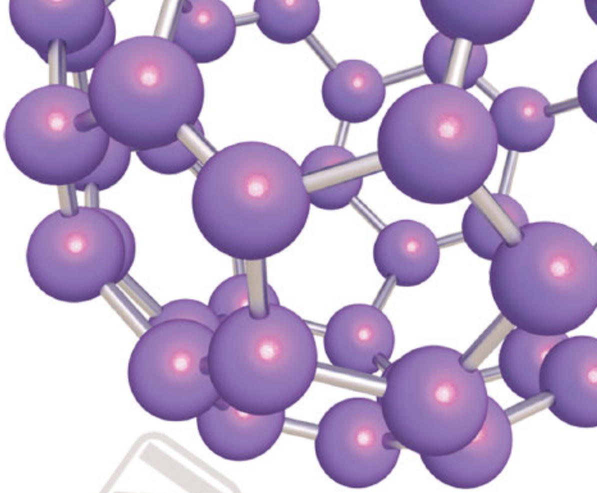


UNIT 5A SOLID STATES

OBJECTIVES

Building on.....

Assessing.....

Preparing for Competition.....

SOLID STATE OF MATTER

The properties of the solids not only depend upon the nature of the constituents but also on their arrangements and the types of forces which hold the constituent particles together in a tightly packed arrangement.

GENERAL CHARACTERISTICS OF SOLID STATE

Some of the important **characteristic properties** of solids are :

(*i*) Solids have definite mass, volume and shape.

(*ii*) The intermolecular distances in solids are short and intermolecular forces are strong.

(*iii*) The constituent particles (atoms, ions or molecules) of solids have fixed positions and can only oscillate about their mean positions.

(*iv*) Solids are almost incompressible and rigid.

(*v*) The density of solids is greater than that of liquids and gases.

(*vi*) Solids diffuse very slowly as compared to liquids and gases.

(*vii*) Most solids become liquids when heated. This process is known as **melting** and the temperature at which a solid changes into a liquid is called the **melting point**. The melting point of a solid depends upon the nature of the solid and melting points of solids vary widely.

CLASSIFICATION OF SOLIDS

Solids can be classified on the basis of nature of order present in the arrangement of constituent particles (atoms, ions or molecules) into two types as:

1. Crystalline solids
2. Amorphous solids

1. Crystalline solids

The substances whose constituent particles (atoms, ions or molecules) are arranged in a definite geometric pattern in three dimensional space *are called* **crystalline solids.**

X-ray diffraction studies of crystalline solids reveal that in these solids, the constituents (atoms, ions or molecules) are arranged in a definite orderly arrangement. The regular arrangement of the constituents extends throughout the three dimensional network of crystals. In other words, the crystalline substances are said to have **long range order**. This means that in crystalline solids, there is a regular pattern or arrangement of particles which repeats itself periodically over the entire crystal. In fact, a crystalline solid consists of a large number of small crystals, each of them having a definite characteristic geometrical shape.

Most of the substances (elements and compounds) form crystalline solids. For example, the elements like copper, silver, iron, sulphur, phosphorus and iodine and common compounds such as sodium chloride, potassium nitrate, zinc sulphide, quartz, etc. all form crystalline solids.

2. Amorphous solids

The substances whose constituent particles are not arranged in any regular arrangement *are called* **amorphous solids** (Greek *amorphos* meaning no form).

The amorphous solids have a random, disordered arrangement of constituents. Therefore, they do not have definite shape or form like crystalline solids. It is observed that some amorphous solids have some orderly arrangement but it is not extended to more than a few Angstrom units. Thus, the amorphous solids are said to have **short range order.** This means that in amorphous solids, a regular and periodically repeating pattern is observed over short distances only. These regular patterns are scattered and in between, the arrangement is disordered.

The common examples of amorphous solids are glass, rubber, plastic, coal, etc.

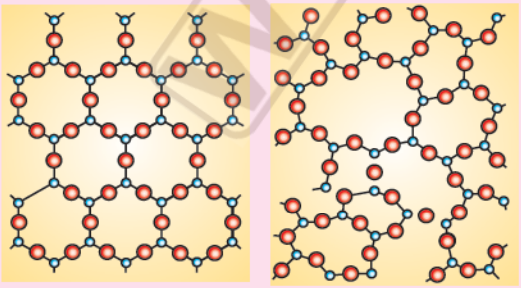
Differences between Crystalline and Amorphous solids

The important differences between crystalline and amorphous solids are :

1. Characteristic geometry. *The crystalline solids have definite regular geometry because of orderly arrangement of constituents (atoms, molecules or ions) in three dimensional space.* On the other hand, amorphous solids do not possess any regular arrangement of constituent particles and therefore, do not have any definite geometric shape.

Structure of quartz (crystalline) and quartz glass (amorphous)

Quartz is a form of SiO_2 (silica). It has tetrahedral SiO_4 units which are orderly arranged in crystalline quartz as shown in Fig. 1 (*a*). In this arrangement, SiO_4 tetrahedra are connected to one another such that oxygen atom of each SiO_4 tetrahedral is shared with another atom. When SiO_2 is melted and the melt is cooled, it forms quartz glass which is amorphous. In this state, the SiO_4 units are randomly joined [Fig 1 (*b*)]. Thus, in quartz (crystalline), SiO_4 units are orderly arranged while in quartz glass (amorphous), the SiO_4 units are randomly arranged. While the two structures are almost identical, yet in case of amorphous quartz glass, there is no long range order. The structure of amorphous solids is similar to that of liquids.



(*a*) Crystalline quartz (*b*) Amorphous quartz glass

Fig.1. Two dimensional structure of (*a*) crystalline quartz and (*b*) quartz glass.

2. Melting points. *The crystalline solids have sharp melting points.* On the other hand, amorphous solids do not have sharp melting points. Therefore, crystalline solids have definite enthalpies of fusion whereas amorphous solids do not have definite enthalpies of fusion. The amorphous solids, in fact, on heating first soften and then melt over a range of temperature. Therefore, amorphous solids can be moulded and blown into various shapes. For example, when glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change into liquid state. Therefore, glass can be moulded and given any desired shape.

It has been observed that on heating and then cooling slowly (*i.e.,* annealing) some amorphous solids become crystalline at some temperature. It is for this reason that **some glass objects from ancient civilizations are found to become milky in appearance.** Milkiness of glass is due to the fact that it undergoes heating during the day and cooling at night (i.e., annealing) over a number of years. As a result, it acquires some crystalline character.

R U Curious...

❑ ***Glass window panes of very old buildings are found to be slightly thicker at the bottom than at the top.***

▸ Glass is an amorphous solid which is super cooled liquid of very high viscosity and behaves more or less like a liquid. The glass flows down very slowly and hence makes the bottom portion slightly thicker.

3. Isotropy and anisotropy. In crystalline substances, some of the physical properties such as electrical conductivity or refractive index have different values when measured along different directions in the same crystals. **Such substances which have physical properties different in different directions** are called **anisotropic.** Thus, *crystalline substances are anisotropic.*

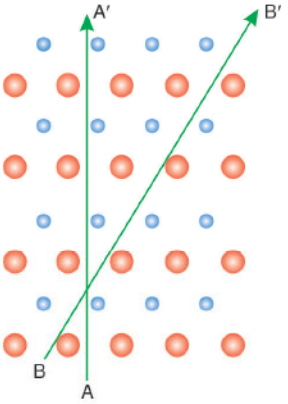


Fig. 2. Anistropy in crystalline substances.

On the other hand, **amorphous substances have physical properties same in all directions** and are called **isotropic.** For example, the velocity of light passing through a crystal varies with the direction in which it is measured. Thus, anisotropy is a strong evidence for the existence of orderly arrangement in crystalline solids. This is shown in Fig 2. In this figure, a simple two dimensional arrangement of two different kinds of atoms is shown. It is clear from the figure that if the properties are measured along two different directions AA′ and BB′, different types of particles come on the way. Along AA′ direction only one type of particles come on the way while along BB′ direction, alternate types of particles come on the way. Hence, the crystalline solids have different physical properties in different directions. In amorphous solids, the constituent particles are arranged at random and in disorderly manner and therefore, all directions are identical and all properties are same in all directions.

4. Cleavage. *Crystalline solids can be cleaved along definite planes.* When cut with a sharp edged tool *(e.g.* knife) they split into two pieces and the newly generated surfaces are plain and smooth. On the other hand, amorphous solids cannot be cleaved along definite planes. When cut with a sharp edged tool (*e.g.*, knife) they undergo irregular breakage and split into two pieces with irregular surfaces. This is shown in Fig 3.

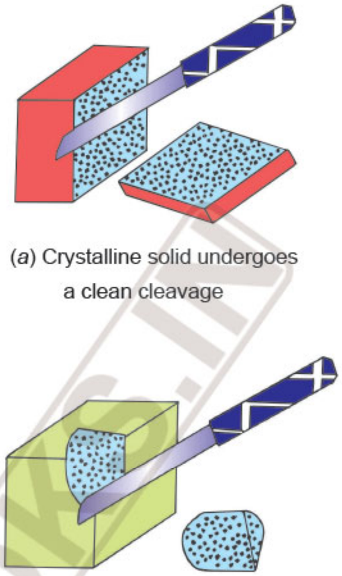


Fig. 3. Cleavage of (*a*) crystalline and (*b*) amorphous solid

Learning Plus

Pseudo solids or Super cooled liquids

Like liquids, amorphous solids have a tendency to flow. Therefore, sometimes these are also called **pseudo solids** or **super cooled liquids.** Glass is a common example of pseudo solid. It softens on heating to a certain temperature. It behaves more or less like a fluid. Pitch is another example of pseudo solid.

Thus, the pseudo solids possess the following characteristics:

(*i*) They do not have sharp melting point but soften over a range of temperature.
(*ii*) They can be easily distorted by applying force.
(*iii*) They can flow slowly under their own weight and lose shape.

The important differences between crystalline solids and amorphous solids are summed up below :

Table 1. Distinction between crystalline and amorphous solids.

Property	Crystalline solids	Amorphous solids
1. Shape	The crystalline solids have definite characteristic shape.	The amorphous solids have irregular shapes.
2. Order in arrangement of constituent particles.	They have regular arrangement of the constituent particles. They are said to exhibit long range order.	They donot have any regular arrangement of the constituent particles. They may have short range order.
3. Melting point	They have sharp and characteristic melting point.	They donot have sharp melting point. They gradually soften over a range of temperature.
4. Enthalpy of fusion	They have a definite and characteristic enthalpy of fusion.	They donot have definite enthalpy of fusion.
5. 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.
6. Anisotropy	They are anisotropic and have different physical properties in different directions.	They are isotropic and have same physical properties in all directions.
7. Nature	They are true solids	They are pseudo solids and supercooled liquids.
Common examples	Copper, silver, iron, common salt, zinc suphide, potassium nitrate, etc.	Glass, rubber, plastics, etc.

REMEMBER

- The substances which show same physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in all directions are called **isotropic substances**.
- The substances which show different physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in different directions are called **anisotropic substances**.

⇒ **Crystalline substances exhibit anisotropy while amorphous substances exhibit isotropy.**

⇒ **Liquids and gases are also isotropic.**

Uses of Amorphous Solids

Amorphous solids such as glass, rubber, plastic, etc. find many uses in our daily lives because of their unique characteristics. For example,

(*i*) The most widely used amorphous solids are *inorganic glasses* which are used in construction, houseware, laboratoryware, etc.

(*ii*) Amorphous silicon is the best photovoltaic material for converting the sunlight into electricity (in photovoltaic cells).

(*iii*) Rubber is also an amorphous solid which is used in making tyres, shoe soles, etc.

(*iv*) A large number of plastics which are amorphous solids are used in making articles of daily use.

CLASSIFICATION OF CRYSTALLINE SOLIDS

The crystalline solids can be classified into following four types depending upon the nature of intermolecular forces operating in them.

1. Molecular solids *2. Ionic solids*
3. Metallic solids *4. Covalent or network solids*

1. Molecular solids

These are crystalline substances in which the constituent particles are molecules. The molecules are held together by dispersion forces or London forces, dipole-dipole forces or hydrogen bonds. These are further subdivided into the following categories :

(*a*) Non-polar molecular solids. *These are those crystalline substances in which the constituent particles are either atoms like those of noble gases (helium, neon, argon, etc.) or non-polar molecules.* For example, solid helium, solid argon, solid hydrogen, solid carbon dioxide, iodine, etc. In these solids, the atoms or molecules are held by weak dispersion forces or London forces.

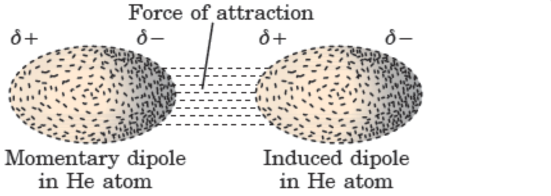


Fig. 4. Weak dispersion or London forces in solid He

These solids have the following characteristics:

(*i*) They are generally soft.

(*ii*) They have low melting points.

(*iii*) They are usually in liquid or gaseous state at room temperature and pressure.

(*iv*) They are non-conductors of electricity because they consist of neutral molecules in solid as well as in dissolved state.

(*b*) Polar molecular solids. *These comprise of molecules of substances formed by polar covalent bonds.* For example, solid HCl, solid SO_2, solid NH_3, etc. The molecules in such solids are held together by relatively stronger dipole - dipole forces.

Fig. 5. Dipole – dipole forces in solid HCl

They have characteristics similar to non-polar covalent molecules as given below :

(*i*) These solids are also soft.

(*ii*) They are non-conductors of electricity.

(*iii*) They have low melting and boiling points. But their melting and boiling points are higher than those of non-polar molecular solids.

(*iv*) Because their melting and boiling points are not very high, most of these are gases or liquids under room temperature and pressure conditions.

(*c*) Hydrogen bonded molecular solids. *The molecules of such solids contain hydrogen bonds between them.* For example, in case of solid water (ice), the negative end of one molecule ($O^{\delta-}$) attracts the positive end of a neighbouring molecule ($H^{\delta+}$) forming hydrogen bond between O and H. These solids contain hydrogen bonds between H and highly electronegative elements; F, O or N. These solids have the following characteristics :

(*i*) They are generally volatile liquids or soft solids under room temperature and normal pressure conditions.

(*ii*) They are non-conductors of electricity.

(*iii*) Their melting and boiling points are generally higher than those of non polar molecular solids and polar molecular solids.

2. Ionic Solids

Ionic solids consist of positively and negatively charged ions arranged in a regular manner throughout the solid. The ions are held together by strong coulombic (or electrostatic) forces. Thus, in ionic solids, the constituent particles are **ions.**

The regular arrangement of ions extends continuously throughout the crystal. For example, in sodium chloride, Na^+ and Cl^- ions have a definite regular arrangement as shown in Fig. 6. In this arrangement, each Na^+ is surrounded by six Cl^- ions and each Cl^- is surrounded by six Na^+ ions.

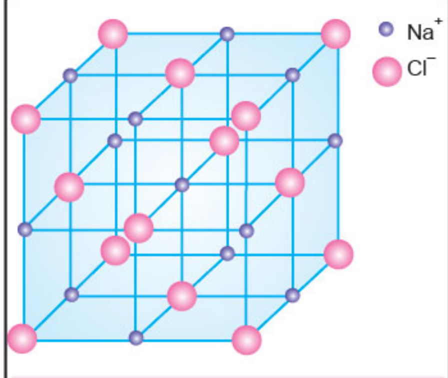


Fig. 6. Structure of sodium chloride.

Similar regular arrangements are also observed in other ionic solids. The main characteristics of ionic crystals are :

(*i*) Ionic solids are very hard and brittle.

(*ii*) They have very high melting and boiling points.

(*iii*) They are poor conductors of electricity and, therefore, are insulators in solid state. This is because in the solid state, the ions are not free to move about. However, in the molten state or when dissolved in water (aqueous solution), the ions become free to move about and they conduct electricity.

(*iv*) They have high enthalpies of vaporisation.

(*v*) Ionic crystals are soluble in water and also in other polar solvents. They are insoluble or very slightly soluble in non-polar solvents such as benzene, carbon tetrachloride, carbon disulphide.

The common examples of ionic crystals are : salts like NaCl, KNO_3, LiF, Na_2SO_4, etc.

3. Metallic solids or crystals

In metallic crystals, the constituent particles are positive ions (called kernels) immersed in a sea of mobile electrons. This is shown in Fig. 7.

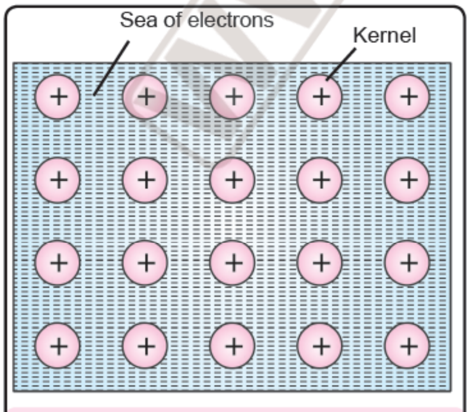


Fig. 7. Electron sea model for a metal.

The electrons in metallic crystals are mobile and are evenly spread throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free mobile electrons are responsible for high electrical and thermal conductivities of metals. When electric field is applied, these electrons flow through the network of positive ions (called *kernels*). Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout the crystal by free electrons. **The forces present between the metal ions** are **metallic bonds**. The main characteristics of metallic crystals are :

(*i*) Metallic crystals may be hard as well as soft.

(*ii*) They are good conductors of heat and electricity.

(*iii*) They have metallic lustre and colour in certain cases.

(*iv*) They are malleable and ductile. Due to malleable nature, they can be beaten into sheets and drawn into wires.

(*v*) They have moderate enthalpies of fusion.

The examples of metallic crystals are **common metals such as nickel, copper and alloys.**

4. Covalent or network solids or crystals

In covalent crystals, the constituent particles are non-metal atoms which are linked to the adjacent atoms by covalent bonds throughout the ***crystal.*** In other words, there is a continuous network of covalent bonds forming a giant three dimensional structure. They are also called **giant molecules.** Covalent bonds are strong and directional in nature and therefore, atoms in these solids are held very strongly at their positions. The important characteristics of covalent crystals are :

(*i*) The covalent crystals are hard.

(*ii*) They have extremely high melting points and may even decompose before melting.

