

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' in Fig. 1.20. Such voids are surrounded by six spheres and are called **octahedral voids**. One such void has been shown separately in Fig. 1.21. 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:** 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 (Fig. 1.22). This sort of arrangement of atoms is found in many metals like magnesium and zinc.

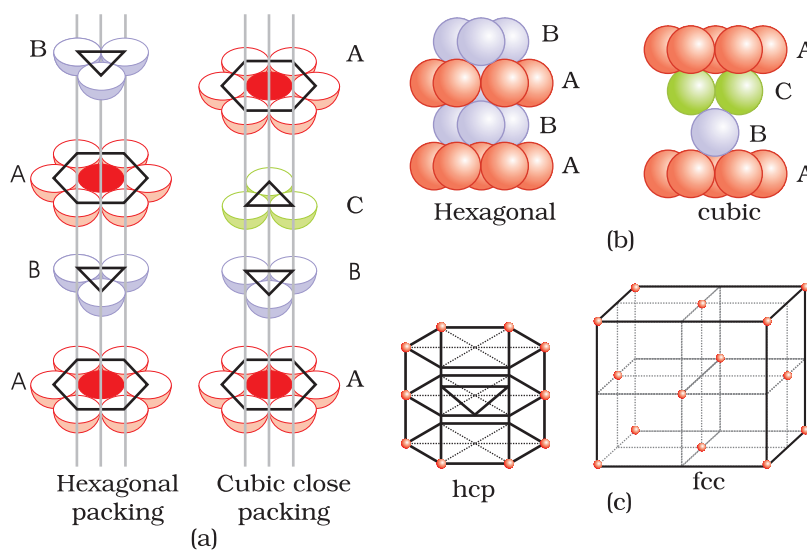
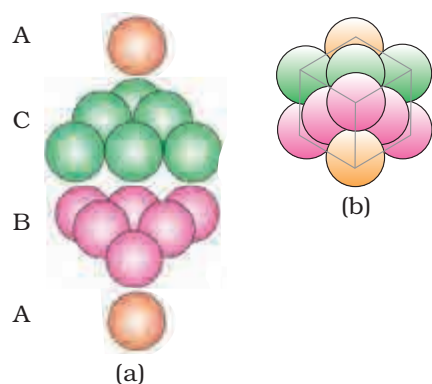


Fig. 1.22
 (a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres
 (b) four layers stacked in each case and (c) geometry of packing.

Fig. 1.23
 (a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.



- (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. 1.22 and 1.23. 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.

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.

1.6.1 Formula of a Compound and Number of Voids Filled

Earlier in the section, we have learnt that when particles are close-packed resulting in either *ccp* or *hcp* structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. 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 tetrahedral voids are occupied, if bigger, then octahedral voids. All octahedral or tetrahedral voids are not occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

Example 1.1

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution

The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

Example 1.2

Atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Solution

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is $2 \times (2/3):1$ or 4:3 and the formula of the compound is A_4B_3 .

Locating Tetrahedral and Octahedral Voids

We know that close packed structures have both tetrahedral and octahedral voids. Let us take *ccp* (or *fcc*) structure and locate these voids in it.

(a) Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice [Fig. 1(a)]. The unit cell is divided into eight small cubes.

Each small cube has atoms at alternate corners [Fig. 1(a)]. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of *ccp* structure. We know that *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

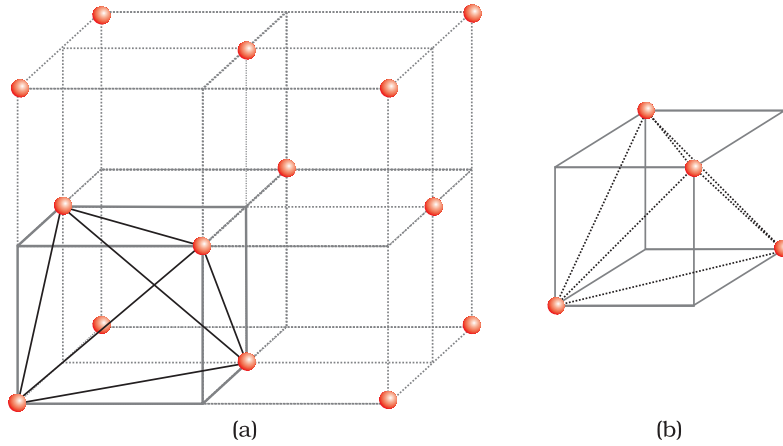


Fig. 1: (a) Eight tetrahedral voids per unit cell of *ccp* structure
(b) one tetrahedral void showing the geometry.

