic properties, substances can be classified into five categories.

(a) **Diamagnetic:** Diamagnetic substances are weakly repelled by the external magnetic field. The atoms of these substances have all paired up electrons. As pairing of electrons cancel their magnetic moments, they lose their magnetic character. NaCl , H_2O , TiO_2 and C_6H_6 are some examples of diamagnetic substances.

(b) **Paramagnetic:** Paramagnetic substances are weakly attracted by the external magnetic field. The atoms of these substances have one or more unpaired electrons. Paramagnetism is temporary and is present as long as external magnetic field is present. O_2 , Fe^{3+} , Cr^{3+} , TiO , VO_2 , Cu^{2+} are some examples of paramagnetic substances.

(c) **Ferromagnetic:** Ferromagnetic substances are strongly attracted by the external magnetic field. In solid state, the metal ions of these substances are grouped together into small regions called domains. Each domain acts as a tiny magnet. When such a substance is placed in a magnetic field all the domains get oriented in the direction of magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet. Thus, besides strong attractions, these substances can be permanently magnetised.

(d) **Antiferromagnetic:** These substances have domain structure similar to that of ferromagnetic substances but their domains are oppositely oriented and cancel out each other's magnetic moment. MnO is an antiferromagnetic substance.

(e) **Ferrimagnetic:** In ferrimagnetic substances due to unequal number of magnetic moment in parallel and antiparallel directions, the net magnetic moment is small. These substances lose ferrimagnetism on heating and become paramagnetic. Fe_3O_4 and ferrites like MgFe_2O_4 and ZnFe_2O_4 are examples of such substances.



Fig. 1.20: Schematic alignment of magnetic moments

➔ **Curie Temperature:** The temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called curie temperature. For iron, the curie temperature is 1033 K, for Ni it is 629 K and for Fe_3O_4 it is 850 K. Below this temperature paramagnetic substances behave as ferromagnetic substances.

17. Electrical Properties: Solids are classified into three groups on the basis of their electrical conductivities:

(a) **Conductors:** These generally include metals. Their conductivity is of the order of 10^4 – 10^7 $\text{ohm}^{-1} \text{m}^{-1}$.

(b) **Semiconductors:** Those solids which have intermediate conductivities ranging from 10^{-6} to 10^4 $\text{ohm}^{-1} \text{m}^{-1}$ are classified as semiconductors. As the temperature rises there is a rise in conductivity because electrons from the valence band jump to conduction band.

(c) **Insulators:** These are solids which have very low conductivity values ranging from 10^{-20} to 10^{-10} $\text{ohm}^{-1} \text{m}^{-1}$.

➔ **Causes of conductance in solids:** In most of the solids conduction takes place due to migration of electrons under the influence of electric field. However, in ionic compounds, it is the ions that are responsible for the conducting behaviour due to their movement.

In metals, conductivity strongly depends upon the number of valence electrons available in an atom. A band is formed due to closeness of molecular orbitals which are formed from atomic orbitals.

If this band is partially filled or it overlaps the higher energy unoccupied conduction band, the electrons can flow easily under applied electric field and the solid behaves as conductor [Fig. 1.21(a)]. If the gap between valence band and next higher unoccupied conduction band is large, electrons cannot jump into it and such a substance behaves as insulator. [Fig. 1.21(b)]