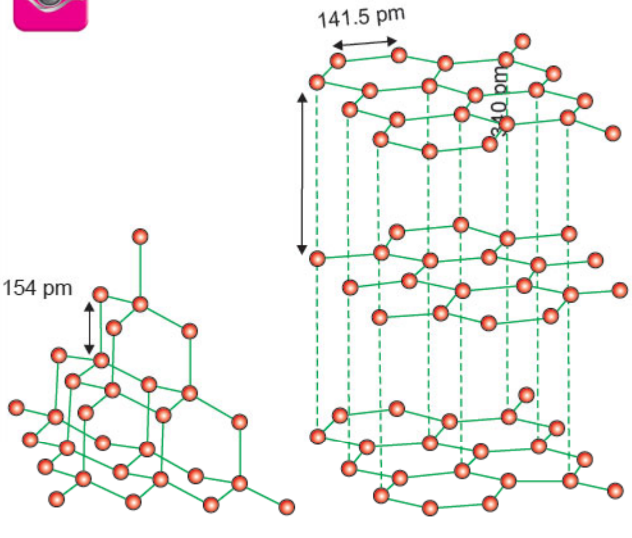
(*iii*) They are poor conductors of electricity and are insulators.

The common examples of covalent crystals are : diamond, carborundum (silicon carbide), quartz (SiO_2), boron nitride (BN), etc.

Diamond is a typical example of covalent crystal. It has a network structure consisting of a very large number of carbon atoms bonded to each other. Each carbon atom is bonded to four other carbon atoms by single covalent bonds. It is clear from Fig. 8 *(a)*, that each carbon atom lies at the centre of a regular tetrahedron and the other four carbon atoms are present at the corners of the tetrahedron. Therefore, there is a three dimensional network of strong covalent bonds. *This makes diamond an extremely hard crystal with very high melting point (3843 K)*. Since all the valence electrons of carbon are strongly held in carbon-carbon bonds, *diamond is a poor conductor of electricity*.

Graphite is also a covalent solid but it is *soft and a good conductor of electricity*. Its **exceptional**

properties are due to its typical structure as shown in Fig. 8 (*b*).



(*a*) Diamond (*b*) Graphite

Fig. 8. Structure of (*a*) diamond and (*b*) graphite

In graphite, carbon atoms are arranged in different layers consisting of hexagonal rings. In these layers, each carbon atom is covalently bonded to three other neighbouring carbon atoms by single covalent bonds in the same layer. The fourth valence electron of each carbon atom is present between different layers and is free to move about. Because of the presence of free electrons, *graphite is a good conductor of electricity.* Further, the different layers are separated by a large distance (340 pm), which is greater than carbon-carbon bond length. This suggests that only weak van der Waals forces are present between these layers and therefore, these layers can slide one over the other. This makes *graphite a soft solid and a good solid lubricant.*

Learning Plus

- In **diamond,** each carbon atom is ***sp***^{3} **hybridised.**
- In **graphite,** each carbon atom is ***sp***^{2} **hybridised.**

R U Curious...

- ***Graphite is a good conductor of electricity, though it is a non-metal.***

❑ Graphite is a covalent solid but it is soft and a good conductor of electricity. Its exceptional behaviour is because of its typical structure having π-delocalised electrons in hexagonal rings which are free to move.

The main characteristics of various types of crystals are summed up in Table 2.

Table 2. Summary of the characteristics of various types of solids

Type of Solid	Constituent particles	Bonding/ attractive forces	Examples	Physical properties: Physical nature	Melting point	Approx binding energy (kJ mol^{-1})	Electrical conductivity
1. Molecular	Small covalent molecules					Less than 40	Insulators
(*i*) Non-polar	Non polar molecules or atoms of noble gases	Dispersion or London forces	Solid CO_2, argon, H_2, I_2, CCl_4, CH_4	Soft	Very low		
(*ii*) Polar	Polar molecules	Dipole- dipole interactions	HCl, SO_2	Soft	Low		
(*iii*) Hydrogen bonded	Molecules containing H bonded to F, O or N	Hydrogen bonding	Ice (H_2O)	Hard	Low		
2. Ionic solids	Positive and negative ions $BaSO_4$, LiF	Strong electrostatic or coulombic forces	NaCl, MgO, BaO, CaF_2, ZnS, KCl,	Hard but brittle	Very high (~ 1500K)	400–4000	Insulators in solid state but conductors in molten state and in aqueous solution.
3. Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding [electric attraction between kernels (positive ions) and electrons]	Common metals (Cu, Ag, Fe, Mg) and some alloys	Hard but malleable and ductile	Moderate to high m pt. (800–1000 K)	70–1000	Good conductors of heat and electricity
4. Covalent or network solids	Atoms	Covalent (electron sharing) bonding	Quartz (SiO_2) SiC, diamond (C) AlN graphite (C)	Hard Soft	Very high (~ 4000K)	150–500	Insulators (except graphite which is conductor)

Learning Plus

- It may be noted that some substances adopt different structural arrangements under different conditions. Such arrangements are called **polymorphs** (meaning *many forms*). For example, diamond and graphite are two different polymorphic forms of carbon.

  Polymorphic forms are also called **allotropes**. These different structures have different properties such as melting point, density, etc. For example, as we know, graphite is soft and a good conductor of electricity while diamond is hard and a poor conductor of electricity.

Isomorphism and Polymorphism

- The existence of two or more crystalline solids having similar chemical composition in the same crystalline form or structure is called isomorphism (*iso*–same, *morphous*–form). For example, Na_3PO_4 and Na_3AsO_4 are isomorphs.
- The existence of a particular substance in more than one crystalline forms is called **polymorphism.** For example, calcium carbonate exists in two crystalline forms known as **calcite** and **aragonite.**

❑ In case of elements, polymorphism is also called **allotropy.**

SOLVED EXAMPLES

❑ **Example 1.**

Classify the following as amorphous or crystalline solids :

(i) Naphthalene (ii) Teflon (iii) Polyurethane (iv) Benzoic acid (v) Potassium nitrate (vi) Cellophane (vii) Polyvinyl chloride (viii) Fibre glass (ix) Copper (x) Zinc sulphide **N.C.E.R.T.**

Solution :

Amorphous solids : (*ii*) Teflon (*iii*) Polyurethane (*vi*) Cellophane (*vii*) Polyvinyl chloride (*viii*) Fibre glass

Crystalline solids : (*i*) Naphthalene (*iv*) Benzoic acid (*v*) Potassium nitrate (*ix*) Copper (*x*) Zinc sulphide.

❑ **Example 2.**

Classify the following solids as ionic, metallic, molecular, network (covalent) or amorphous :

(i) Tetraphosphorus decaoxide (P_4O_{10}) (ii) Graphite (iii) SiC (iv) Brass (v) Rubidium (vi) I_2 (vii) Ammonium phosphate, $(NH_4)_3PO_4$ (viii) LiBr (ix) Si (x) Plastics (xi) P_4 (xii) Solid CO_2. **N.C.E.R.T.**

Solution : The solids are classified as :

Ionic : $(NH_4)_3PO_4$, LiBr
Metallic : Brass, Rubidium
Molecular : P_4O_{10}, I_2, P_4, solid CO_2
Network (covalent) : Graphite, SiC, Si
Amorphous : Plastics.

CRYSTAL LATTICE OR SPACE LATTICE AND UNIT CELL

The crystalline solids have definite orderly arrangement of their constituent particles in three dimensions. The positions of these particles in a crystal, relative to one another, are usually shown by points. The arrangement of an infinite set of these points is called **space lattice**. The positions which are occupied by the atoms, ions or molecules in the crystal lattice are called **lattice points** or **lattice sites.**

To understand space lattice, let us first learn about two dimensional lattices and then three dimensional lattices.

A. Two Dimensional Lattices

A **two dimensional lattice** *is a regular arrangement of constituent particles (atoms, ions or molecules) in a plane.* A two dimensional pattern is shown in Fig. 9 (*a*) and the lattice is shown by points in Fig. 9 (*b*).

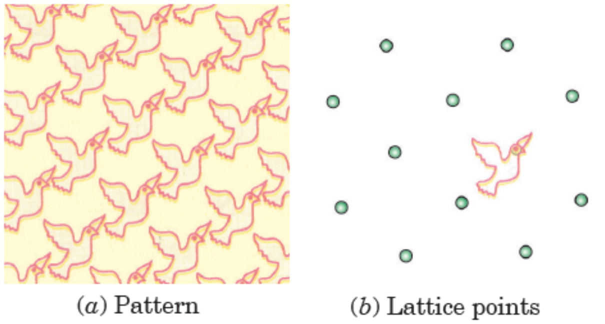
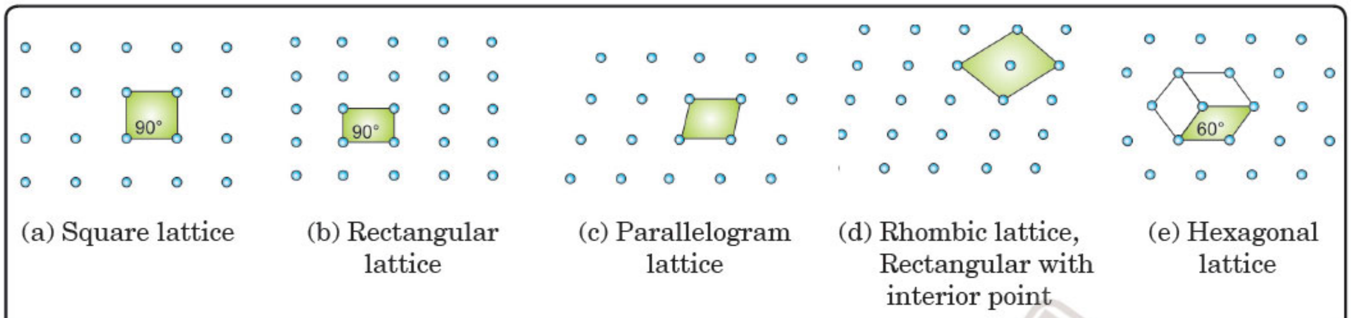

(*a*) Pattern (*b*) Lattice points

Fig. 9. Two dimensional pattern

There are **five types of two dimensional lattices.** These are, square, rectangular, parallelogram, rhombic and hexagonal lattice as shown in Fig. 10 ahead. These differ in symmetry of the arrangement of points. *The hexagonal lattice has the most symmetrical arrangement of points while parallelogram lattice has the least symmetrical arrangement* of points.



(a) Square lattice (b) Rectangular lattice (c) Parallelogram lattice (d) Rhombic lattice, Rectangular with interior point (e) Hexagonal lattice

Fig. 10. Five different two dimensional lattices.

Because of the regular repeating arrangement of the points in a two dimensional lattice, we need only to describe a small part of the lattice (called **motif**) in order to specify it completely. For example, we select four points in two dimensional lattice and connect them to give a parallelogram. This smallest part is known as **unit cell.** We can generate the complete lattice by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge as shown in Fig. 11.

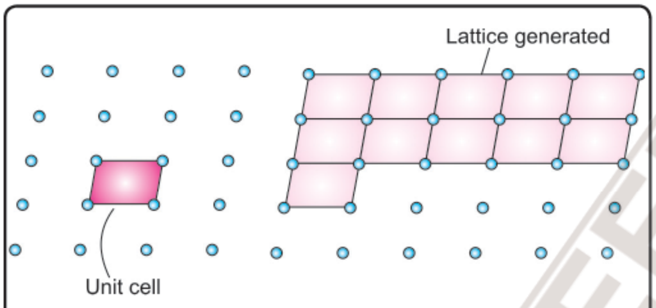


Fig. 11. (*a*) A unit cell (*b*) The complete lattice generated by repeatedly moving the unit cell in the direction of its cell edges by distance equal to cell edge.

Thus, **the unit cell gives the shape of the entire lattice.** However, it may be noted that for any given lattice, the unit cells may be chosen in many different ways. This is because a lattice contains a very large number of atoms and numerous identical points may be found. Naturally, a question arises. "What are the characteristics of this unit cell?" The most convenient cell is the smallest unit cell which has the full symmetry of the lattice. For the square, rectangular and parallelogram lattices, the unit cells chosen are the square, the rectangle and the parallelogram respectively. However, for the hexagonal lattice the unit cell is a rhombus with an angle of 60°.

For the rhombic lattices, a rectangular unit cell with an interior point is generally selected. A cell with an interior point is called a **centered unit cell.** The unit cells which do not contain any interior point are called **primitive unit cells.**

Thus, we see that for describing a two dimensional lattice, we must specify the unit cell by the lengths of the edges and the angles between them.

Thus, the five two dimensional lattices and their unit cells are :

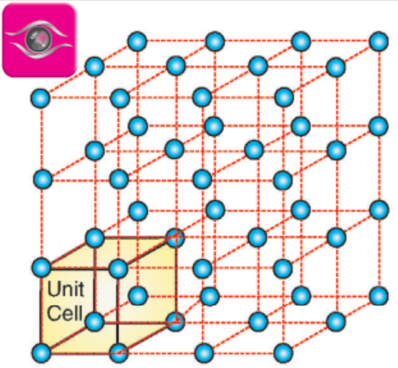
Two dimensional lattice	Unit cell
(*a*) Square lattice	Square
(*b*) Rectangular lattice	Rectangle
(*c*) Parallelogram lattice	Parallelogram
(*d*) Rhombic lattice	Rectangular with an interior point
(*e*) Hexagonal lattice	Rhombus with an angle of 60°

B. Three Dimensional Crystal Lattice

The crystalline solids have definite three dimensional arrangement of constituent particles (atoms, ions or molecules). If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically by depicting each particle by a point, the arrangement is called crystal lattice or space lattice. Thus, **a crystal lattice** is a

> ***regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.***

A three dimensional crystal lattice is shown in Fig. 12.



Space Lattice Showing Unit Cell

Fig. 12. Three dimensional lattice.

Like two dimensional lattice, if we carefully look a crystal lattice, it is observed that we can select a group of lattice points (a smallest three dimensional portion) which is repeated over and over again in the whole crystal lattice. This smallest repeating pattern (motif) is called the unit cell. Thus, a **unit cell** may be defined as :

the smallest three dimensional repeating portion of a space lattice which when repeated over and again in different directions produces the complete crystal lattice.

This smallest repeating pattern (unit cell) represents the shape of the entire crystal. We can generate the complete lattice by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge. In fact, the crystal may be considered to consist of an infinite number of unit cells. The unit cell in the above crystal lattice is shown by solid lines.

Parameters of a Unit cell

A unit cell is characterized by

(*i*) its dimensions (lengths) along the three edges as a, b and c. These edges may or may not be mutually perpendicular.

(*ii*) angles α, β and γ between the pair of edges. The angle α is between the edges b and c, angle β is between the edges c and a and angle γ is between the edges a and b. Thus, a unit cell is characterized by six parameters, a, b, c, α, β and γ. The parameters of a unit cell are shown in Fig. 13. The complete crystal lattice can be obtained by extending the unit cell in all the three directions.

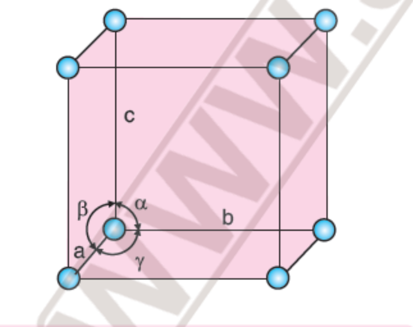


Fig. 13. Parameters of a unit cell.

Characteristics of a Crystal Lattice

Let us sum up the characteristics of a crystal lattice. The following are the characteristics of a crystal lattice.

(*i*) Each point in a crystal lattice is called lattice point or lattice site.

(*ii*) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(*iii*) The three dimensional arrangement of lattice points represents a crystal lattice.

(*iv*) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Types of Unit Cells

There are basically two types of unit cells constituting different crystal systems. These are :

(*i*) *Primitive or simple unit cells*

(*ii*) *Non primitive or centred unit cells.*

(*i*) Primitive unit cells. *These are unit cells which have points (or particles) only at the corners.* These are also called **simple unit cells.**

(*ii*) Non-primitive *or* **centred unit cells.** *These are unit cells which have points (or particles) at the corners as well as at some other positions.*

The centred unit cells are of three types :

(*a*) **Face centred unit cells** *in which the points are present at the corners as well as at the centre of each face.*

(*b*) **Body centred unit cells** *in which the points are present at all the corners as well as at the body centre of the unit cell.*

(*c*) **End centred unit cells** *in which the points are present at all the corners and at the centre of two opposite faces.*

Seven Crystal Systems

When a unit cell in a crystal lattice has lattice points only at its corners it is called a **simple** or **primitive unit cell.** In all, there are **seven types** of *simple or primitive* unit cells among crystals. These unit cells are characterised by the axial lengths a, b and c and the angles α, β and γ. These are called **seven crystal systems** or **crystal habits.** These are shown in Fig. 14. All crystals can be placed in one of these seven crystal systems. These are :

1. Cubic. All the three axes are of equal length and are at right angles to each other ($a = b = c$, all angles $= 90°$).

2. Tetragonal. The three axes are at right angles to each other but only the two axes are equal ($a = b \neq c$, all angles $= 90°$).

3. Orthorhombic. It has three unequal axes which are at right angles to each other ($a \neq b \neq c$, all angles $= 90°$).

4. Monoclinic. The three axes are of unequal length and two angles are of 90° ($a \neq b \neq c$, two angles $= 90°$ and one angle $\neq 90°$).

5. Hexagonal. It has two edges of equal length ($a = b$) and two angles of 90° and one angle of 120° ($a = b \neq c$, two angles of 90° and one angle of 120°).

6. Rhombohedral or trigonal. The three axes are of equal length which are inclined at the same angle but the angle is not equal to 90° ($a = b = c$, all three angles equal but not equal to 90°).

7. Triclinic. The three axes are of unequal length, and all angles are different but none is perpendicular to any of the others ($a \neq b \neq c$, all angles different and none equal to 90°).

These seven crystal systems are shown in Fig. 14 and are summed up in Table 3.

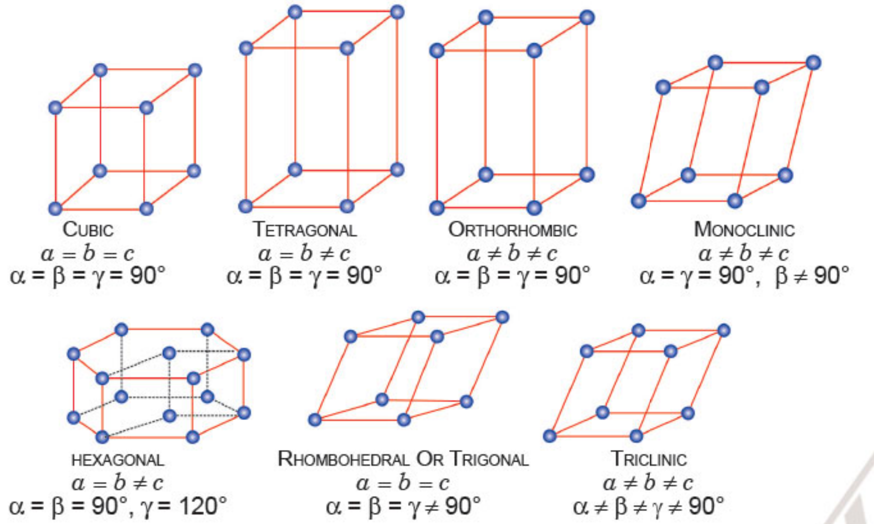


Fig. 14. The seven crystal systems.