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(a)]. The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges [Fig. 2(b)]. It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only $\frac{1}{4}$ th of each void belongs to a particular unit cell.

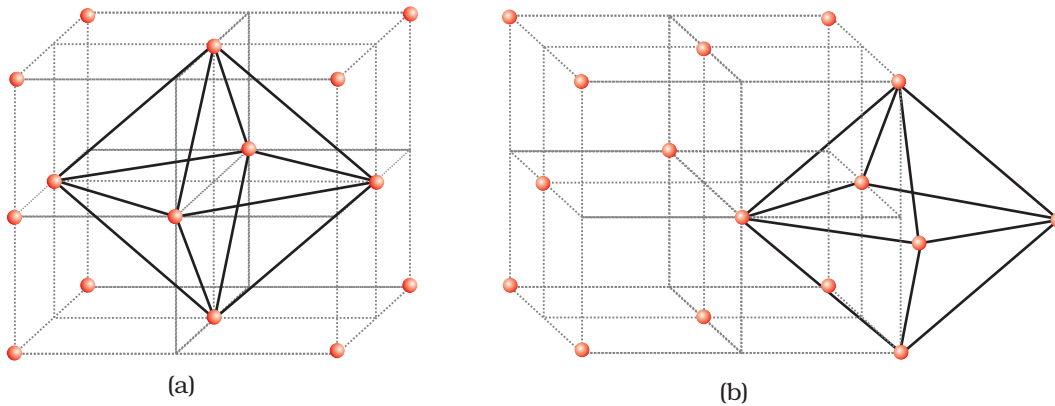


Fig. 2: Location of octahedral voids per unit cell of *ccp* or *fcc* lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

∴ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in hcp and ccp Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.24 let the unit cell edge length be 'a' and face diagonal AC = b.

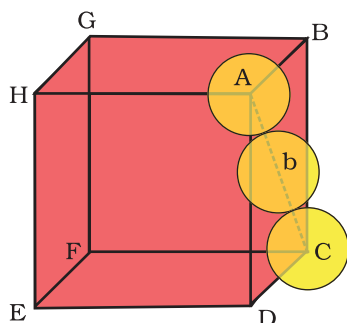


Fig. 1.24: Cubic close packing other sides are not provided with spheres for sake of clarity.

In ΔABC

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

$$= a^2 + a^2 = 2a^2 \text{ or}$$

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

If r is the radius of the sphere, we find

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

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

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

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 $(2\sqrt{2}r)^3$.

Therefore,

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

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

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

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.25, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

$$\begin{aligned} \text{In } \triangle EFD, \\ b^2 &= a^2 + a^2 = 2a^2 \\ b &= \sqrt{2}a \end{aligned}$$

$$\begin{aligned} \text{Now in } \triangle AFD \\ c^2 &= a^2 + b^2 = a^2 + 2a^2 = 3a^2 \\ c &= \sqrt{3}a \end{aligned}$$

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.

$$\begin{aligned} \text{Therefore, } \sqrt{3}a &= 4r \\ a &= \frac{4r}{\sqrt{3}} \end{aligned}$$

$$\text{Also we can write, } r = \frac{\sqrt{3}}{4} a$$

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\frac{4}{3}\right)\pi r^3$.

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

Therefore,

$$\begin{aligned} \text{Packing efficiency} &= \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}} \% \\ &= \frac{2 \times \left(\frac{4}{3}\right)\pi r^3 \times 100}{\left[\left(\frac{4}{\sqrt{3}} r\right)^3\right]} \% \\ &= \frac{(8/3)\pi r^3 \times 100}{64/(3\sqrt{3})r^3} \% = 68\% \end{aligned}$$

1.7.3 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 (Fig. 1.26).

Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$$a = 2r$$

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

Since a simple cubic unit cell contains only 1 atom

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

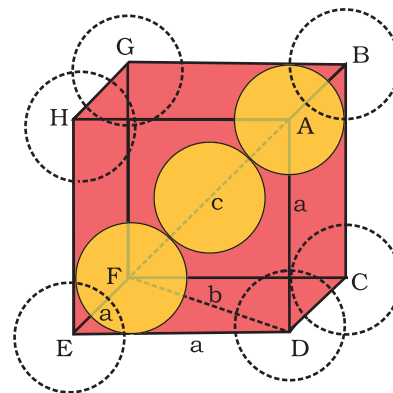
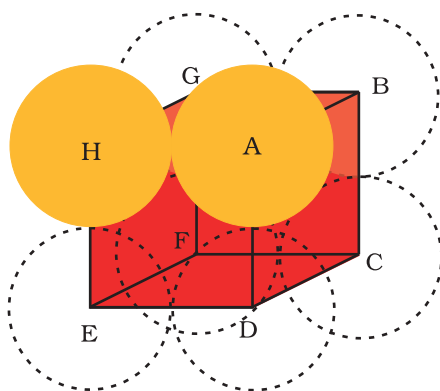


Fig. 1.25: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

Fig. 1.26
Simple cubic unit cell.
The spheres are in contact with each other along the edge of the cube.



∴ Packing efficiency

$$\begin{aligned}
 &= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\% \\
 &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 \\
 &= 52.36\% = 52.4\%
 \end{aligned}$$

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

1.8 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:

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

Mass of the unit cell

$$= \text{number of atoms in unit cell} \times \text{mass of each atom} = z \times m$$

(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:

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

Therefore, density of the unit cell

$$\begin{aligned}
 &= \frac{\text{mass of unit cell}}{\text{volume of unit cell}} \\
 &= \frac{z \cdot m}{a^3} = \frac{z \cdot M}{a^3 \cdot N_A} \quad \text{or} \quad d = \frac{zM}{a^3 N_A}
 \end{aligned}$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (d , z , M , a and N_A), if any four are known, we can determine the fifth.

Example 1.3 An element has a body-centred cubic (*bcc*) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm³. How many atoms are present in 208 g of the element?

Solution

$$\begin{aligned}
 \text{Volume of the unit cell} &= (288 \text{ pm})^3 \\
 &= (288 \times 10^{-12} \text{ m})^3 = (288 \times 10^{-10} \text{ cm})^3 \\
 &= 2.39 \times 10^{-23} \text{ cm}^3
 \end{aligned}$$

Volume of 208 g of the element

$$= \frac{\text{mass}}{\text{density}} = \frac{208\text{g}}{7.2\text{g cm}^{-3}} = 28.88\text{ cm}^3$$

Number of unit cells in this volume

$$= \frac{28.88\text{cm}^3}{2.39 \times 10^{-23}\text{ cm}^3 / \text{unit cell}} = 12.08 \times 10^{23} \text{ unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell) \times 12.08×10^{23} unit cells
= 24.16×10^{23} atoms

X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3 , calculate the atomic mass of copper.

Example 1.4

In case of *fcc* lattice, number of atoms per unit cell, $z = 4$ atoms

Solution

$$\text{Therefore, } M = \frac{d N_A a^3}{z}$$

$$= \frac{8.92\text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ atoms mol}^{-1} \times (3.608 \times 10^{-8}\text{ cm})^3}{4 \text{ atoms}}$$

$$= 63.1 \text{ g/mol}$$

Atomic mass of copper = 63.1 u

Silver forms *ccp* lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

Example 1.5

Since the lattice is *ccp*, the number of silver atoms per unit cell = $z = 4$

Solution

$$\text{Molar mass of silver} = 107.9 \text{ g mol}^{-1} = 107.9 \times 10^{-3} \text{ kg mol}^{-1}$$

$$\text{Edge length of unit cell} = a = 408.6 \text{ pm} = 408.6 \times 10^{-12} \text{ m}$$

$$\text{Density, } d = \frac{z.M}{a^3 \cdot N_A}$$

$$= \frac{4 \times (107.9 \times 10^{-3} \text{ kg mol}^{-1})}{(408.6 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})} = 10.5 \times 10^3 \text{ kg m}^{-3}$$
$$= 10.5 \text{ g cm}^{-3}$$

Intext Questions

- 1.14** What is the two dimensional coordination number of a molecule in *square close-packed* layer?
- 1.15** A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

- 1.16 A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?
- 1.17 Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?
- 1.18 An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of the cubic unit cell?