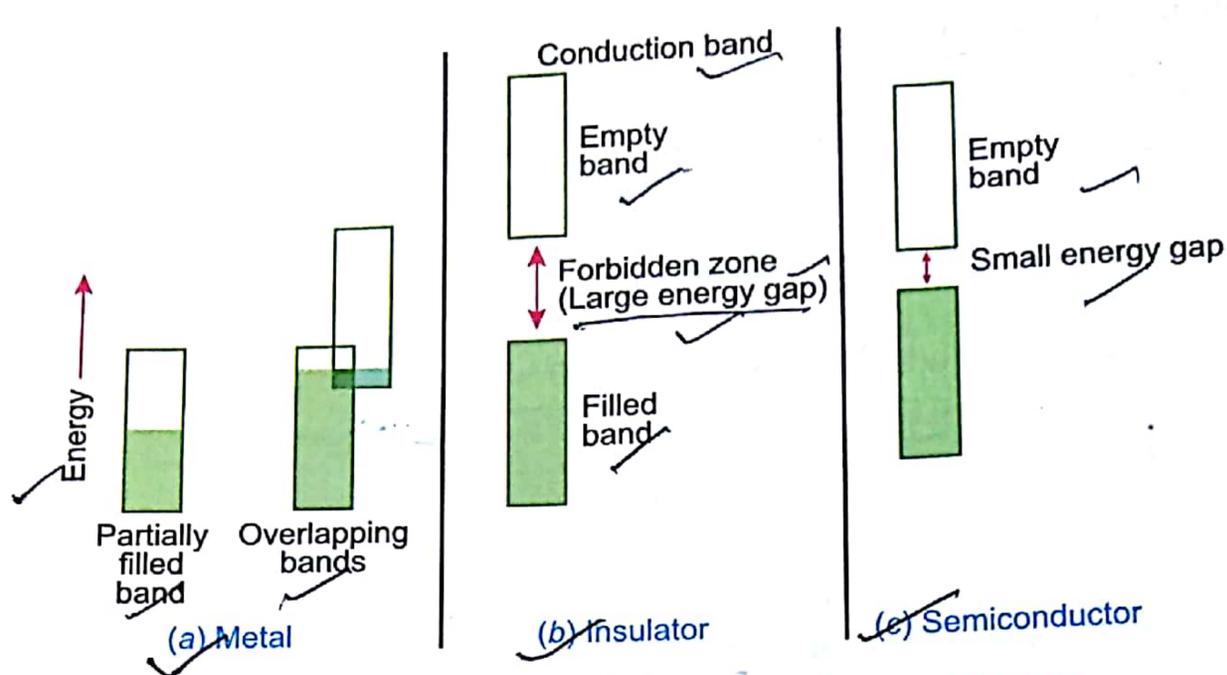


Fig. 1.21: Distinction among metals, insulators and semiconductors

If the gap between the valence band and conduction band is small, some electrons may jump from valence band to the conduction band. Such a substance shows some conductivity and it behaves as a semiconductor [Fig. 1.21(c)]. Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump from valence to conduction band. Silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

(e) **Doping:** It is a process by which impurity is introduced in semiconductors to enhance their conductivity.

➔ ***n*-type semiconductor:** When silicon or germanium crystal is doped with a Group 15 element like P or As, the dopant atom forms four covalent bonds like a Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and contributes its share towards electrical conduction. Thus, silicon or germanium doped with P or As is called *n*-type semiconductor, *n* indicates negative charge of electron since it is the electron that conducts electricity [Fig. 1.22(b)].

➔ ***p*-type semiconductor:** When silicon or germanium is doped with a group 13 element like B or Al, the dopant atom forms three covalent bonds, but at the place of fourth electron a hole is created. This hole moves through the crystal like a positive charge giving rise to electrical conductivity. Thus, Si or Ge doped with B or Al is called *p*-type semiconductor (*p* stands for positive hole), since it is the positive hole that is responsible for conduction [Fig. 1.22(c)].

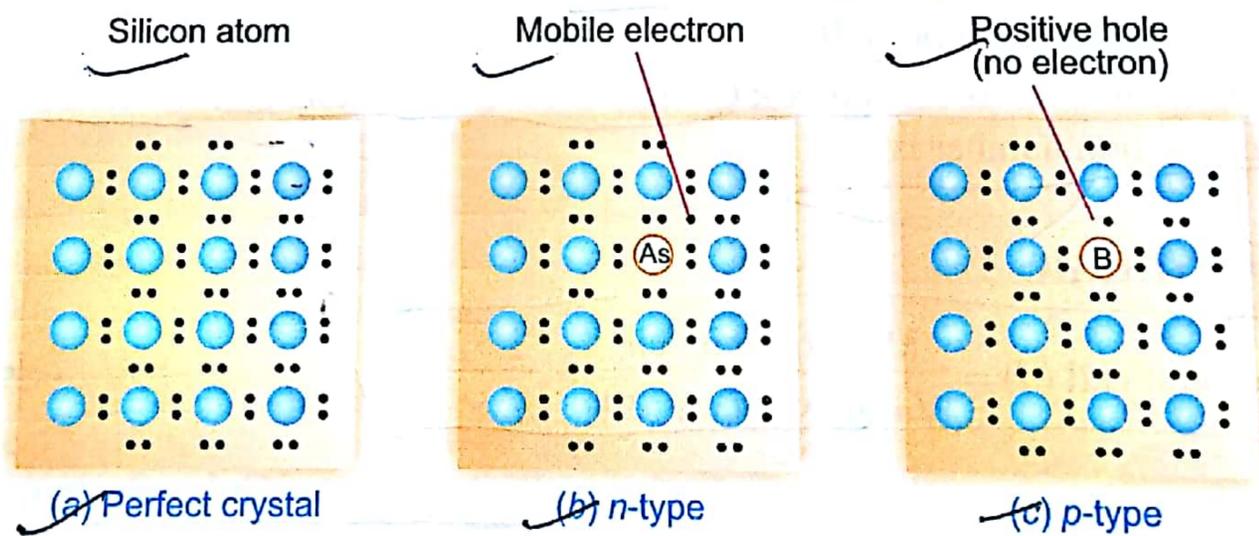


Fig. 1.22: Creation of *n*-type and *p*-type semiconductors

- ➔ **Diode:** Diodes are made by the combination of *n*-type and *p*-type semiconductors. They are used as rectifiers.
- ➔ **Transistors:** These are used to detect or amplify radio or audio signals. They consist of *pnp* or *npn* sandwich semiconductors.
- ➔ **Photodiode:** These are diodes which are capable of converting light energy into electrical energy and are used in solar cells.