REMEMBER

It may be noted that among the seven crystal systems :

⇒ **Cubic is the most symmetrical while**

⇒ **Triclinic is the most unsymmetrical system**

The characteristics of the seven crystal systems are summed up in Table 3.

Table 3. The seven crystal systems.

System	Possible Variations	Axial distances	Axial angles	Examples
Cubic	Primitive Body-centred Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, KCl, Zinc blende, Cu, Ag
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, $PbCO_3$, $BaSO_4$
Monoclinic	Primitive End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4 \cdot 10H_2O$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Graphite, ZnO, BeO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), $NaNO_3$, cinnabar (HgS), quartz, Sb
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3.

It may be noted that all crystals do not have simple lattices *i.e.,* having lattice points only at the corners. In addition, there are some lattices which are different from the simple lattice. For example, if we consider a cubic system, which is simplest of all these seven systems, it is observed that a cube has three types of lattices.

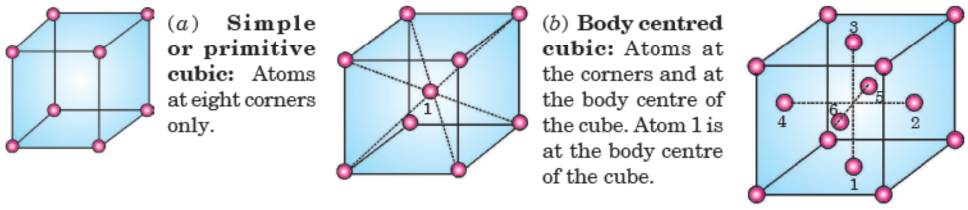
Types of Cubic Lattices

There are three types of cubic unit cells or lattices. These are :

1. Simple or Primitive. *It has points at all the corners of the unit cell.* A primitive cubic unit cell is shown in Fig. 15 (*a*). It consists of one atom at each of the eight corners.

2. Body centred cubic unit cell (*bcc*). *It has points at all the corners as well as at the body centre of the cube* [Fig. 15 (*b*)]. It is labelled as ***bcc***. As shown in the figure, in a body centred cubic unit cell, there are eight atoms at the corners and one at the centre.

3. Face centred cubic unit cell (*fcc*). In this case, *there are points at all the corners as well as at the centre of each face.* It is shown in Fig 15 (*c*). It is labelled as ***fcc***. As shown in the figure, it has eight atoms at the corners and six atoms at the centre of faces.



(*a*) **Simple or primitive cubic:** Atoms at eight corners only.

(*b*) **Body centred cubic:** Atoms at the corners and at the body centre of the cube. Atom 1 is at the body centre of the cube.

(*c*) **Face centred cubic:** Atoms at the corners and centre of each face. Atoms 1, 2, 3, 4, 5, and 6 are present at the centres of six faces (atom 5 corresponds to atom at the centre of back face and atom 6 corresponds to the centre of front face.)

Fig. 15. Three types of cubic lattices.

Similarly, if we consider the other lattices, in addition to simple lattices for other systems, it is observed that there are 14 different types of space lattices. These are known as **14 Bravais lattices** after the name of French mathematician who first described them. These are given in Fig. 16.

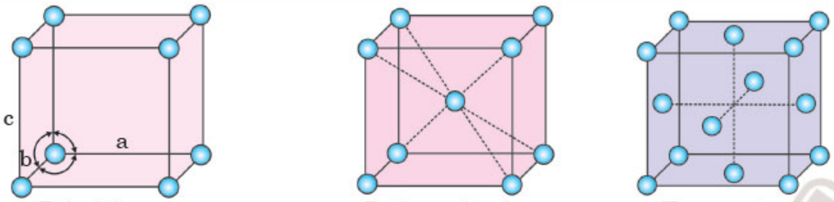
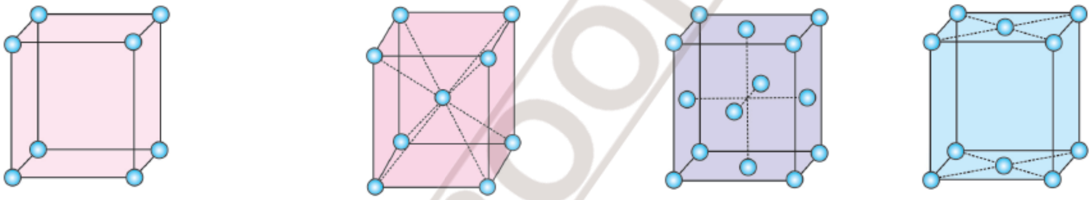
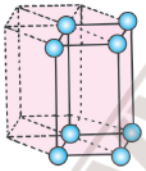
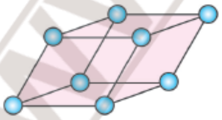
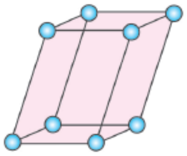
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	 Primitive Body-centred Face-centred
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	 Primitive Body-centred
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	 Primitive Body-centred Face-centred End-centred
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	 Primitive End-centred
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	 Primitive The full hexagonal prism is shown, although the unit cell is just the part shown in solid lines.
Rhombohedral or trigonal $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	 Primitive **REMEMBER** There are **seven crystal systems and fourteen Bravais lattices**
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	 Primitive

Fig. 16. Unit cells of 14 Bravais lattices.

NOTE

It may be noted that there is another type of non-primitive unit cell known as **end centred unit cell**. In this case, there are points (or atoms) at all the corners and at the centres of any two opposite faces.

- There is no end centred cubic unit cell.
- Only orthorhombic and monoclinic crystal systems have end centred unit cells.

TYPES OF CUBIC CRYSTALS AND NUMBER OF ATOMS PER UNIT CELL

We know that a crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule or ion). In different types of unit cells, the particles may be at the corners, at the body centre or, at the centre of faces. Since every unit cell in a crystalline solid is adjacent to other unit cells, most of the atoms (or constituent particles) are shared by neighbouring unit cells. As a result, only some portion of each atom belongs to a particular unit cell. For example, in all types of cubic cells, each corner atom belongs to eight adjacent unit cells as shown in Fig 17(*c*), four unit cells in the same layer and four unit cells of the upper layer. Therefore, only **1/8th of an atom** (or molecule or ion) actually belongs to a particular unit cell.

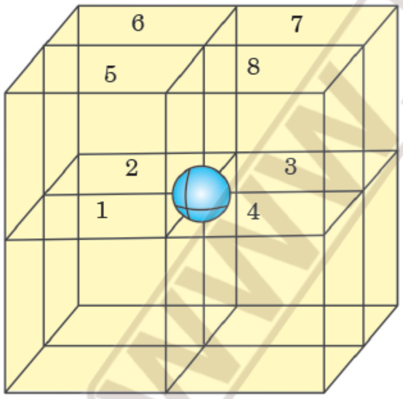


Fig. 17(*a*). A corner atom in cubic unit cell is shared by 8 unit cells.

Similarly, each face centred atom is shared by two unit cells (shown in Fig. 17*b*) and only **1/2 of an atom** (or molecule or ion) belongs to a particular unit cell.

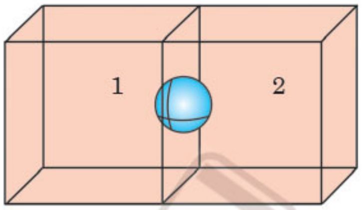


Fig. 17(*b*). A face centred atom in a cubic unit cell is shared by two unit cells.

An atom at the body centre of a unit cell is not shared by other unit cells and it **completely belongs to the unit cell** (Fig. 17*c*).

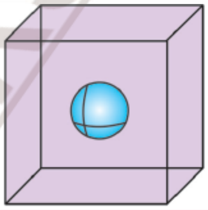


Fig. 17(*c*). A body centred atom in any cubic unit cell is not shared by any other unit cell.

Thus, the contribution of each atom to the unit cell is :

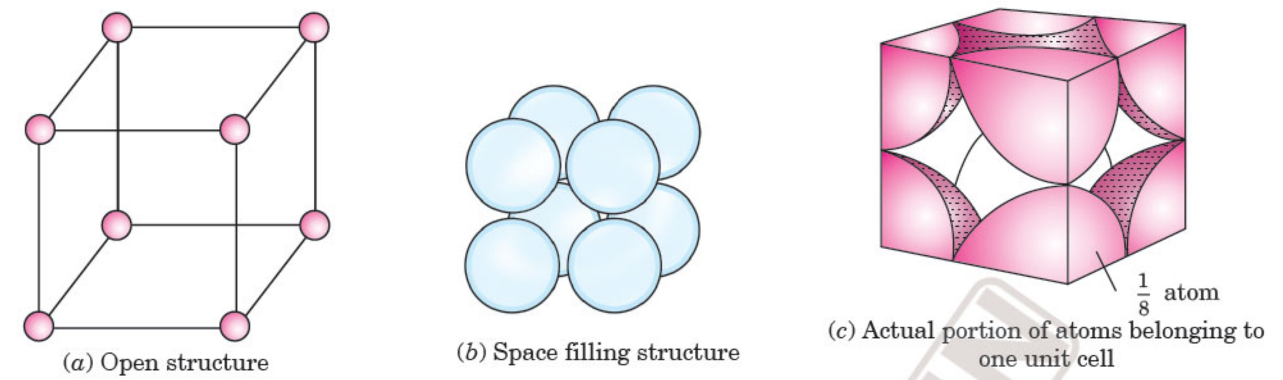
at corner = $\frac{1}{8}$; at the face = $\frac{1}{2}$; within the body = 1

For simplicity assume that the constituent particle is an atom. The unit cell may be represented in **three different ways.**

(*a*) Each small sphere in figure represents only the centre of the particle occupying that position and not its actual size. Such type of structures are called **open structures**. It is easier to follow the arrangement of particles in open structures [Fig. 18 (*a*)].

(*b*) **Space filling representation** of the unit cell with actual particle size [Fig. 18 (*b*)]. This gives a more realistic picture showing how the particles actually pack within the solid.

(*c*) **Actual portion** of different atoms present in a unit cell [Fig. 18 (*c*)].



(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 18. Simple cubic arrangement and number of spheres per unit cell.

Let us now **calculate number of atoms** in different types of cubic unit cells.

(*i*) **Simple** or **primitive cubic unit cell**

In this unit cell, *the points (atoms, ions or molecules) are present at all the corners of a cube.* This is shown in Fig. 18 (*a*). It is clear from Fig. 18 (*c*) that atom present at each corner contributes 1/8 to each cube because it is shared by 8 cubes. Now, there are 8 atoms at the corners.

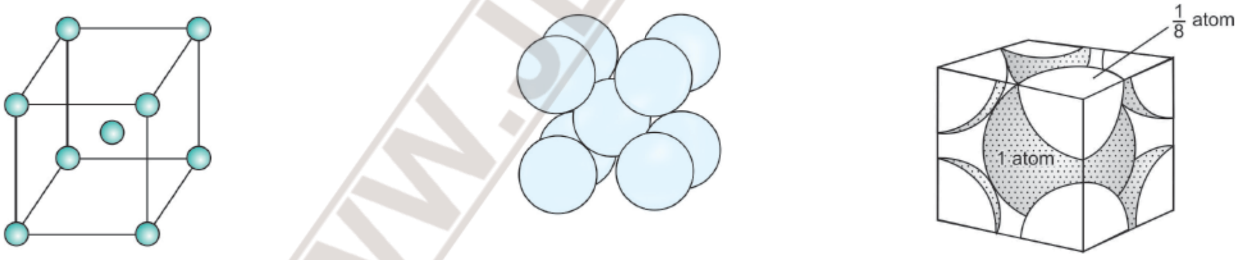
Thus, the number of atoms present in each unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = \mathbf{1\ atom.}$$

Thus, **simple or primitive cubic unit cell has one atom per unit cell.**

(*ii*) **Body centred cubic unit cell**

It has points at all the corners as well as at the body centre of the cube. It is shown in Fig. 19. It is clear from the figure that there are eight atoms at the corners and each is shared by 8 unit cells so that the contribution of each atom at corner is 1/8. In addition, there is one atom in the body of the cube as shown in Fig. 19 (*c*) which is not shared by any other cube.



(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 19. Body centred cubic unit cell.

Thus, the number of atoms present at the corners per unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = 1$$

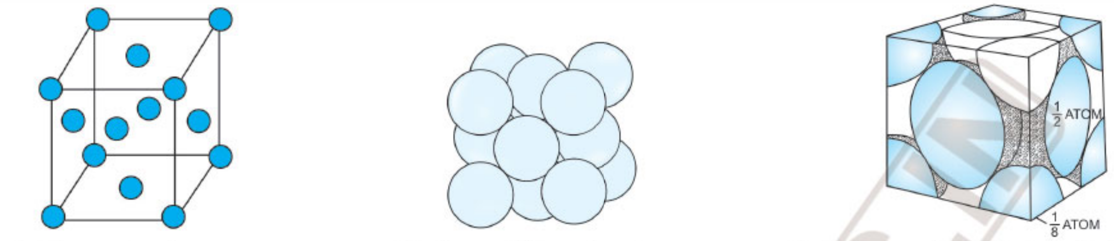
The number of atoms present at the centre of the cube = 1

∴ Total number of atoms in *bcc* arrangement = 1 + 1 = **2**.

Thus, **a body centred cubic unit cell has two atoms per unit cell.**

(*iii*) **Face centred cubic unit cell.**

This is also called cubic close packed unit cell. *It has points at all the corners as well as at the centre of each of the six faces.* It is shown in Fig. 20(*a*). In this arrangement, there is one atom at each of the eight corners. It is clear from Fig. 20 (*b*) that atom present at each corner contributes 1/8 to each cube because it is shared by 8 cubes. In addition, there are six atoms at the faces of the cube and each is shared by two unit cells. Therefore, the contribution of each atom at the face per unit cell is 1/2 [Fig. 20 (*c*)].



(*a*) Open structure (*b*) Space filling structure (*c*) Actual portion of atoms belonging to one unit cell

Fig. 20. Cubic close packed or face centred cubic arrangement and share of each atom per unit cell.

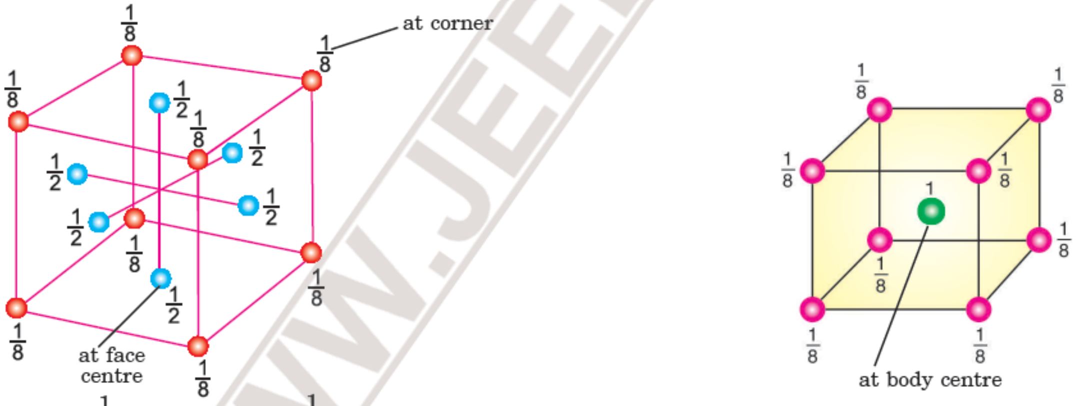
Thus, the number of atoms present at corners per unit cell = 8 corner atoms × $\frac{1}{8}$ atom per unit cell = 1

The number of atoms present at faces per unit cell = 6 atoms at the faces × $\frac{1}{2}$ atom per unit cell = 3

∴ Total number of atoms in ccp or fcc arrangement = 1+ 3 = 4

Thus, **a face centred cubic unit cell has four atoms per unit cell.**

The contribution of atoms and total number of atoms in different types of cubic unit cells are summarized below :



Contribution $\frac{1}{8}$ at corners and $\frac{1}{2}$ at face centres of the atoms in a face centred cell

Contribution of 1 at the body centre

Fig. 21. Contribution of atoms in a cubic unit cell.

REMEMBER

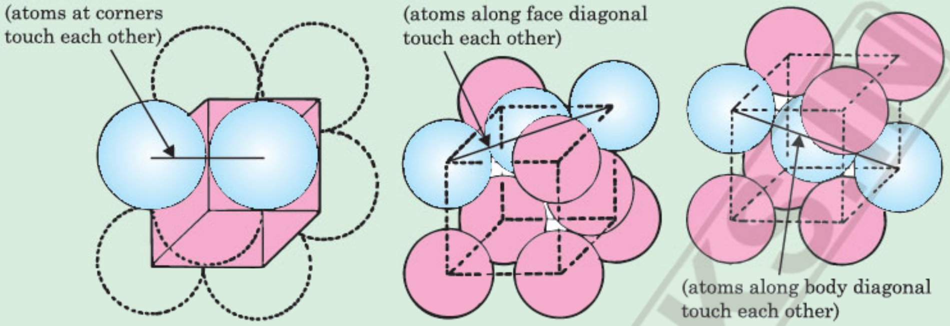
Unit cell	**No. of atoms at corners**	**No. of atoms at faces**	**No. of atoms in centre**	**Total**
Simple cubic or primitive cell	$8 \times \frac{1}{8}$	0	0	1
Body centred cubic	$8 \times \frac{1}{8}$	0	1	2
Face centred cubic	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	0	4

NOTE

It is important to remember that the **atoms (or spheres) at the corners of a simple cube touch each other** [Fig. 22 (*a*)]. However, the atoms at the corners of face centred cube and body centred cube donot touch each other. It may be seen that

- in the face centred cube, the **atoms along the face diagonal of the cube touch each other** [Fig. 22(*b*)].
- in the body centred cube, the **atoms along the body diagonal of the cube touch each other** [Fig. 22(*c*)].

  However, for simplicity, the atoms (or spheres) are shown only at the corners in the figures.



The blue coloured spheres represent the spheres which are touching each other.

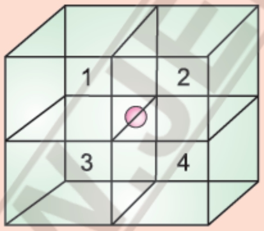
(a) Simple cubic (b) Face centred cubic (c) Body centred cubic

Fig. 22

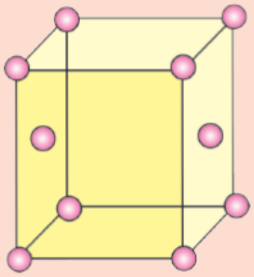
Learning Plus

- **Can you guess the contribution of an atom at the edge centre?**

  An atom present on the edge is shared by four unit cells as shown below:



Therefore, **contribution of each atom on the edge** = 1/4



- **How many atoms will be present in an end centred orthorhombic unit cell?**

  An edge centred orthorhombic unit cell has eight atoms at the corners and two atoms at the centres of two end faces.