1.9 Imperfections in Solids

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of 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*. We shall confine our discussion to point defects only.

1.9.1 Types of Point Defects

Point defects can be classified into three types : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

(a) 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** (Fig. 1.27). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

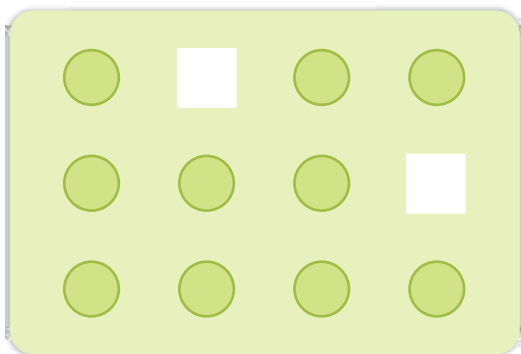


Fig. 1.27: Vacancy defects

(ii) *Interstitial Defect*: When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have **interstitial defect** (Fig. 1.28). 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*: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 1.29). It creates a *vacancy defect* at its original site and an **interstitial defect** at its new location.

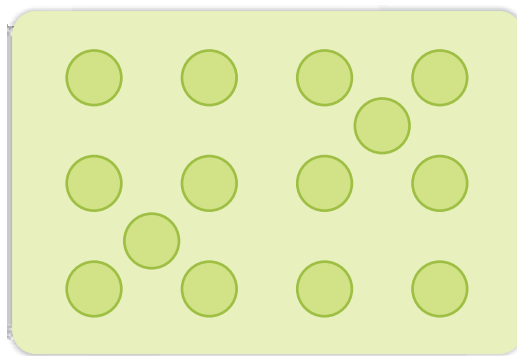


Fig. 1.28: Interstitial defects

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.

(iv) *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 (Fig. 1.30).

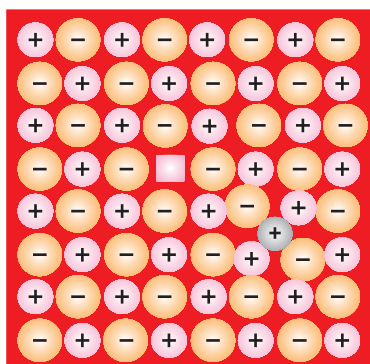


Fig. 1.29: Frenkel defects

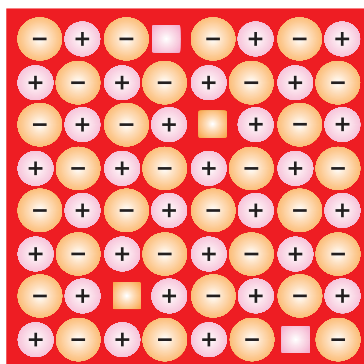


Fig. 1.30: Schottky defects

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 cm^3 at room temperature. In 1 cm^3 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

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig.1.31). 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.

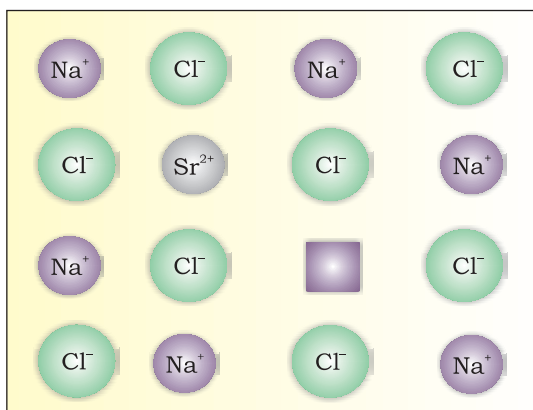


Fig. 1.31: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. 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. 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. 1.32). 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).

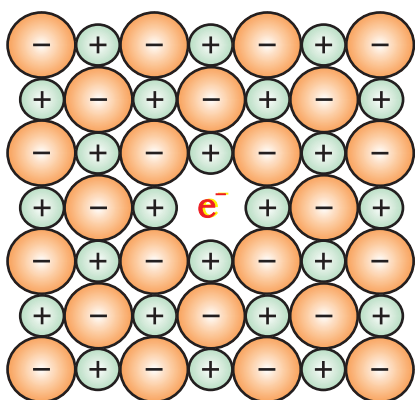
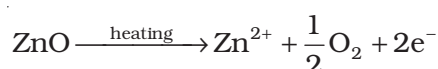


Fig. 1.32: An F-centre in a crystal

- *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.