  Therefore, total number of atoms per unit cell in end centred unit cell is 8 (corners) × $\frac{1}{8}$ + 2 (end centres) × $\frac{1}{2}$ = **2 atoms**.

▸ It may be noted that there is **no end centred cubic unit cell.**

RELATIONSHIP BETWEEN THE NEAREST NEIGHBOUR DISTANCE (d) AND RADIUS OF ATOM (r) AND THE EDGE OF UNIT CELL (a) FOR PURE ELEMENTS

1. Simple cubic

In a simple cubic arrangement, the atoms at the corners touch each other [Fig. 23].

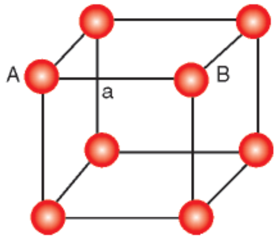


Fig. 23 Simple cubic.

Distance between the nearest neighbours,

$$d = AB = a$$

Radius, $r = d/2 = a/2$

2. Face centred cubic

In a face centred cubic arrangement, the three atoms along the face diagonal touch each other [Fig. 24].

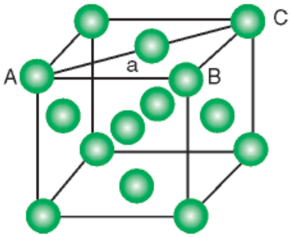


Fig. 24 Face centred cubic.

Distance between the nearest neighbours, $d = \frac{AC}{2}$

Now in right angled ΔABC

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

$$AC^2 = a^2 + a^2 = 2a^2 \quad \text{or} \quad AC = \sqrt{2}\,a$$

$$\therefore \qquad d = \frac{\sqrt{2}\,a}{2} = \frac{a}{\sqrt{2}}$$

Radius, $r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$

3. Body centred cubic

In a body centred cubic arrangement, three atoms along the body diagonal touch each other [Fig. 25].

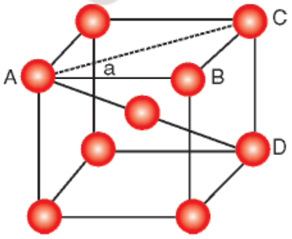


Fig. 25 Body centred cubic.

Distance between nearest neighbours, $d = \frac{AD}{2}$

In right angled ΔABC

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

$$AC^2 = a^2 + a^2 \text{ or } AC = \sqrt{2}\,a$$

Now in right angled ΔADC,

$$AD^2 = AC^2 + DC^2$$

$$AD^2 = \left(\sqrt{2}\,a\right)^2 + a^2 = 3a^2 \text{ or } AD = \sqrt{3}\,.a$$

$$\therefore \qquad d = \frac{\sqrt{3}a}{2}$$

Radius, $r = \frac{d}{2} = \frac{\sqrt{3}}{4}a.$

REMEMBER

The relationship between the nearest neighbour distance and radius of atom (for crystals of pure elements) and the edge of unit cell (a) is summed up below :

Unit cell	Distance between nearest neighbour (d)	Radius (r)
Simple cubic	a	$\frac{a}{2}$
Face centred cubic	$\frac{a}{\sqrt{2}}$ or 0.707 a	$\frac{a}{2\sqrt{2}}$ or 0.3535 a
Body centred cubic	$\frac{\sqrt{3}}{2}a$ or 0.866 a	$\frac{\sqrt{3}}{4}a$ or 0.433 a

It may be noted that for pure elements, $r = \frac{d}{2}$.

SOLVED EXAMPLES

☐ **Example 3.**

A cubic unit cell is made up of X and Y elements. If X are present on the corners of the cube and Y are present on centres of faces of cube, then find the formula of the compound. *(Hr. S.B. 2018)*

Solution : In a cube, X atoms are at the 8 corners, each shared by 8 cubes. Therefore,

The number of X atoms in the unit cell is 8/8 = 1.

Y atoms are at the centres of 6 faces and each face is shared by two cubes. Therefore,

The number of Y atoms = 6/2 = 3

The formula of the compound = XY_3.

☐ **Example 4.**

If three elements P, Q and R crystallise in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centres and R atoms at the centre of the edges, then write the formula of the compound.

(Pb. S.B. 2002)

Solution : As P atoms are present at the 8 corners of the cube. Therefore,

No. of P atoms in the unit cell = $8 \times \frac{1}{8} = 1$

Q atoms are present at the cube centres,

No. of Q atoms in the unit cell = 1

R atoms are present at the edges. Since there are 12 edges and atom at each edge is shared by four atoms. Therefore,

No. of R atoms in the unit cell = $12 \times \frac{1}{4} = 3$

∴ The formula of the compound = $\mathbf{PQR_3}$.

☐ **Example5.**

Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f c c) structure. (Atomic mass of Al = 27 g mol⁻¹).

(A.I.S.B. 2017, D.S.B. 2017)

Solution :

$$\text{Moles of aluminium} = \frac{8.1}{27}\,\text{mol}$$

$$\text{No. of atoms of Al in 8.1 g} = \frac{8.1}{27} \times 6.022 \times 10^{23}$$

$$\text{No. of atoms in one unit cell} = 4(fcc)$$

$$\text{No. of unit cells} = \frac{8.1}{27} \times \frac{6.022 \times 10^{23}}{4}$$

$$= \mathbf{4.5 \times 10^{22}}.$$

☐ **Example 6.**

Tungsten crystallizes in body centred cubic unit cell. If edge of the unit cell is 316.5 pm, what is the radius of the tungsten atom ?

(D.S.B. 2012, CBSE Sample Paper 2017-18)

Solution : If a is the edge length of *bcc* unit cell, then radius of an atom,

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

Here, $a = 316.5$ pm

$$\therefore \quad r = \frac{\sqrt{3}}{4} \times 316.5 \text{ pm}$$

$$= \mathbf{137.04 \text{ pm}}$$

☐ **Example 7.**

Aluminium crystallizes in a fcc structure. Atomic radius of the metal is 125 pm. Calculate the edge length of the unit cell of the metal?

(A.I.S.B. 2013, Karnataka S.B.2014)

Solution : In a face centred cubic structure, radius (r), is related to length of the side (a) as:

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

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

$$r = 125 \text{ pm}$$

$$\therefore \quad a = 2 \times 125 \times 1.414$$

$$= \mathbf{353.3 \text{ nm.}}$$

Practice Problems

1. A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at the body centre. What is the formula of the compound ? *(D.S.B.2006, CBSE Sample Paper 2008)*
2. When atoms are placed at the corners of all 12 edges of a cube, how many atoms are present per unit cell ?
3. A unit cell consists of a cube in which there are A atoms at the corners and B atoms at the face centres and A atoms are missing from 2 corners in each unit cell. What is the simplest formula of the compound ? *(Pb. S.B. 2011)*
4. A compound of X and Y crystallizes in the cubic structure in which Y atoms are at the corners and X atoms are at the alternate faces of the cube. Find the formula of the compound. *(Pb. S.B. 2011, Meghalaya S.B. 2013)*
5. Gold crystallizes in the face centred cubic lattice. Calculate the approximate number of unit cells in 2 mg of gold. (atomic mass of gold = 197 u).
6. Xenon crystallizes in the face centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and radius of xenon atom ?
7. The length of the unit cell edge of a body centred cubic metal crystal is 352 pm. Calculate the radius of an atom of the crystal. *(Nagaland S.B. 2013)*
8. Calculate the atomic radius of elementary silver which crystallises in face centred cubic lattice with unit cell edge length 4.086×10^{-10}m. *(Assam S.B. 2016)*
9. A solid has a structure in which W atoms are present at the corners of the cubic unit cell, O atoms are located at the cube edges and Na atoms are present at cube centres. What is the formula of the compound ?
10. CsCl crystallizes in cubic structure in which Cl^- ions are at the corners and Cs^+ ions occupy centre of the unit cell. If radii of Cs^+ and Cl^- ions are 1.69Å and 1.81Å respectively, calculate the edge length of the unit cell.
11. Tungsten crystallizes in body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten (Atomic mass of tungsten = 184 u). *(Pb. S.B. 2013)*
12. Sodium crystallizes in a *bcc* unit cell. Calculate the approximate number of unit cells in 9.2 g of sodium (Atomic mass of Na = 23 u). *(C.B.S.E. Sample Paper 2011, Assam S.B. 2013)*
13. Gold (atomic radius = 0.144 nm) crystallizes in face centred unit cell. What is the length of the side of the cell? *(Meghalaya S.B. 2017)*

14. In a face centred cubic arrangement of A and B atoms, A atoms occupy the corners and B atoms occupy the face centres of the unit cell. If one of the atoms is missing from the corner in each unit cell, what is the simplest formula of the compound?

Answers to Practice Problems

1. XY	**2.** 1
3. AB_4	**4.** XY
5. 1.528×10^{18} unit cells	**6.** 438.5 pm, 219.25 pm
7. 152.416 pm	**8.** 1.44×10^{-10} m
9. $NaWO_3$	**10.** 4.04 Å
11. 2.45×10^{21} unit cells	**12.** 1.2044×10^{23} unit cells
13. 0.407 mm	**14.** A_7B_{24}

Hints & Solutions on page 57A

CLOSE PACKED STRUCTURES

In the formation of crystals, the constituent particles (atoms, ions or molecules) get *closely packed together*. The closely packed arrangement is that in which *maximum available space is occupied leaving minimum vacant space*. This corresponds to a state of maximum possible density. The closer the packing, the greater is the stability of the packed system.

We know that the constituent particles of crystals may be of varying shapes and, therefore, the mode of closest packing of particles will vary according to their shapes and sizes. However for understanding, we can use identical hard spheres of equal size to represent atoms in a metal in terms of closest packing of identical spheres.

We can build up the three dimensional structure in three steps :

(*a*) Close Packing in one Dimension

There is only one way of arranging spheres in one dimensional close packed structure in which the spheres are placed in a horizontal row touching each other. This is shown in Fig. 26.

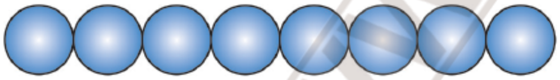


Fig. 26. Close packing of spheres in one dimension.

As can be seen in this arrangement, each sphere is in contact with two of its neighbours.

The *number of nearest neighbours of a particle* is called its co-ordination number.

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

(*b*) Close Packing in two Dimensions

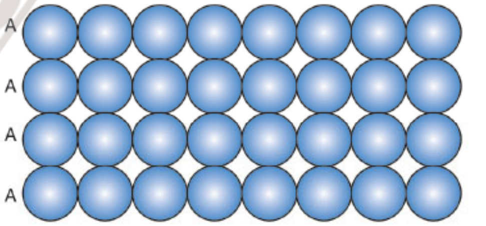
Two dimensional close packed structure can be generated by placing the rows of close packed spheres. The rows can be combined in the following **two ways** with respect to the first row to build a crystal plane.

(*i*) Square close packing or AAA... type arrangement in two dimensions.

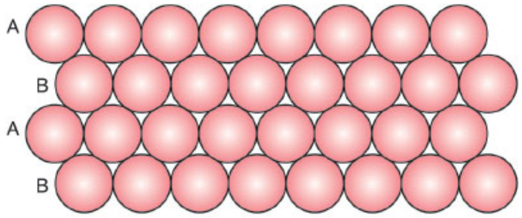
The spheres are packed in such a way that the rows have a horizontal as well as vertical alignment. In this arrangement, the spheres of second row are exactly above those of the first row. The second row is exactly same as the first one. If we label the first row as 'A' type, the second row is also 'A' type. Similarly, we may place more rows to get AAA.... ..... type arrangement as shown in Fig. 27 (*a*). In this arrangement, the spheres are found to form squares. This type of packing is also called ***square close packing in two dimensions.***

(*ii*) Hexagonal close packing or ABABA... type arrangement in two dimensions.

The spheres are packed in such a way that the spheres in the second row are placed in the depressions between the spheres of the first row. Similarly, the spheres in the third row are placed in the depressions between the spheres of the second row and so on. In this arrangement, the second row is different from the first row. But the spheres in third row are aligned with those of the first row. Similarly, the spheres of fourth row are aligned with those of second row. If the arrangement of spheres in first row is called 'A' type, the one in the second row is different and may be called 'B' type. Now, the arrangement of spheres of third row is same as that of first row, and therefore, it is also called 'A' type. Similarly, fourth row is called 'B' type. Hence the arrangement is called ABAB........ type. This type of arrangement is also called *hexagonal close packing of spheres in two dimensions* and is shown in Fig. 27.(*b*) (arrangement II).



Arrangement I
(*a*) Square close packing occupies 52.4% of available space



Arrangement II
(*b*) Hexagonal close packing occupies 60.4% of available space

Fig. 27. Packing of spheres in two dimensions.

A comparison of two ways of packing of spheres shows that in arrangement I, the spheres are less closely packed than in arrangement II. It has been calculated that in arrangement I, only 52.4% of the available space is occupied by the spheres. In the second arrangement, 60.4% of the space is occupied. Therefore, the arrangement II is more efficient and leaves less space unoccupied by spheres. Thus, arrangement II is more economical and it represents a close packing of spheres.

It can be seen that in arrangement I, each sphere is in contact with four other spheres as shown in Fig. 28 (*a*). On the other hand, each sphere is in contact with six other similar spheres in arrangement II as shown in Fig. 28 (*b*).

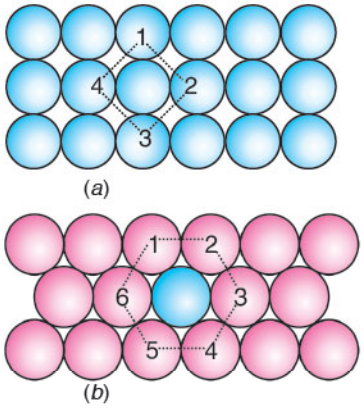


Fig. 28. (*a*) A sphere in square close packing is in contact with four spheres. (*b*) A sphere in hexagonal close packing is in contact with six spheres.

Thus, in two dimensional close packing, the co-ordination number of each sphere in arrangement I (square close packing) is **four** and in arrangement II (hexagonal close packing) is **six**. Thus, the arrangement II represents closest packing of spheres in a layer.

(*c*) Close Packing in Three Dimensions

We can now build other layers over the first layer to extend the packing in three dimensions. This can be done by building layers on square packed and hexagonal close-packed arrangement of first layer. Let us see what types of three dimensional close packing can be obtained from these two types of arrangements. Let us mark the sphere in the first layer as A.

(*i*) Three dimensional close packing from two dimensional square close packed layers

For placing the second square close packed layers above the first row, follow the same procedure that was followed when one row was placed adjacent to the other row. The second layer is placed over the first layer such that these spheres of the second layers are exactly above those of first layer. In this arrangement, spheres of both layers are perfectly aligned horizontally as well as vertically. Similarly, we may place more layers one above the other. This is shown in Fig. 29 (*a*). If the arrangement of spheres in the first layer is called 'A' type, the other layers will also be 'A' type because they have same arrangement. This type of packing is referred to as AAA......type. This type of packing is also called **simple cubic packing** and its unit cell is the primitive unit cell as shown in Fig. 29 (*b*).

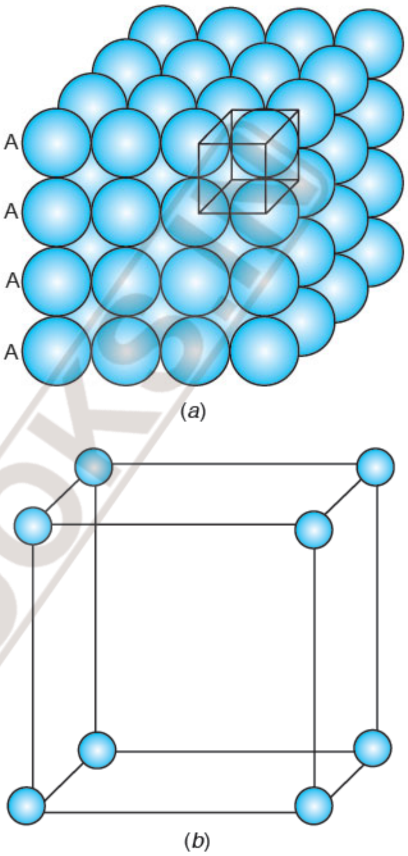


Fig. 29. Simple cubic lattice formed by AAA.... arrangement.

(*ii*) Three dimensional close packing from two dimensional hexagonal close packed layers.

As we have already seen that for two dimensional packing, hexagonal close packing is more efficient packing. Let us consider a three dimensional packing above this layer.

Let us mark the spheres in the first layer as A. It is clear from Fig. 30(*a*) that in the first layer there are some empty spaces or hollows called **voids.** These are triangular in shape. These triangular voids are of two types marked as *a* and *b*. All the hollows are equivalent but the spheres of second layer may be placed either on hollows which are marked *a* or on other set of hollows marked *b*. It may be noted that it is not possible to place spheres on both types of hollows. Let us place the spheres on hollows marked *b* to make the second layer which may be labelled as *B* layer. Obviously the holes marked *a* remain unoccupied while building the second layer. The second layer is indicated as dotted circles in Fig. 30 (*b*).

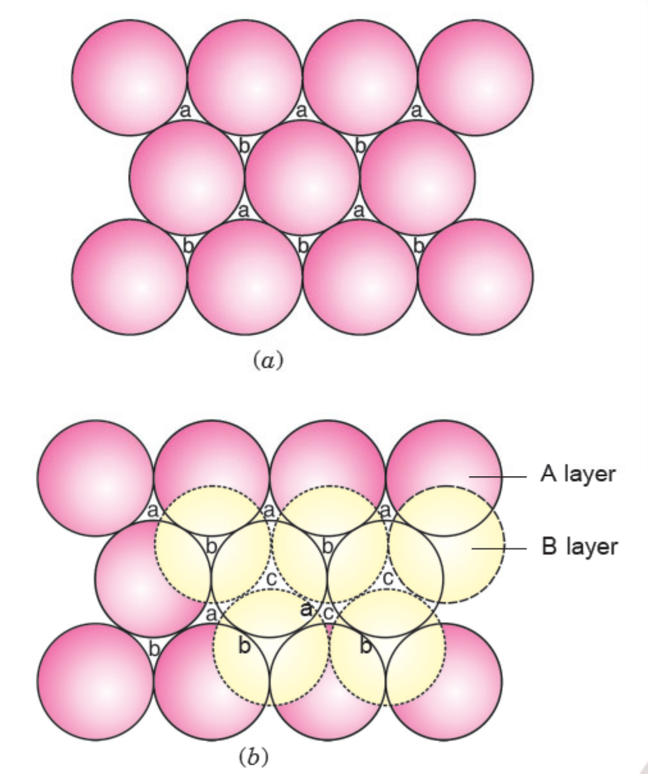


Fig. 30. Packing of second layer (*b*) on first layer (*a*).

It is clear from Fig. 30 (*b*) that the two types of voids are not similar. The '*c*' type of voids are triangular but '*a*' type of voids of the second layer are a combination of two triangular voids (one each of first layer and second layer) with the vertex of one triangle upwards and the vertex of other triangle downwards.

Whenever a sphere of second layer is placed above the void of first layer, 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. **The voids '*c*' represent tetrahedral voids.**

The voids '*a*' are double triangular voids. The triangular void in the second layer are above the triangular voids in the first layer and the triangular shapes of these voids donot overlap. Such voids are surrounded by six spheres and are called **octahedral voids.**

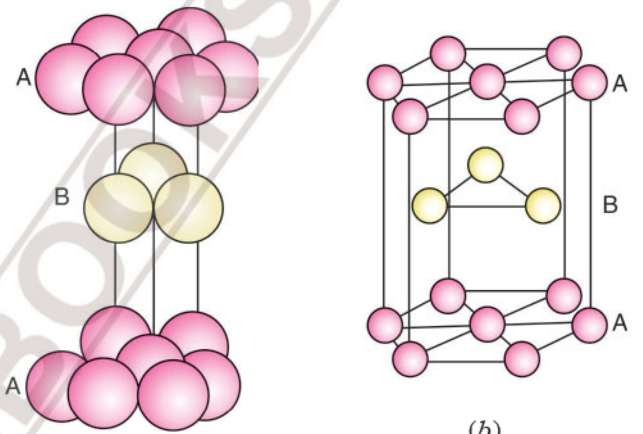
Now the third layer can be build up by placing spheres above tetrahedral voids marked (*c*) or octahedral voids marked (*a*).

(*i*) Covering tetrahedral voids

When a third layer is to be added, again there are two types of hollows available. One type of hollows marked '*a*' are unoccupied hollows of the first layer. The other type of hollows are hollows in the second layer (marked *c*). Thus, there are **two alternatives** to build the third layer.

The third layer of spheres may be placed on the tetrahedral voids marked (*c*) of the second layer. In this arrangement, the spheres of the third layer lie directly above those in the first layer. In other words, *third layer becomes exactly identical to the first layer* (labelled A). This is shown in Fig. 31. This type of packing is referred to as ABABA.... arrangement. This type of packing is also known as **hexagonal close packing.** It is abbreviated as ***hcp***. For simplicity, *hcp* arrangement can be drawn as shown in Fig. 31 (*b*).

Metals like magnesium, molybdenum, beryllium, zinc, etc. adopt this type of arrangement.



(*a*) *hcp* arrangement (*b*)

Fig. 31. ABABA... or *hcp* arrangement of spheres. Metals like magnesium, zinc, etc. adopt this type of arrangement.

(*ii*) Covering octahedral voids

The second way to pack spheres in the third layer is to place them over octahedral voids marked '*a*' (unoccupied hollows of first layer). This gives rise to a new layer labelled as C. However, it can be shown that the spheres in the fourth layer will correspond to those in the first layer. This is shown in Figs. 32 (*a*) and 32 (*b*). This gives the ABCABCA.....type of arrangement. It is also known as **cubic close packing** and is abbreviated as ***ccp.*** For simplicity ccp arrangement can be drawn as shown in Fig. 32(*c*). It is clear from Fig. 32 (*c*) that there is *a* sphere at the centre of each face of the cube. Therefore, this arrangement is also known as **face centred cubic arrangement** and is abbreviated as ***fcc.*** Metals like copper, iron, nickel, aluminium, gold and silver crystallise in this type of structure.

It may be noted that both types of packing are equally economical though these have different forms. In both cases, 74% of the available volume is occupied by the spheres.

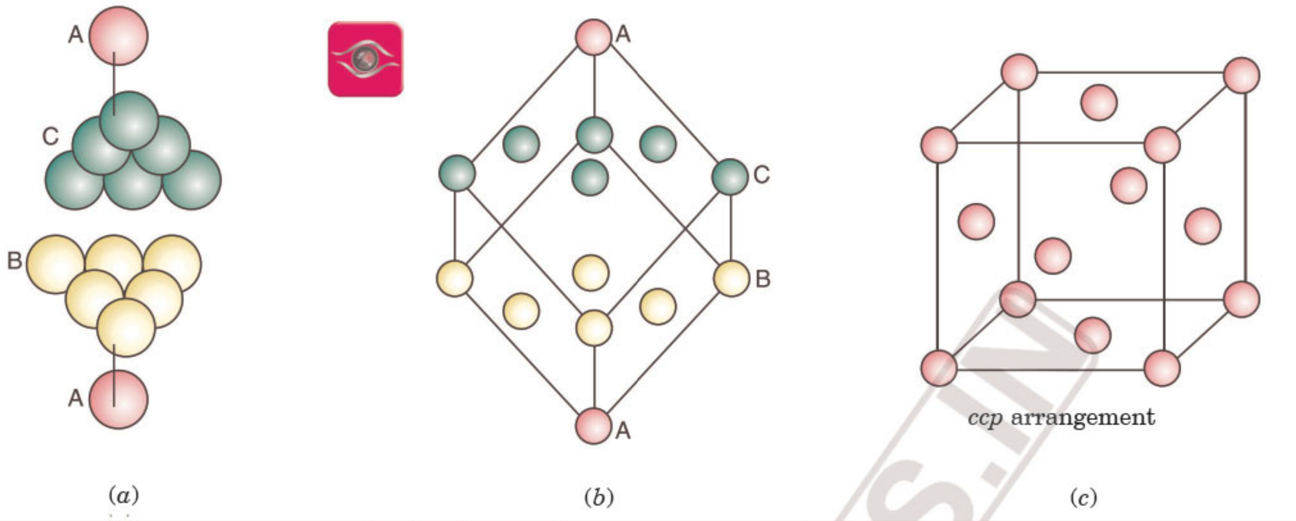


Fig. 32. ABCABCA... or *ccp* arrangement of spheres.

Learning Plus

- **Number of atoms per unit cell in *hcp*.**

❑ In *hcp* arrangement, Fig. 31 (*b*), there are 12 atoms at the corners, 2 at face centres and 3 atoms are present in the body. In *hcp*, each corner is shared by six unit cells, therefore, contribution of atom at the corner is 1/6; each atom at the face centre is shared by 2 unit cells and therefore, contribution of atom at the face centre is 1/2; the atom within the body contributes to that unit cell only. Thus,

No. of atoms per unit cell =

$$12 \text{ (at corners)} \times \frac{1}{6} + 2 \text{ (face)} \times \frac{1}{2} + 3 \text{ (body)} \times 1$$

$$= 2 + 1 + 3 = 6 \text{ atoms/unit cell.}$$

INTERSTITIAL VOIDS OR INTERSTITIAL SITES

In the close packing of spheres, certain hollows or voids are left vacant. These holes or voids in the crystals are called **interstitial voids** or **interstitial sites.** Two important interstitial voids are (*i*) *tetrahedral* (*ii*) *octahedral.*

We have learnt during packing of spheres that after arranging two layers (A and B) we find two types of voids (marked *a* and *c*). The void '*c*' is created by four spheres and is called tetrahedral void. The void '*a*' is created by six spheres in contact and is called octahedral void. These are shown in Fig. 33 marking them as *t* and *o*.

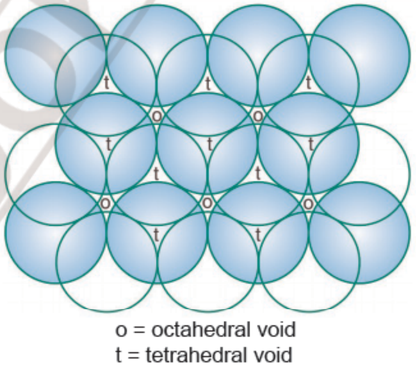


Fig. 33. Tetrahedral and octahedral voids in close packing arrangement.

(*i*) **Tetrahedral void or site .** A sphere in the second layer is placed above three spheres touching one another in the first layer. This is shown in Fig.34. The centres of these spheres lie at the apices of a tetrahedron. It may be noted that the shape of the void is not tetrahedral, but the arrangement around this void is tetrahedral. Thus, *the vacant space among four spheres having tetrahedral arrangement* is called **tetrahedral void** or **tetrahedral site.**

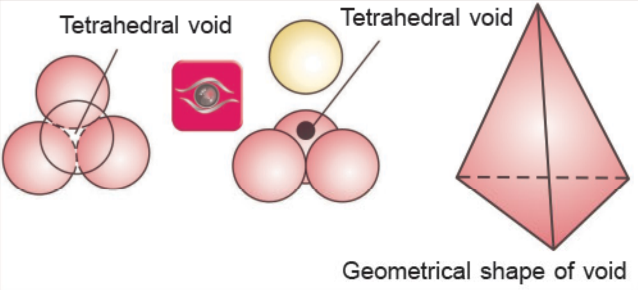


Fig. 34. Tetrahedral void.

(*ii*) **Octahedral void or site.** This type of void or site is formed at the centre of six spheres. It is shown in Fig. 35.

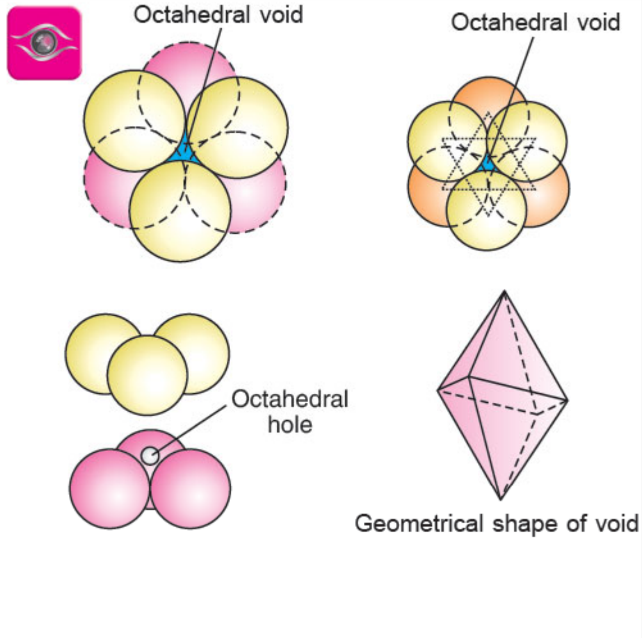


Fig. 35. Octahedral void.

From the figure, it is clear that each octahedral void is produced by two sets of equilateral triangles which point in opposite directions. Thus, *the void formed by two equilateral triangles with apices in opposite direction* is called **octahedral void** or **octahedral site**. This void is, therefore, surrounded by 6 spheres lying at the vertices of a regular octahedron.

Number of octahedral and tetrahedral voids or sites. There are two tetrahedral voids for each sphere and there is only one octahedral void for each sphere. Thus, in a close packed structure of N spheres, there are :

tetrahedral voids = 2N
octahedral voids = N
total number of tetrahedral and octahedral voids = 3N

Learning Plus

The presence of interstitial voids or interstitial sites play an important role in chemistry of transition metals. The transition metals can easily accommodate the small non-metallic atoms such as hydrogen, boron, carbon and nitrogen because of spaces between the metal atoms. These compounds are called **interstitial compounds.**

Coordination Number

The number of spheres which are touching a given sphere is called **the coordination number.** Thus, **coordination number** is

the number of closest (or nearest) neighbours of any constituent particle in the crystal lattice.

As already discussed in *hcp* and *ccp* arrangements, a sphere is in direct contact with 6 other spheres in the same plane of the central atom. It touches three spheres in the layer above it and three spheres in the layer below it. Thus, its coordination number in *hcp* and *ccp* arrangements is 12 as shown in Fig. 36.

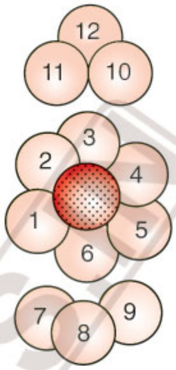


Fig. 36. Coordination number of 12 in *hcp* and *ccp* arrangement.

It may be noted that coordination numbers of 4, 6, 8 and 12 are very common in various types of crystals.

EFFICIENCY OF PACKING OR PACKING EFFICIENCY

In whatever way, the constituent particles (atoms, molecules or ions) are packed, there is always some free space left in the form of voids. The **packing efficiency** is

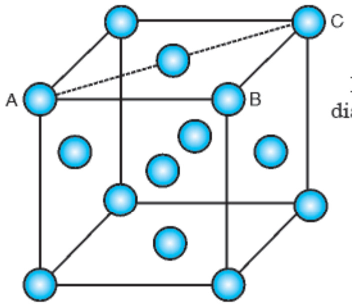
the percentage of total space filled by the particles.

Alternatively, it may also be expressed as **packing fraction. It is the fraction of total space filled by the particles.** Both types of close packing (*hcp* and *ccp*) are equally efficient and occupy 74% of the available volume. On the other hand, in body centred cubic structure, the efficiency is 68% while in simple cubic structure, it is only 52.4%.

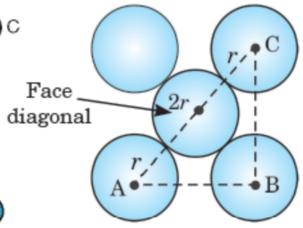
Let us calculate the packing efficiencies in different structures.

(*a*) In cubic close packing or face centred cubic arrangement

Suppose the edge length of the unit cell = a
and radius of each sphere = r



ccp arrangement



top view of *ccp* arrangement (spheres along face diagonal are touching)

It is clear from the figure that there are 8 spheres at the corners and six spheres at the faces.

No. of spheres in unit cell $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

As spheres along face diagonal are touching, it is evident from the figure,

$$AC = 4r$$

Consider ΔABC. Since it is right angled triangle,

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

$\therefore$ Face diagonal, $AC = \sqrt{2} \cdot a$

$\therefore \sqrt{2}.a = 4r$ or $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$

Volume of a unit cell

$$= a^3 = (2\sqrt{2}\,r)^3 = 16\sqrt{2}\,r^3$$

Total volume of 4 spheres

$$= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

Packing efficiency

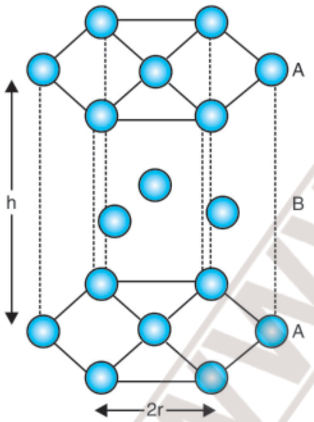
$$= \frac{\text{Volume of four spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

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

$$= \frac{\pi}{3\times\sqrt{2}} \times 100 = \frac{3.142}{3\times 1.414} \times 100 = 74\%$$

$\therefore$ **Volume occupied in *fcc* or *ccp* arrangement = 74%**

(*b*) In hexagonal close packing (*hcp*) arrangement



hexagonal close packed arrangement

Suppose radius of each sphere $= r$

From the figure, it is clear, that $a = 2r$

Volume of unit cell can be calculated as:

Volume of unit cell = Base area × Height (h)

Base area of regular hexagon = 6 × Area of equilateral triangle

$$= 6 \times \frac{\sqrt{3}}{4}a^2$$

$$= 6 \times \frac{\sqrt{3}}{4}(2r)^2 = 6 \times \sqrt{3}\,r^2$$

Height of unit cell $= 4r.\sqrt{\frac{2}{3}}$

Volume of unit cell$= 6\sqrt{3}\,r^2 \times 4r.\sqrt{\frac{2}{3}} = 24\sqrt{2}\,r^3$

No. of atoms in *hcp* unit cell $= 12 \times \frac{1}{6}$(corners) $+ 2 \times \frac{1}{2}$(face centres) + 3 (in body) = 6

Volume of 6 spheres $= 6 \times \frac{4}{3}\pi r^3 = 8\pi r^3$

Packing efficiency

$$= \frac{\text{Volume occupied by spheres in unit cell}}{\text{Volume of } hcp \text{ unit cell}} \times 100$$

$$= \frac{8\pi r^3}{24\sqrt{2}\,r^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = \frac{3.142}{3\times 1.414} \times 100$$

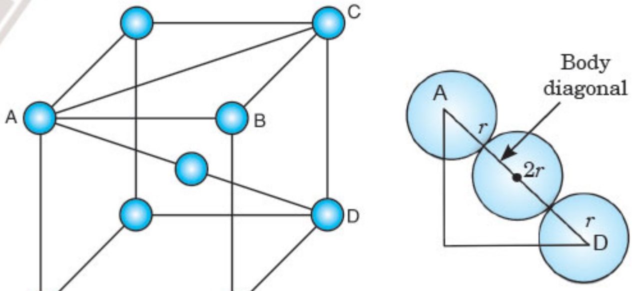
$$= 0.74 \times 100 = 74\%$$

$\therefore$ **Volume occupied in hcp arrangement = 74%**

(*c*) In body centred cubic (*bcc*) arrangement

Suppose the edge length $= a$

Radius of each sphere $= r$



View of body diagonal AD

bcc arrangement (spheres along body diagonal are touching)

It is clear from figure that there are 8 spheres at the corners and one in the body of the unit cell.

No. of spheres per unit cell

$$= 8 \times \frac{1}{8} + 1 = 2$$

It is evident from the figure that spheres along body diagonal are touching so that,

$$AD = 4r$$

Consider right angled ΔABC,

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

$$\therefore \quad AC^2 = 2a^2$$

Similarly in right angled ΔACD,

$$\text{Body diagonal, } AD^2 = AC^2 + CD^2$$

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

$$\therefore \quad AD = \sqrt{3}.a$$

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

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

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

$$\text{Volume of a sphere} = \frac{4}{3}\pi r^3$$

$$\text{Total volume of two spheres} = 2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$$

Packing efficiency

$$= \frac{\text{Volume of two spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

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

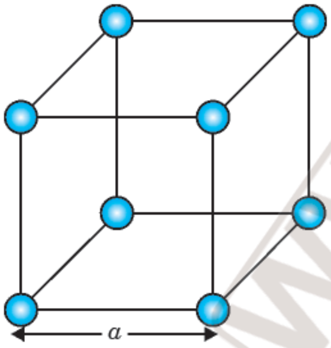
$$= \frac{3.142 \times 1.732}{8} \times 100 = 68\%$$

∴ **Volume occupied in *bcc* arrangement = 68%**

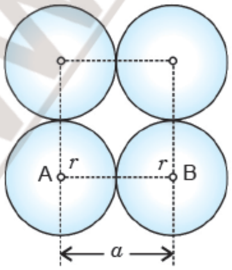
(*d*) In a simple cubic unit cell

Suppose the edge length of the unit cell = a

Radius of the sphere = r



simple cubic arrangement



(spheres along the edge are touching)

Since the spheres are touching each other along the edge, $a = 2r$

Now, there are eight spheres at the corners of the cube.