Now there is excess of zinc in the crystal and its formula becomes Zn_{1+x}O. The excess Zn²⁺ 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 Fe²⁺ cations are missing and the loss of positive charge is made up by the presence of required number of Fe³⁺ ions.

1.10 Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10⁻²⁰ to 10⁷ ohm⁻¹ m⁻¹. Solids can be classified into three types on the basis of their conductivities.

- *Conductors:* The solids with conductivities ranging between 10⁴ to 10⁷ ohm⁻¹ m⁻¹ are called conductors. Metals have conductivities in the order of 10⁷ 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⁻¹m⁻¹.
- (iii) *Semiconductors* : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm⁻¹m⁻¹.

1.10.1 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. 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 (Fig. 1.33 a).

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 (Fig. 1.33 b).

1.10.2 Conduction of Electricity in Semiconductors

In case of semiconductors, the gap between the valence band and conduction band is small (Fig. 1.33 c). 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**.

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

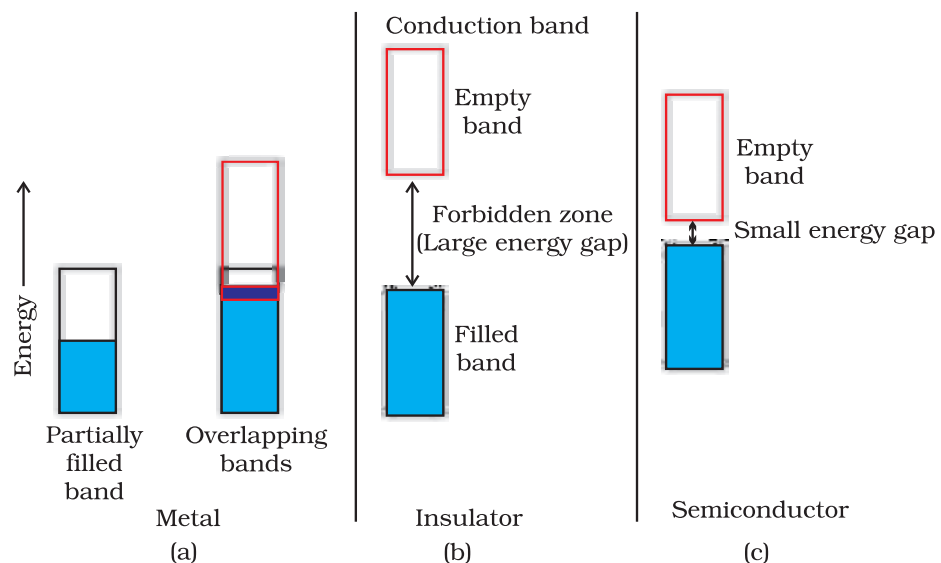


Fig. 1.33
Distinction among
(a) metals
(b) insulators and
(c) semiconductors.
In each case, an unshaded area represents a conduction band.

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 (Fig. 1.34 a). 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 (Fig. 1.34 b). 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** (Fig. 1.34 c). 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 it happens, 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.