Each sphere at the corner is shared by eight unit cells and the contribution per unit cell is 1/8 so that

$$\text{Number of spheres per unit cell is } 8 \times \frac{1}{8} = 1$$

$$\text{Volume of sphere} = \frac{4}{3}\pi r^3$$

$$\text{Volume of cube} = a^3 = (2r)^3 = 8r^3$$

Packing efficiency

$$= \frac{\text{Volume of one sphere}}{\text{Total volume of cubic unit cell}} \times 100$$

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

$$= \frac{\pi}{6} \times 100 = \frac{3.142 \times 100}{6}$$

$$= 52.37\% \quad \text{or} \quad 52.4\%$$

∴ **Volume occupied in simple cubic arrangement = 52.4%**

SIZES OF TETRAHEDRAL AND OCTAHEDRAL VOIDS

As we have already learnt, in the close packed structures (*hcp* or *ccp*), there are two common types of voids :

(*i*) octahedral voids

(*ii*) tetrahedral voids

The radii of the voids in these close packed structures are related to the sizes of the spheres present in the packing. Let us calculate the radii of these voids in relation to the radii of the atoms in close packing.

Relationship between radius of octahedral void and radius of atoms in close packing.

An octahedral void is shown in Fig. 37. Though an octahedral void is surrounded by six spheres, only four are shown. The spheres present above and below the void are not shown. Let us assume that the length of the unit cell is a cm and radius of octahedral void (shown by sphere) is r and the radius of sphere is R.

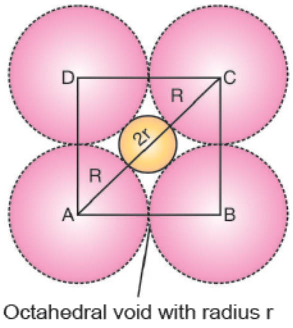


Fig. 37. A cross-section of an octahedral void.

If the length of the unit cell is a cm, then

In right angled ΔABC,

$$AB = BC = a \text{ cm}$$

The diagonal AC is :

$$AC = \sqrt{AB^2 + BC^2}$$

$$= \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

also $$\frac{AC}{AB} = \frac{\sqrt{2}\, a}{a}$$

$$= \frac{\sqrt{2}}{1}$$

Now, $$AB = 2R$$

$$AC = R + 2r + R = 2R + 2r$$

$$\therefore \quad \frac{2R + 2r}{2R} = \frac{\sqrt{2}}{1}$$

or $$1 + \frac{r}{R} = \frac{\sqrt{2}}{1}$$

or $$\frac{r}{R} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

or $$r = 0.414\ R$$

Thus, *for an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.*

Relationship between radius of the tetrahedral void and radius of atoms in close packing.

A tetrahedral void may be represented by placing four spheres at the alternate corners of a cube as shown in Fig. 38.

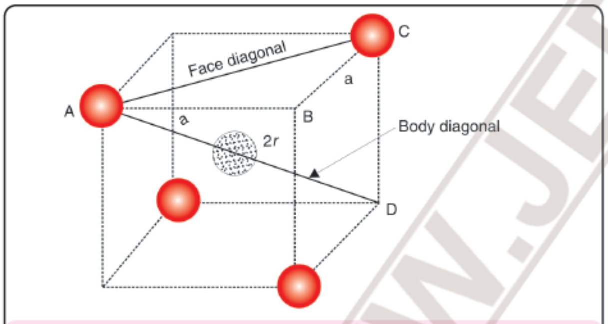


Fig. 38. A tetrahedral void.

It may be noted that a stable tetrahedral arrangement has four spheres at the corners touching each other. However, for simplicity, the spheres are shown by distant circles. Actually all the spheres are touching one another. Let us assume that the length of each side of the cube is a cm and radius of tetrahedral void (shown by a sphere) is r and the radius of sphere is R.

In the figure, AC is a face diagonal.

In right angled ΔABC,

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

or $$AC = \sqrt{AB^2 + BC^2}$$

$$= \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

As spheres A and C at the face diagonal (though shown by distant circles) are actually touching each other so that

$$AC = R + R = 2R$$

$$\therefore \quad 2R = \sqrt{2}\, a \text{ or } R = \frac{\sqrt{2}a}{2} \qquad ...(i)$$

Now in the right angled triangle, ΔACD, AD is body diagonal and

$$AD^2 = AC^2 + CD^2$$

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}\, . a$$

The tetrahedral void is present at the centre of the body diagonal AD so that half the length of this diagonal is equal to the sum of the radii of R and r. Thus,

$$R + r = \frac{AD}{2} = \frac{\sqrt{3}a}{2} \qquad ...(ii)$$

Dividing eq. (*ii*) by eq. (*i*), we get

$$\frac{R + r}{R} = \frac{\sqrt{3}a}{2} \times \frac{2}{\sqrt{2}a} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

or $$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}}$$

$$= \frac{1.732 - 1.414}{1.414} = 0.225$$

or $$r = 0.225\ R$$

Thus, *for an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere.*

Thus, **we observe that a tetrahedral void is much smaller than the octahedral void.**

Radius Ratio of Cations and Anions and Stability of Ionic Solids

In case of ionic solids, usually anions are present in the close packed arrangement and cations occupy voids. ***The number of oppositely charged ions surrounding each ion*** is called its **coordination number**. Therefore, the relation between the size of the void and the sphere in the close packed arrangement is expressed in terms of radius of cation to that of anion.

The ratio of the radius of the cation to the radius of the anion is called **radius ratio.**

Thus, $$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r_+}{r_-}$$

For cations occupying the tetrahedral voids,

$r_+ = 0.225\ r_-$ or $r_+/r_- = 0.225$

For cations occupying the octahedral voids,

$r_+ = 0.414\ r_-$ or $r_+/r_- = 0.414$

The ratio of the radius of cation and the radius of anion *i.e.*, radius ratio (r_+/r_-) plays an important role in determining the structures of ionic solids and coordination number of ions. As is clear, for the cations to occupy tetrahedral void, the limiting lowest value of r_+/r_- is 0.225 and to occupy octahedral void, it is 0.414. In other words, for tetrahedral coordination, the radius ratio should be in the range of 0.225 – 0.414. Similarly, it has been calculated that for stable arrangement of cations occupying octahedral voids (*i.e.*, coordination number 6), the radius ratio should be more than 0.414 in the range of 0.414–0.732. If the radius ratio (r_+/r_-) is more than 0.732 (in the range 0.732–1.0), the cations occupy cubic voids (coordination number 8). Similarly, below 0.225, the cations occupy simple trigonal voids. The possible coordination numbers and structural arrangements of anions around cations for different r_+/r_- values are given below :

Radius ratio (r_+/r_-)	Possible coordination number arrangement	Structural	Structural type	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS	ZnS, CuCl, CuBr, CuI BaS, HgS
0.414 – 0.732	6	Octahedral	NaCl	NaCl, MgO, NaBr, CaS, CaO
0.732 – 1.0	8	Cubic	CsCl	CsCl, CsBr, TlBr, NH_4Br

The application of radius ratio rule may be illustrated by the following examples :

SOLVED EXAMPLES

❑ **Example 8.**

The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict whether the coordination number of Na^+ ion is 6 or 4.

(Pb. S.B. 2017)

Solution : Radius of Na^+ = 95 pm

Radius of Cl^- = 181 pm

$$\text{Radius ratio, } \frac{r_+}{r_-} = \frac{r(\text{Na}^+)}{r(\text{Cl}^-)} = \frac{95}{181} = 0.524$$

The radius ratio lies between 0.414 – 0.732. Hence, Na^+ ions prefer to occupy **octahedral holes** having coordination number 6.

❑ **Example 9.**

Br^- ions form a close packed structure. If the radius of Br^- ion is 195 pm, calculate the radius of the cation that just fits into the tetrahedral hole. Can a cation having a radius of 82 pm be slipped into the octahedral hole of the crystal A^+Br^- ? (A.I.S.B. 2003)

Solution : Radius of the cation just fitting into the tetrahedral hole

$$= \text{Radius of tetrahedral hole} = 0.225 \times r_{Br^-}$$

$$= 0.225 \times 195 = \mathbf{43.875\ pm}$$

For the cation A^+ with radius, 82 pm

$$\text{Radius ratio} = \frac{r_+}{r_-} = \frac{82\text{ pm}}{195\text{ pm}} = 0.4205$$

Since the radius ratio (r_+/r_-) lies in the range 0.414–0.732, hence the cation A^+ can be slipped into octahedral hole of the crystal A^+Br^-.

Practice Problems

15. The atomic radii of Cs^+ and Cl^- ions are 1.69 Å and 1.81 Å respectively. Predict the coordination number of Cs^+ ion and structure of CsCl.

16. A solid AB has NaCl structure. If the radius of cation A is 100 pm, what is the radius of anion B ? (*Pb.S.B.2017*)

17. If the radius of Br^- ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole ?

Answers to Practice Problems

15. 8, cubic

16. 136.6 to 241.6 pm.

17. $< 7.53 \times 10^{-2}$ nm

Hints & Solutions on page 57A

FORMULA OF A COMPOUND AND NUMBER OF VOIDS FILLED

In the case of simple ionic compounds, generally two types of arrangements are possible. These are *cubic close packed* (*ccp*) or *face centred cubic* (*fcc*) arrangement and *hexagonal close packed* (*hcp*) *arrangement*. The larger ions (*i.e.,* anions) adopt these arrangements. The other kinds of ions (*i.e.,* cations) occupy different voids. As we have learnt, there are two types of voids : tetrahedral and octahedral; which are generally occupied.

From the description of the close packed structures and the types of voids occupied, we can easily draw inferences regarding the structures of simple ionic compounds. For example, consider a compound of general formula AB in which the B ions form a close packed lattice. There are two possibilities :

(*i*) Since there is only one octahedral void per atom in a close packed lattice, all the octahedral voids will be occupied by A^+ ions. In this case, the number of A^+ ions and B^- ions will be same. Sodium chloride has this type of structure in which Cl^- ions form a cubic close packed structure and Na^+ ions occupy all the octahedral voids.

(*ii*) There are two tetrahedral voids per atom in a close packed lattice. This means that there are two tetrahedral voids available for every B^- ion. To form the compound AB, only one half of the tetrahedral voids will be occupied. Zinc blende (ZnS) has this type of structure, in which S^{2-} ions form cubic close packed lattice and Zn^{2+} ions occupy one half of the tetrahedral voids.

If, on the other hand, the formula of the compound is A_2B in which B^- ions adopt cubic close packed lattice, then all the tetrahedral voids will be occupied by A^+ ions. Since there are two tetrahedral voids per atom, and all the voids are occupied, there will be two A^+ ions for each B^- ion. Sodium oxide adopts this type of structure. This structure is also known as **antifluorite structure**.

Alternatively, if A^+ ions (though smaller in size than B^- ions) adopt cubic close packed structure and B^- ions occupy all the tetrahedral voids, then the formula of the compound is AB_2. Calcium fluoride has similar type of structure. The structure is known as **fluorite structure**.

The structures of some common ionic solids are summed up in Table 4.

Competition Plus

The arrangement of atoms, ions or molecules in crystals is determined by X-rays diffraction studies. For detail, refer **Competition File** (Page 78A).

Table 4. Summary of the structures of ionic solids.

Compound	Description	Co-ordination number	Other Examples
NaCl	*ccp* arrangement of Cl^-, Na^+ in all the octahedral sites	$Na^+ = 6$ $Cl^- = 6$	Li, Na, K halides, AgCl, AgBr, MgO, CaO
ZnS (Zinc blende)	*ccp* arrangement of S^{2-}, Zn^{2+} in alternative tetrahedral sites	$Zn^{2+} = 4$ $S^{2-} = 4$	BeS, CuCl, CuBr, CuI
CsCl	Simple cubic arrangement of Cl^-, Cs^+ in cubic sites	$Cs^+ = 8$ $Cl^- = 8$	CsBr, CsI TlCl, TlBr
CaF_2	*ccp* arrangement of Ca^{2+}, F^- occupy all tetrahedral sites	$Ca^{2+} = 8$ $F^- = 4$	SrF_2, BaF_2, CaF_2, CdF_2
Na_2O	*ccp* arrangement of O^{2-}, Na^+ occupy all tetrahedral sites	$Na^+ = 4$ $O^{2-} = 8$	Li_2O, K_2S

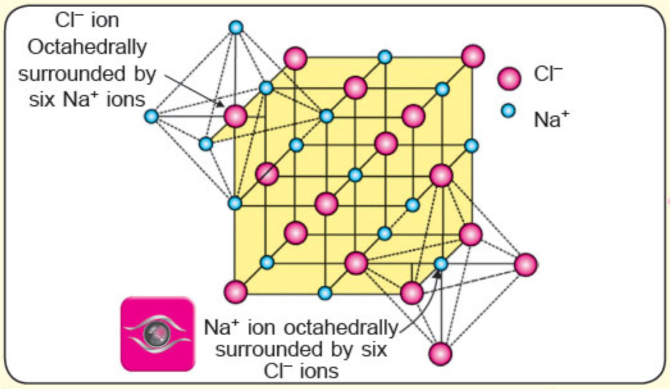
Effect of Temperature and Pressure on Crystal Structures

At ordinary temperatures and pressures, chlorides, bromides and iodides of Li, Na, K and Rb as well as some of the halides of silver possess the sodium chloride type structure. In this, the coordination number of both the negative and positive ions are 6 : 6. On the application of high pressure, these change to CsCl type structure in which the coordination number of ions become 8 : 8. Therefore, **the high pressure increases the coordination number.** On the other hand, on heating to about 760 K, the CsCl structure transforms to the NaCl structure.

$$\underset{(6\,:\,6\ \text{coordination})}{\text{NaCl structure}} \underset{760\text{K}}{\overset{\text{High pressure}}{\rightleftharpoons}} \underset{(8\,:\,8\ \text{coordination})}{\text{CsCl structure}}$$

Similarly, NH_4Cl, NH_4Br and NH_4I transform from CsCl structure to the NaCl structure at 457 K, 411 K and 253 K respectively.

STRUCTURES OF SOME COMMON IONIC COMPOUNDS



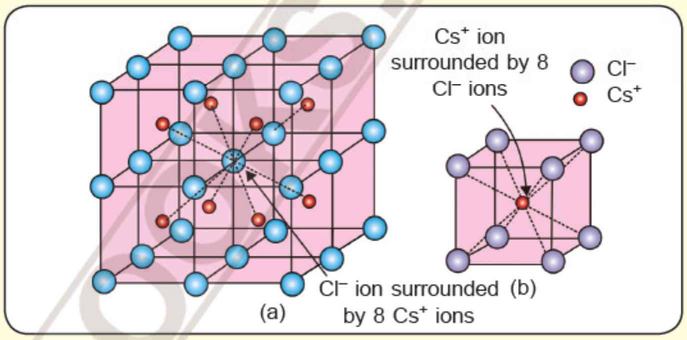
Sodium chloride (NaCl)

Sodium chloride (NaCl)

- Cl^- ions have ccp or fcc arrangement (*i.e.* Cl^- ions occupy all the corners and all the face centres of the cube)
- Na^+ ions occupy all octahedral sites (*i.e.* Na^+ ions are present at the body centre and edge centres)
- C.N. of Na^+ = 6
- C.N. of Cl^- = 6

Cesium chloride (CsCl)

- Cl^- ions have simple cubic arrangement (*i.e.* present at all the corners of the cube)
- Cs^+ ions occupy cubic sites (*i.e.* occupy the centre of the cube)
- C.N. of Cs^+ = 8
- C.N. of Cl^- = 8

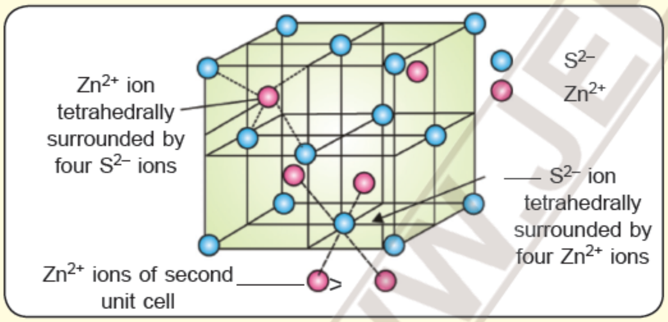


Cesium chloride (CsCl)

Zinc sulphide (ZnS)

- S^{2-} ions have *ccp* or *fcc* arrangement (*i.e.* S^{2-} ions occupy all the corners and all the face centres of the cube)
- Zn^{2+} ions occupy half of the tetrahedral sites
- C.N. of Zn^{2+} = 4
- C.N. of S^{2-} = 4

- **It may be noted that ZnS exists in two forms; zinc blende and wurtzite. In zinc blende, S^{2-} ions have *ccp* or *fcc* arrangement (as shown) but in wurtzite S^{2-} ions have *hcp* arrangement. The arrangement of Zn^{2+} ions is same in both *i.e.* occupy half the tetrahedral sites.**

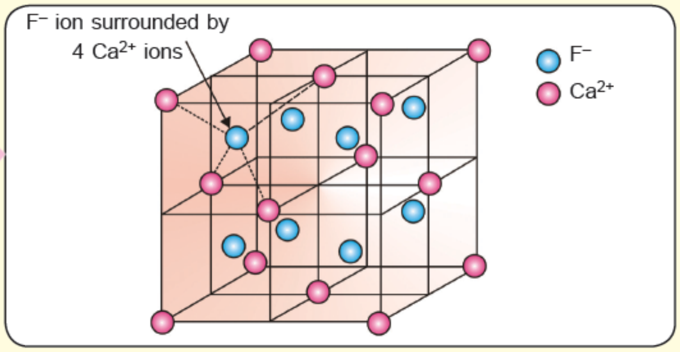


Zinc sulphide (ZnS)

Calcium fluoride (CaF_2)

- Ca^{2+} ions in ccp arrangement (*i.e.* Ca^{2+} ions occupy all the corners and all the face centres of the cube)
- F^- ions occupy all tetrahedral sites
- C.N. of Ca^{2+} = 8
- C.N. of F^- = 4

- This structure is called **fluorite structure.** Sodium oxide (Na_2O) has structure reverse of fluorite structure. O^{2-} ions are arranged in ccp arrangement and Na^+ ions occupy all the tetrahedral sites. It is called **antifluorite structure**.



Calcium fluoride (CaF_2)

Learning Plus

Structure of diamond.

- Diamond has same overall geometry as zinc blende but with all atoms identical. It has face centred cubic (fcc) structure with four more atoms which are present in alternate tetrahedral voids.
  There are 8 carbon atoms per unit cell in diamond as calculated below:
  Diamond has 8 carbon atoms at the corners (each contributing 1/8), 6 atoms at faces (each contributing 1/2) of the cube and 4 atoms at tetrahedral sites (not shared by any other). Thus

$$\text{Total number of atoms per unit cell} = 8 \text{ (at corners)} \times \frac{1}{8} + 6 \text{ (at faces)} \times \frac{1}{2} + 4 \text{ (at tetrahedral sites)} \times 1$$

$$= 1 + 3 + 4 = \mathbf{8 \text{ atoms}}$$

SOLVED EXAMPLES

❑ Example 10.

A compound is formed by two elements P and Q. Atoms of Q (as anions) make hcp lattice and those of the element P (as cations) occupy all the tetrahedral voids. What is the formula of the compound? *(Kerala S.B. 2014)*

Solution : Atoms Q adopt *hcp* arrangement and there are two tetrahedral sites per Q atom. Since all the tetrahedral sites are occupied by P atoms, this means that there are two P atoms for each Q atom.

Thus, the formula of the compound = $\mathbf{P_2Q}$.

❑ Example 11.

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

N.C.E.R.T. *(Assam S.B. 2017)*

Solution : Atoms B adopt hcp arrangement and there are two tetrahedral sites per atom of B. Since 2/3rd of the tetrahedral sites are occupied by atoms of element A, then for each atom of B, the number of A atoms will be 2 × 2/3 = 4/3.

$$\text{Ratio of atoms A and B} = \frac{4}{3} : 1 = 4 : 3$$

$\therefore$ Formula of compound : $\mathbf{A_4B_3}$.

❑ Example 12.

In a cubic close packed structure of mixed oxides, the lattice is made up of oxide ions, one-eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one-half of octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide ?

Solution : In a close packed arrangement, there is one octahedral and two tetrahedral voids corresponding to each atom constituting the lattice. Therefore, if

Number of oxide ions (O) per unit cell = n

Number of tetrahedral voids per oxide ion in lattice

$$= n \times 2 = 2n$$

$$\text{No. of divalent } (A^{2+}) \text{ ions} = \frac{1}{8} \times 2n = \frac{n}{4}$$

Number of octahedral voids per oxide ion in lattice

$$= n \times 1 = n$$

$$\text{No. of trivalent } (B^{3+}) \text{ ions} = n \times \frac{1}{2} = \frac{n}{2}$$

$$\text{Ratio of A : B : O} = \frac{n}{4} : \frac{n}{2} : n$$

$$\text{or} = 1 : 2 : 4$$

$\therefore$ Formula of the compound = $\mathbf{AB_2O_4}$.

❑ Example 13.

The mineral spinel has the molecular formula Mg Al_2O_4. In this, oxide ions are present in ccp arrangement, Mg^{2+} ions occupy the tetrahedral voids while Al^{3+} ions occupy the octahedral voids. Calculate the percentage of

(i) tetrahedral voids occupied by Mg^{2+} ions

(ii) octahedral voids occupied by Al^{3+} ions.

Solution : According to the formula $MgAl_2O_4$, there are 4 oxide ions, $1Mg^{2+}$ and 2 Al^{3+} ions per formula unit. If 4 oxide ions are in *ccp* arrangement, there will be 4 octahedral voids and 8 tetrahedral voids. Thus, 1 Mg^{2+} ion is present in one of the 8 tetrahedral voids and 2 Al^{3+} ions are present in 2 octahedral voids out of 4 available.

(*i*) Percentage of tetrahedral voids occupied by Mg^{2+} ions

$$= \frac{1}{8} \times 100 = 12.5\%$$

(*ii*) Percentage of octahedral voids occupied by Al^{3+} ions

$$= \frac{2}{4} \times 100 = 50\%$$

Practice Problems

18. A solid is made of two elements X and Y. Atoms X are in fcc arrangement and Y atoms occupy all the octahedral sites and alternate tetrahedral sites. What is the formula of the compound ?

19. A compound is formed by two elements X and Y. Atoms of 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? ***N.C.E.R.T.***

20. A compound is formed by two elements M and N. The element N forms ccp and M atom occupy 1/3 of the tetrahedral voids. What is the formula of the compound ? ***N.C.E.R.T.*** *(Pb.S.B. 2013, D.S.B. 2015)*

21. In a crystalline solid, anions Y are arranged in ccp arrangement. Cations X are equally distributed between tetrahedral and octahedral voids. If all the octahedral voids are occupied, what is the formula of the solid ?

22. In a metallic oxide, oxide ions are arranged in cubic close packing. One sixth of the tetrahedral voids are occupied by cations P and one third of octahedral voids are occupied by the cations Q. Deduce the formula of the compound. *(Pb.S.B. 2018)*

23. In corrundum, oxide ions are arranged in *hcp* arrangement and the aluminium ions occupy 2/3 of the octahedral voids. What is the formula of corrudum ?

Answers to Practice Problems

18. XY_2.
19. XY.
20. M_2N_3.
21. X_2Y.
22. PQO_3.
23. Al_2O_3.

Hints & Solutions on page 57A

Learning Plus

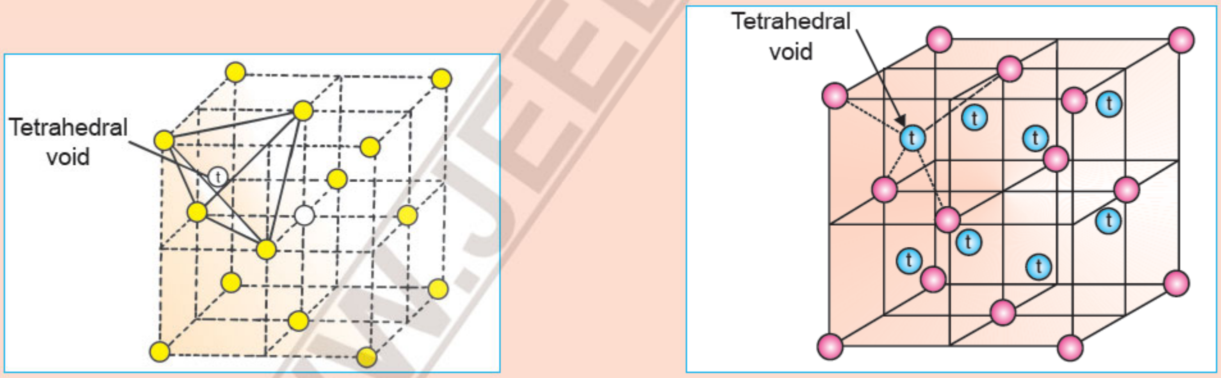
LOCATING TETRAHEDRAL AND OCTAHEDRAL VOIDS

We have learnt that close packed structures have both tetrahedral and octahedral voids. Let us visualize these voids in *ccp* (or *fcc*) structures.

▸ Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice. It has atoms at all the corners of the cube and at the centre of each face as shown in Fig.1(*a*). If we see carefully, we observe that the unit cell has eight small cubes. Each small cube has atoms at alternate corners. Therefore, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. **The centre of the small cube becomes tetrahedral void.** Thus, there is one tetrahedral void in each small cube. Since there are eight small cubes and therefore, there are **eight tetrahedral voids in *ccp* unit cell.**

We know that *ccp* structure has 4 atoms per unit cell. Thus, **the number of tetrahedral voids is twice the number of atoms.** In Fig. 1(*a*) only one tetrahedral site is shown while in Fig 1 (*b*) eight tetrahedral voids in *ccp* structure are shown.



(*a*) One tetrahedral void in *ccp* structure. (*b*) Eight tetrahedral voids in *ccp* structure.

Fig.1. Locating tetrahedral voids in *ccp* structure.

▸ Locating Octahedral Voids

Let us consider the unit cell of *ccp* or *fcc* lattice. It has atoms at all the corners and at the centre of each face as shown in Fig. 2(*a*). If we carefully see, we observe that the body centre of the cube, O, is not occupied but it is surrounded by six atoms on centre of six faces. If these face centres are joined, they make an octahedron. Thus, the centre of this octahedron *i.e.*, point O becomes octahedral void.

In addition to body centre, there is an octahedral void at the centre of each edge as shown Fig. 2(*b*). It is also surrounded by six atoms as shown in Fig. 2(*b*).

Thus in a *ccp* unit cell, there are 12 octahedral voids located on edges and 1 at the body centre of the cube. Now, each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. This means that 1/4th of each void belongs to a particular unit cell.

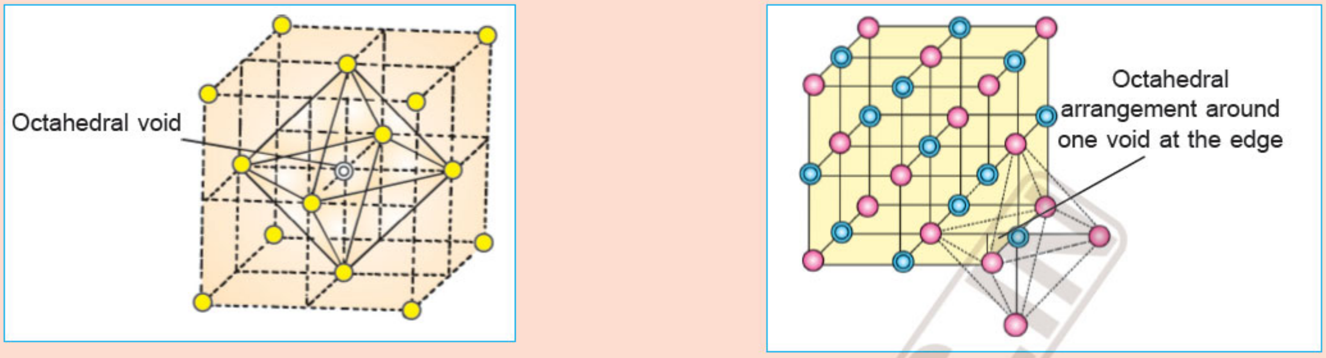
Thus, in ccp structure, the number of octahedral voids are :

Octahedral void at the body centre of the cube = 1

Octahedral voids at the edges = $12 \times \frac{1}{4} = 3$

∴ Total number of octahedral voids = 1 + 3 = 4

We know that in *ccp* structure, each unit cell has 4 atoms. Therefore, **the number of octahedral voids are same as the number of atoms.**



(*a*) Octahedral void at body centre of *ccp* unit cell (*b*) 12 octahedral voids at the edges in *ccp* unit cell (shown ●)

Fig.2. Locating octahedral voids in *ccp* structure.

Advanced Levels PROBLEMS

Accelerate Your Potential (for JEE Advance)

Problem 1. In a crystalline solid, anions Y^- are arranged in *hcp*. Cation X^+ are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the compound ?

Solution Suppose the number of anions, $Y^- = N$

$$\text{Then number of octahedral voids} = N$$

$$\text{Number of tetrahedral voids} = 2N$$

Since octahedral and tetrahedral voids are equally occupied by cations X^+ and all the octahedral voids are occupied, then N cations X^+ are present in octahedral voids and N cations X^+ are present in tetrahedral voids. Thus,

$$\text{No. of cations present} = N + N = 2N$$

$$\text{Ratio of cations and anions} = 2:1$$

$$\therefore \quad \text{Formula of the compound} = X_2Y.$$

Problem 2. In a face centred lattice of X and Y, X atoms are present at the corners while Y atoms are at face centres.

(*a*) What is the formula of the compound ?

(*b*) What would be the formula of the compound if:

(*i*) one of the X atoms is missing from a corner in each unit cell,

(*ii*) two atoms of X are missing from the corners,

(*iii*) one of the X atoms from a corner is replaced by Z atoms (also monovalent) ?

Solution (*a*) No. of X atoms in the unit cell = $8 \times 1/8 = 1$

$$\text{No. of Y atoms in the unit cell} = 6 \times \frac{1}{2} = 3$$

$$\text{Formula} = \mathbf{XY_3}$$

(*i*) If one X atom is missing, no. of X atoms = 7/8

Formula $X_{7/8}Y_3$ or $\mathbf{X_7Y_{24}}$

(*ii*) If two X atoms are missing, no. of X atoms = 6/8 = 3/4

$$\text{Formula} = X_{3/4}Y_3 \text{ or } = \mathbf{XY_4}$$

(*iii*) No. of X atoms = 7/8, No. of Z atoms = 1/8

No. of Y atoms = 3

$$\text{Formula} = X_{7/8}Y_3Z_{1/8} \text{ or } \mathbf{X_7Y_{24}Z}$$

Problem 3. In a normal spinel structure, O^{2-} ions form *fcc* packing and 1/8 of the tetrahedral sites are occupied by divalent metal, A^{2+} ions and half of the octahedral sites are occupied by trivalent metal B^{3+} ions, what is the ratio of tetrahedral/octahedral sites:

(*i*) occupied in spinel structure

(*ii*) not occupied in spinel structure

Solution Since O^{2-} ions form *fcc* structure, there will be four O^{2-} ions per unit cell. Therefore,

$$\text{No. of octahedral sites} = 4$$

$$\text{No. of tetrahedral sites} = 4 \times 2 = 8$$

(*i*)
$$\text{No. of tetrahedral sites occupied} = 8 \times \frac{1}{8} = 1$$

$$\text{No. of octahedral sites occupied} = 4 \times \frac{1}{2} = 2$$

$$\therefore \quad \frac{\text{Tetrahedral sites}}{\text{Octahedral sites}} = \frac{1}{2} \text{ or } 1:2$$

(*ii*)
$$\text{No. of tetrahedral sites unoccupied} = 8 - 1 = 7$$

$$\text{No. of octahedral sites unoccupied} = 4 - 2 = 2$$

$$\therefore \quad \frac{\text{Tetrahedral sites}}{\text{Octahedral sites}} = \frac{7}{2} \text{ or } 7:2$$

add on

Conceptual Questions 1A

Q.1. A metal crystallizes in a body centred cubic structure. If 'a' is the edge length of its unit cell, 'r' is the radius of the sphere. What is the relationship between 'r' and 'a'? ***(CBSE Sample Paper 2017-18)***

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

Q.2. If the radius of the octahedral void is 'r' and radius of the atoms in close packing is 'R'. What is the relation between 'r' and 'R'? ***(CBSE Sample Paper 2017-18)***

Ans. $r = 0.414$ R.

Q.3. In a close packing of N spheres, how many
(*i*) tetrahedral, and (*ii*) octahedral sites are present?

Ans. (*i*) Tetrahedral = 2N, (*ii*) Octahedral = N.

Q.4. Arrange simple cubic, body centred cubic, face centred cubic and hexagonal close packing in the increasing order of packing efficiency.

Ans. Simple cubic < body centred cubic < face centred cubic = hexagonal close packing.

Q.5. (*a*) What is meant by the term coordination number?
(*b*) What is the coordination number of atoms:
(*i*) in a cubic close packed structure (*ii*) in a body centred cubic structure?

Ans. (*a*) Coordination number is the number of nearest neighbours of any constituent particle in the crystal lattice.
(*b*) (*i*) 12 (*ii*) 8.

Q.6. The ions of NaF and MgO all have the same number of electrons and the internuclear distances are about the same (235 pm and 215 pm). Why then are the melting points of NaF and MgO so different (992°C and 2642°C)?

Ans. In MgO, both the ions carry two units of charge (Mg^{2+}, O^{2-}) whereas in NaF, each ion carries only one unit charge (Na^+F^-). Therefore, there are stronger electrostatic forces of attraction in MgO and, hence, more energy is required to overcome these forces. Thus, its melting point is high.

Q.7. Name the (*i*) most symmetrical and (*ii*) most unsymmetrical crystal system.

Ans. (*i*) Most symmetrical crystal system : Cubic
(*ii*) Most unsymmetrical crystal system : Triclinic.

Q.8. How many atoms can be assigned to its unit cell if an element forms (*i*) a body centred cubic cell and (*ii*) face centred cubic cell? ***(A.I.S.B. 2005)***

Ans. (*i*) 2 (*ii*) 4.

Q.9. What is the maximum coordination number of an atom in a hcp crystal structure of an element.? ***(D.S.B. 2005)***

Ans. 12.

Q.10. Which network solid is an exceptionally good conductor of electricity?

Ans. Graphite, a network solid is a good conductor of electricity.

Q.11. How are unit cell and space lattice related?

Ans. Space lattice is obtained by repeating the unit cell in three dimensions. The spatial arrangement, stoichiometry and density of unit cell and space lattice are equivalent.

Q.12. Pick out the odd ones from the following sets :
(*i*) Sulphur, Argon, Solid CO_2, Diamond ; (*ii*) SiC, Quartz, BaO, Graphite

Ans. (*i*) Diamond because all others are molecular solids.
(*ii*) BaO because all others are covalent solids.

Q.13. What is the two dimensional coordination number of a molecule in square packed layer? ***N.C.E.R.T. (Meghalaya S.B. 2017)***

Ans. 4.

Q.14. Solid A is very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it ? *N.C.E.R.T.*

Ans. Covalent or network solid like quartz (SiO_2) or SiC.

Q.15. What type of solids are electrical conductors, malleable and ductile ? *N.C.E.R.T.*

Ans. Metallic solids.

Q.16. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure ? *(CBSE Sample Paper 2007)*

Ans. 1 mole

Q.17. What is the total number of atoms per unit cell in a face centred cubic structure ? *(A.I.S.B., 2008, D.S.B. 2008)*

Ans. 4.

Q.18. Some of the very old glass objects appear slightly milky instead of being transparent. Why ? *(A.I.S.B.2007)*

Ans. This is because of some crystallization in that region.

Q.19. An ionic compound AB_2 possesses CaF_2 type crystal structure. Write the co-ordination numbers of A^{2+} and B^- ions in crystals of AB_2. *(D.S.B. 2000)*

Ans. C. N. of $A^{2+} = 8$; C. N. of $B^- = 4$.

Q.20. An iron oxide crystallizes in a hexagonal close packed arrangement of oxide ions with two out of every three octahedral voids occupied by iron. Give the formula of the iron oxide. *(Meghalaya S.B. 2014)*

Ans. In a close packed arrangement, there is one octahedral site corresponding to each atom constituting the lattice. Therefore,

$$\text{No. of oxide ions per unit cell in hcp arrangement} = 6$$

$$\text{No. of octahedral holes} = 6 \times 1 = 6$$

$$\text{No. of iron ions} = 6 \times \frac{2}{3} = 4$$

$$\text{Formula of the compound} = Fe_4O_6 \text{ or } Fe_2O_3.$$

Q.21. If three elements X, Y and Z crystallize in a cubic solid with X atoms at the corners, Y atoms at the cube centres and Z atoms at the faces of the cube, then write the formula of the compound.

Ans. Atom X per unit cell $= 8 \times \frac{1}{8} = 1$

Atom Y per unit cell = 1

Atom Z per unit cell $= 6 \times \frac{1}{2} = 3$

$\therefore$ Formula of the compound $= XYZ_3$

Q.22. In a solid 'AB', 'A' atoms have *ccp* arrangement and B atoms occupy all the octahedral sites. If all the face centred atoms along one of the axes are removed, then what will be the resultant stoichiometry of the compound?