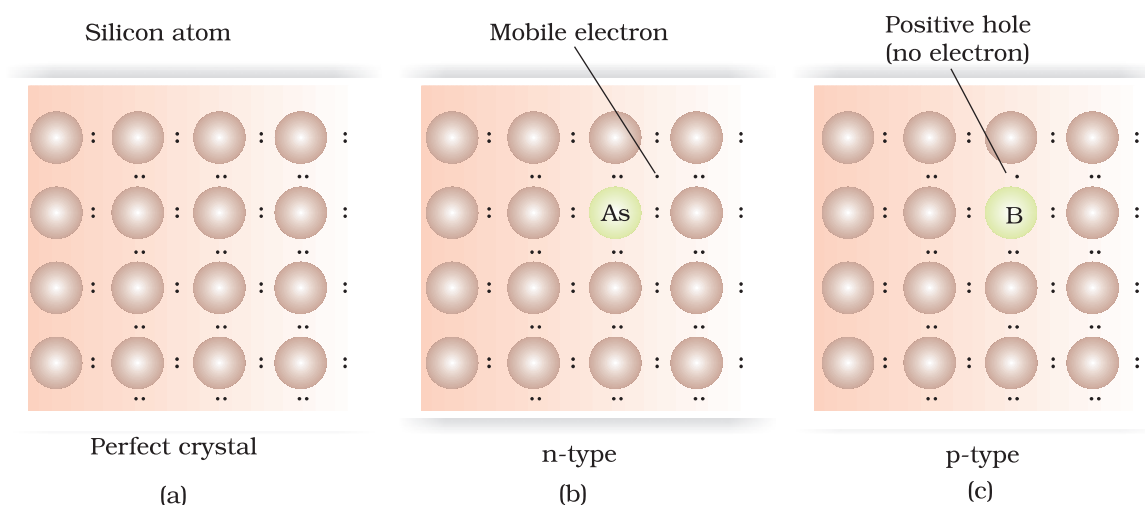


Fig. 1.34: Creation of *n-type* and *p-type* semiconductors by doping groups 13 and 15 elements.

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.

Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13 – 15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO₂ and ReO₃ behave like metals. Rhenium oxide, ReO₃ is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO₂, VO₃ and TiO₃ show metallic or insulating properties depending on temperature.

1.11 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. Its magnetic moment originates

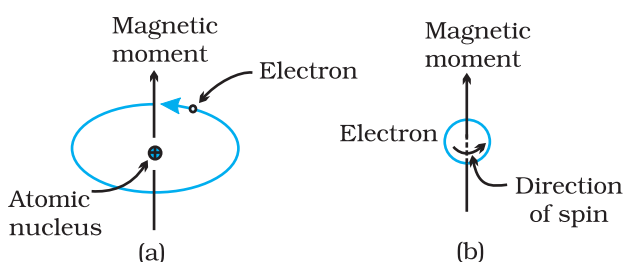


Fig.1.35: Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.

from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis (Fig. 1.35). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called **Bohr magneton**, μ_B . It is equal to $9.27 \times 10^{-24} \text{ A m}^2$.

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.

- (i) **Paramagnetism:** Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O₂, Cu²⁺, Fe³⁺, Cr³⁺ are some examples of such substances.

- (ii) *Diamagnetism*: Diamagnetic substances are weakly repelled by a magnetic field. H_2O , NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.
- (iii) *Ferromagnetism*: A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field (Fig. 1.36 a) 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.
- (iv) *Antiferromagnetism*: Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment (Fig. 1.36 b).
- (v) *Ferrimagnetism*: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers (Fig. 1.36c). They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like MgFe_2O_4 and ZnFe_2O_4 are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

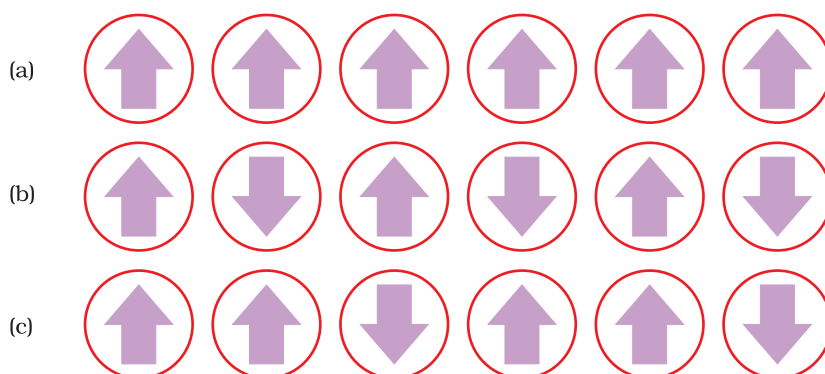


Fig 1.36: Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.

- 1.19** What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?
- 1.20** What type of stoichiometric defect is shown by:
(i) ZnS (ii) AgBr
- 1.21** Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.
- 1.22** Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.
- 1.23** A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?
- 1.24** What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Summary

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them. In **amorphous** solids, the arrangement of constituent particles has only **short range order** and consequently they behave like **super cooled liquids**, do not have sharp melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have sharp melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of **crystalline** solids depend upon the nature of interactions between their constituent particles. On this basis, they can be divided into four categories, namely: **molecular**, **ionic**, **metallic** and **covalent** solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each **lattice point** gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called **Bravais lattices**. Each lattice can be generated by repeating its small characteristic portion called **unit cell**. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either **primitive** which have particles only at their corner positions or **centred**. The centred unit cells have additional particles at their body centre (**body-centred**), at the centre of each face (**face-centred**) or at the centre of two opposite faces (**end-centred**). There are seven types of **primitive unit** cells. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen **Bravais lattices**.

Close-packing of particles result in two highly efficient lattices, **hexagonal close-packed (hcp)** and **cubic close-packed (ccp)**. The latter is also called face-centred cubic (**fcc**) lattice. In both of these packings 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less

efficient packing of particles. While in **body-centred cubic lattice (bcc)** 68% space is filled, in simple cubic lattice only 52.4 % space is filled.

Solids are not perfect in structure. There are different types of **imperfections** or **defects** in them. Point defects and line defects are common types of defects. Point defects are of three types - **stoichiometric defects**, **impurity defects** and **non-stoichiometric defects**. **Vacancy defects** and **interstitial defects** are the two basic types of stoichiometric point defects. In ionic solids, these defects are present as **Frenkel** and **Schottky defects**. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of **metal excess type** and **metal deficient type**. Sometimes calculated amounts of impurities are introduced by **doping in semiconductors** that change their electrical properties. Such materials are widely used in electronics industry. Solids show many types of magnetic properties like **paramagnetism**, **diamagnetism**, **ferromagnetism**, **antiferromagnetism** and **ferrimagnetism**. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures.

Exercises

- 1.1 Define the term 'amorphous'. Give a few examples of amorphous solids.
- 1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?
- 1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.
 - (i) Tetra phosphorus decoxide (P_4O_{10})
 - (ii) Ammonium phosphate $(NH_4)_3PO_4$
 - (iii) SiC
 - (iv) I_2
 - (v) P_4
 - (vi) Plastic
 - (vii) Graphite
 - (viii) Brass
 - (ix) Rb
 - (x) LiBr
 - (xi) Si
- 1.4
 - (i) What is meant by the term 'coordination number'?
 - (ii) What is the coordination number of atoms:
 - (a) in a cubic close-packed structure?
 - (b) in a body-centred cubic structure?
- 1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.
- 1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

- 1.7 How will you distinguish between the following pairs of terms:
(i) Hexagonal close-packing and cubic close-packing?
(ii) Crystal lattice and unit cell?
(iii) Tetrahedral void and octahedral void?
- 1.8 How many lattice points are there in one unit cell of each of the following lattice?
(i) Face-centred cubic
(ii) Face-centred tetragonal
(iii) Body-centred
- 1.9 Explain
(i) The basis of similarities and differences between metallic and ionic crystals.
(ii) Ionic solids are hard and brittle.
- 1.10 Calculate the efficiency of packing in case of a metal crystal for
(i) simple cubic
(ii) body-centred cubic
(iii) face-centred cubic (with the assumptions that atoms are touching each other).
- 1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.
- 1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?
- 1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium using its atomic mass 93 u.
- 1.14 If the radius of the octahedral void is r and radius of the atoms in close-packing is R , derive relation between r and R .
- 1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .
- 1.16 Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?
- 1.17 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.
- 1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?
- 1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.
- 1.20 Classify each of the following as being either a p-type or a n-type semiconductor:
(i) Ge doped with In
(ii) Si doped with B.

- 1.21 Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?
- 1.22 In terms of band theory, what is the difference
(i) between a conductor and an insulator
(ii) between a conductor and a semiconductor?
- 1.23 Explain the following terms with suitable examples:
(i) Schottky defect (ii) Frenkel defect (iii) Interstitials and (iv) F-centres.
- 1.24 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(i) What is the length of the side of the unit cell?
(ii) How many unit cells are there in 1.00 cm³ of aluminium?
- 1.25 If NaCl is doped with 10⁻³ mol % of SrCl₂, what is the concentration of cation vacancies?
- 1.26 Explain the following with suitable examples:
(i) Ferromagnetism
(ii) Paramagnetism
(iii) Ferrimagnetism
(iv) Antiferromagnetism
(v) 12-16 and 13-15 group compounds.

Answers to Some Intext Questions

- 1.14 4
- 1.15 Total number of voids = 9.033×10^{23}
Number of tetrahedral voids = 6.022×10^{23}
- 1.16 M₂N₃
- 1.18 ccp