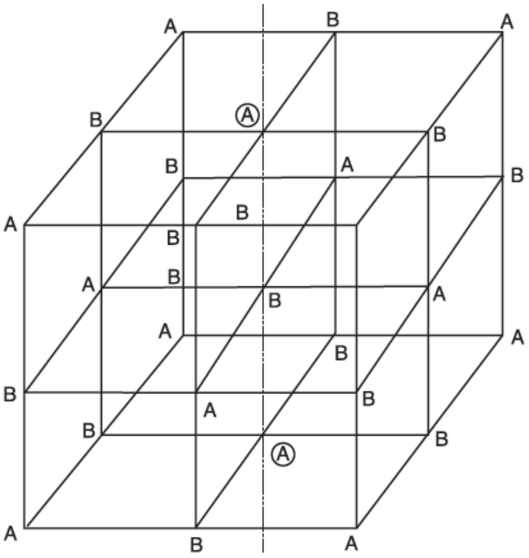
Ans. In *ccp* type structure, there are 8A at the corners of the cube and 6A atoms on the face centres. If all the face centred atoms along one of the axes are removed, it means removal of 2A atoms. Therefore, only 4 atoms will be left on faces.

$$\text{No. of A atoms per unit cell} = 8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 3$$

No. of B atoms in *ccp* structure are 12 at edge centred and 1 at body centre. Therefore,

$$\text{No. of B atoms per unit cell} = 12 \times \frac{1}{4} + 1 = 4$$

$\therefore$ Stoichiometry of compound $= A_3B_4$.



2Ⓐatoms along one axis are removed.

Q.23. Both diamond and rhombic sulphur are covalent solids but the latter has very low melting point than the former. Explain why ?

Ans. Diamond is a network covalent solid with strong interatomic forces whereas sulphur is a molecular solid consisting of puckered eight membered rings (S_8) held together by weak van der Waals forces.

Q.24. Write a feature which will distinguish a metallic solid from an ionic solid. ***(D.S.B. 2010)***

Ans. Metallic solids are good conductors of heat and electricity whereas ionic solids are insulators in solid state but conductors in molten state and in aqueous solution.

Q.25. Write a distinguishing feature of metallic solids. ***(A.I.S.B. 2010)***

Ans. Metallic solids are good conductors of heat and electricity.

Q.26. What is the difference between glass and quartz while both are made up from SiO_4 tetrahedra? Under what conditions could quartz be converted into glass ?

Ans. Glass is an amorphous solid while quartz is a crystalline solid. On melting quartz and then rapidly cooling *i.e.*, annealing, quartz is converted to glass.

Q.27. What difference in behaviour between the glass and sodium chloride would you expect to observe if you break off a piece of either cube ?

Ans. The glass (an amorphous solid) would break irregularly, usually in curved shapes because its component molecules are not arranged in an ordered pattern. On the other hand, sodium chloride (an ionic solid) would break off along flat surfaces parallel to the faces of the cube because the planes of its component ions are parallel to the faces of the crystalline cube.

Q.28. KF has *ccp* structure. Calculate the radius of the unit cell if the side of the cube or edge length is 400 pm. How many F^- ions and octahedral voids are there in the unit cell ? ***(CBSE Sample Paper 2011)***

Ans. For *ccp* lattice, $r = \frac{a}{2\sqrt{2}} = \frac{400}{2 \times 1.414} = \mathbf{141.4\ pm}$

There are four F^- ions and four octahedral voids.

Q.29. What is the relationship between the edge length *(a)* of the unit cell and radius *(r)* of an atom in a face centred unit cell? ***(Meghalaya S.B. 2013)***

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

Q.30. How will you show that glass is a supercooled liquid ?

Ans. On being heated, glass has the property to flow like liquids. If we examine carefully the window panes of old buildings, we observe that they become slightly thicker at the bottom than at the top. This is because glass flows down very slowly and makes the bottom portion slightly thicker. Hence, glass is called supercooled liquid.

CALCULATIONS INVOLVING UNIT CELL DIMENSIONS

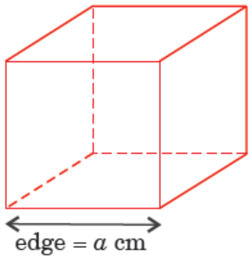
From the dimensions of the unit cell, it is possible to calculate the volume of the unit cell. From the knowledge of the density of unit cell, we can calculate the mass of atoms in the unit cell or vice-versa.

If we know the edge of a cubic crystal of an element or compound, we can easily calculate its density as described below :

Consider a unit cell of edge '*a*' (cm)

The length of the edge of the cell = *a* cm

Volume of unit cell = a^3 cm^3



$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} \quad \text{... }(i)$$

Mass of unit cell

= Number of atoms in a unit cell × Mass of each atom = Z × *m* ... *(ii)*

where Z = number of atoms in unit cell and

m = mass of each atom

Mass of an atom present in unit cell,

$$m = \frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{M}{N_A}$$

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

Substituting in eq. (*i*), we get

$$\boxed{\text{Density} = \frac{Z \times M}{a^3 \times N_A}\ \text{g cm}^{-3}}$$

If edge length '*a*' is in pm, then

Edge length = *a* pm

= $a \times 10^{-12}$ m = $a \times 10^{-10}$ cm

$$\text{Volume of unit cell} = (a \times 10^{-10}\ \text{cm})^3 = a^3 \times 10^{-30}\ \text{cm}^3$$

So, the formula becomes

$$\text{Density of unit cell} = \frac{Z \times M}{a^3 \times 10^{-30} \times N_A}\ \text{g cm}^{-3}$$

where 'a' is in pm.

In terms of SI units, if a is in metres and M is in kg mol^{-1}, then

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}\ \text{kg m}^{-3}$$

Density of unit cell is the same as the density of the substance. If the density of the element is known by other method, Avogadro number or number of atoms in a given amount of element can be easily calculated.

The density of solids can be used in different ways.

NOTE

It may be noted that the relation considers the cubic crystals of elements. However, for cubic crystals of ionic compounds, the formula is the same except that in the case of ionic compounds, Z is the number of formula units present in one unit cell and M is formula mass.

Solving Numerical Problems

KEY FORMULAE AND UNITS

Density of unit cell (and hence density of a crystal),

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

where a is edge of unit cell in **cm**

N_A = Avogadro number (6.022×10^{23})

M = Atomic mass of element or formula mass of the compound.

Z = No. of atoms present per unit cell or formula units

e.g. for *fcc*, Z = 4,

for bcc, Z = 2,

for simple cubic, Z = 1.

SOLVED EXAMPLES

A. Unit Cell Dimensions and Density

☐ **Example 14.**

An element having bcc geometry has atomic mass 50u. Calculate the density of the unit cell, if its edge length is 290 pm.

(Mizoram S.B. 2015, Pb. S.B. 2015, 2016)

Solution : Length of edge, a = 290 pm

$= 290 \times 10^{-10}$ cm

Since it is *bcc* arrangement,

No. of atoms in the unit cell, Z = 2

Atomic mass of the element, M = 50 g mol^{-1}

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{2 \times 50\ \text{g mol}^{-1}}{(290 \times 10^{-10}\text{cm})^3 \times (6.022 \times 10^{23}\text{mol}^{-1})}$$

$$= \mathbf{6.81\ g\ cm^{-3}}.$$

☐ **Example 15.**

Copper crystallizes with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. (Atomic mass of Cu = 63.55 u and Avogadro's number, $N_A = 6.02 \times 10^{23}$ mol^{-1}). *(A.I.S.B. 2012)*

Solution : For a *fcc* unit cell, edge length (a) is related to radius of atom as :

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

or $a = 2\sqrt{2}.r = 2 \times 1.414 \times 127.8$

$= 361.42$ pm

or $= 361.42 \times 10^{-10}$ cm

Since the lattice is *fcc*, the number of copper atoms per unit cell, Z = 4.

$$\text{Density,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

$M = 63.55$ u, $N_A = 6.02 \times 10^{23}$

$$\therefore \quad \rho = \frac{4 \times 63.55}{(361.42 \times 10^{-10})^3 \times (6.02 \times 10^{23})}$$

$$= \mathbf{8.94\ g\ cm^{-3}}$$

☐ **Example 16.**

Sodium has body centred cubic structure having nearest neighbour distance 365.9 pm. Calculate its density. (Atomic mass of sodium = 23 g mol^{-1}.)

Solution : For the *bcc* structure, edge length is related to nearest neighbour distance (d) as

$$d = \frac{\sqrt{3}}{2}a \quad \text{or} \quad a = \frac{2d}{\sqrt{3}}$$

$$\therefore \quad a = \frac{2 \times 365.9}{1.732} = 422.5\ \text{pm} = 422.5 \times 10^{-10}\ \text{cm}$$

$$\text{Density,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

Z = 2 (for *bcc*), M = 23 g mol^{-1}, $N_A = 6.02 \times 10^{23}$

$$\therefore \quad \rho = \frac{2 \times 23}{(422.5 \times 10^{-10})^3 \times (6.02 \times 10^{23})} = \mathbf{1.01 g\ cm^{-3}}$$

☐ **Example 17.**

An element crystallizes in a fcc lattice with cell edge of 250 pm. Calculate its density if 300 g of this element contain 2×10^{24} atoms. (D.S.B. 2016)

Solution : Length of edge, $a = 250 \text{ pm} = 250 \times 10^{-12} \text{ m}$

$= 250 \times 10^{-10} \text{ cm}$

$$\text{Volume of unit cell} = (250 \times 10^{-10} \text{ cm})^3 = 15.625 \times 10^{-24} \text{ cm}^3$$

Mass of unit cell = No. of atoms in unit cell × Mass of each atom

Since the element has fcc arrangement, the number of atoms per unit cell, $Z = 4$

$$\text{Mass of an atom} = \frac{300}{2 \times 10^{24}} \text{ g}$$

$$\therefore \quad \text{Mass of unit cell} = \frac{300}{2 \times 10^{24}} \times 4 = 6.0 \times 10^{-22} \text{ g}$$

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{6.0 \times 10^{-22} \text{ g}}{15.625 \times 10^{-24} \text{ cm}^3} = \mathbf{38.4 \text{ g cm}^{-3}}$$

❑ Example 18.

A metal having atomic mass 50 g mol^{-1} has a body centred cubic crystal structure. The density of metal is 5.96 g cm^{-3}. Find the volume of the unit cell.

(H.P.S.B. 2001, Pb S.B. 2016 Mizoram S.B. 2013, 2018)

Solution : If a is the edge length of the unit cell, then volume of unit cell, $V = a^3$

Density of unit cell, $\rho = 5.96 \text{ g cm}^{-3}$

Atomic mass of the metal, $M = 50 \text{ g mol}^{-1}$

No. of atoms per unit cell, $Z = 2$ (*bcc*)

$$\text{Now,} \quad \text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$\text{or} \quad \rho = \frac{Z \times M}{V \times N_A}$$

$$\text{or} \quad V = \frac{Z \times M}{\rho \times N_A}$$

$$\therefore \quad \text{Volume} = \frac{2 \times (50 \text{ g mol}^{-1})}{(5.96 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = \mathbf{27.86 \times 10^{-24} \text{ cm}^3}.$$

B. Lattice Type from Density and Unit Cell Dimensions

❑ Example 19.

The density of chromium metal is 7.2 g cm^{-3}. If the unit cell is cubic with edge length of 289 pm, determine the type of unit cell (simple, body centred or face centred) [Atomic mass of Cr = 52 a.m.u., N$_A$ = 6.02 × 10^{23} mol^{-1}]. (Pb. S. B. 2014, 2017)

Solution : Length of the edge $= 289 \text{ pm} = 289 \times 10^{-12} \text{ m} = 289 \times 10^{-10} \text{ cm}$

Atomic mass of Cr, $A = 52 \text{ g mol}^{-1}$

Density of metal, $\rho = 7.2 \text{ g cm}^{-3}$

$$\text{Now,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$7.2 \text{ g cm}^{-3} = \frac{Z \times 52 \text{ g mol}^{-1}}{(289 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$\text{or} \quad Z = \frac{(7.2 \text{ g cm}^{-3}) \times (289 \times 10^{-10} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(52 \text{ g mol}^{-1})}$$

$= \mathbf{2.01}$

Since the unit cell contains 2 atoms, it is **body centred cubic (*bcc*).**

❑ Example 20.

An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05 × 10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the unit cell ? (D.S.B. 2015)

Solution : Density of unit cell, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$\rho = 2.7 \text{ g cm}^{-3}$, $a = 4.05 \times 10^{-8} \text{ cm}$, $M = 27 \text{ g mol}^{-1}$, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad 2.7 = \frac{Z \times 27}{(4.05 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$\text{or} \quad Z = \frac{2.7 \times (4.05 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{27} = 4.0$$

Since $Z = 4$, the unit cell is face centred cubic (*fcc*) unit cell.

C. Atomic Mass and Number of Atoms from Density and Unit Cell Dimensions

❑ Example 21.

An element with density 11.2 g cm^{-3} forms a fcc lattice with edge length of 4 × 10^{-8} cm. Calculate the atomic mass of the element.

(D. S. B. 2014, Pb. S.B. 2016)

Solution : Edge length of the unit cell

$a = 4 \times 10^{-8} \text{ cm}$

$\text{Density} = 11.2 \text{ g cm}^{-3}$

No. of atoms per unit cell in *fcc* lattice, $Z = 4$

$$\text{Density,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$11.2 \text{ g cm}^{-3} = \frac{4 \times M}{(4 \times 10^{-8} \text{cm})^3 \times (6.02 \times 10^{23} \text{mol}^{-1})}$$

$$\text{or} M = \frac{(11.2 \text{ g cm}^{-3}) \times (4 \times 10^{-8} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})}{4}$$

$= 107.9 \text{ g mol}^{-1}$

Atomic mass of element **= 107.9 u.**

❑ Example 22.

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 cm^{-3}. How many atoms are present in 208 g of the element ? (D.S.B. 2006, Pb.S.B. 2007)

Solution : Edge length of the unit cell $= 288 \text{ pm}$

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

$$\text{Volume of the unit cell} = (288 \times 10^{-10})^3 \text{ cm}^3 = 2.39 \times 10^{-23} \text{ cm}^3$$

$$\text{Mass of element} = 208 \text{ g}$$
$$\text{Density of element} = 7.2 \text{ g cm}^{-3}$$
$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}}$$
$$\text{Volume of element} = \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}} = 28.89 \text{ cm}^3$$

Number of unit cells in this volume

$$= \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$
$$= \frac{28.89 \text{ cm}^3}{2.39 \times 10^{-23} \text{cm}^{-3} / \text{ unit cell}}$$
$$= 12.08 \times 10^{23} \text{ unit cells}$$

Since the structure is *bcc*, number of atoms present in a unit cell = 2

The number of atoms in 208 g of the element

$$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23} \text{ atoms}$$

or $$\mathbf{= 2.416 \times 10^{24} \text{ atoms}}$$

❑ **Example 23.**

An element E crystallizes in body centred cubic structure. If the edge length of the cell is 1.469 × 10^{-10} m and the density is 19.3 g cm^{-3}, calculate the atomic mass of this element. Also calculate the radius of an atom of the element.

(CBSE Sample Paper 2007)

Solution : Edge length of the unit cell, $a = 1.469 \times 10^{-10}$ m = 1.469×10^{-8} cm

Density, $\rho = 19.3 \text{ g cm}^{-3}$

Since it is body centred, Z = 2

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$$19.3 \text{ g cm}^{-3} = \frac{2 \times M}{(1.469 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$\text{or } M = \frac{(19.3 \text{ g cm}^{-3}) \times (1.469 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{2}$$

$$= 18.42 \text{ g mol}^{-1}$$

∴ Atomic mass = **18.42** u.

For a *bcc* structure, radius of an atom,

$$r = \frac{\sqrt{3}}{4} \cdot a = \frac{1.732 \times 1.469 \times 10^{-10} \text{m}}{4}$$

$$= \mathbf{6.36 \times 10^{-11} \text{ m}}$$

D. The Avogadro Constant from Density and Unit Cell Dimensions

❑ **Example 24.**

Calculate the value of Avogadro number from the following data :

Density of NaCl = 2.165 g cm^{-3}, distance between Na^+ and Cl^- ions in NaCl crystal = 281 pm.

(A.I.S.B. 2004, H.P.S.B. 2005, Pb. S.B. 2011, Hr. S.B. 2017 Nagaland S.B. 2018)

Solution : Sodium chloride has face centred cubic structure. Therefore, the number of formula units or molecules per unit cell, Z = 4

$$\text{Let Avogadro number} = N_A$$
$$\text{Molar mass of NaCl} = 23 + 35.5 = 58.5 \text{ g mol}^{-1}$$

Since distance between Na^+ and Cl^- ions is 281 pm, the length of edge is double the distance between Na^+ and Cl^- ions.

$$\text{Edge of unit cell} = 2 \times 281 \text{ pm} = 562 \text{ pm}$$

or $$= 562 \times 10^{-12} \text{ m} = 562 \times 10^{-10} \text{ cm}$$

Density, $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$$2.165 \text{ g cm}^{-3} = \frac{4 \times (58.5 \text{ g mol}^{-1})}{(562 \times 10^{-10} \text{cm})^3 \times N_A}$$

or $$N_A = \frac{4 \times (58.5 \text{ g mol}^{-1})}{(2.165 \text{ g cm}^{-3}) \times (562 \times 10^{-10} \text{cm})^3}$$

$$= \mathbf{6.09 \times 10^{23} \text{ mol}^{-1}}.$$

E. Unit Cell Dimensions and Ionic Radii from Density

❑ **Example 25.**

The compound CuCl has fcc structure like ZnS. Its density is 3.4 g cm^{-3}. What is the length of the edge of the unit cell ? *(Mizoram S.B. 2014)*

Solution : CuCl has cubic close packed or face centred cubic structure like ZnS. The number of formula units or molecules of CuCl per unit cell = 4.

$$\text{Let length of each edge} = a \text{ cm}$$
$$\therefore \text{ Volume of the cube} = a^3 \text{ cm}^3$$
$$\text{Density of the cell} = 3.4 \text{ g cm}^{-3}$$

Formula mass of CuCl, M = 63.5 + 35.5 = 99

Density $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$$3.4 \text{ g cm}^{-3} = \frac{4 \times (99 \text{ g mol}^{-1})}{a^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

or $$a^3 = \frac{4 \times (99 \text{ g mol}^{-1})}{(3.4 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$= 193.4 \times 10^{-24} \text{ cm}^3$$

∴ $$a = \mathbf{5.78 \times 10^{-8} \text{ cm or 578 pm.}}$$

❑ **Example 26.**

An element A crystallises in fcc structure. 200 g of this element has 4.12 × 10^{24} atoms. The density of A is 7.2 g cm^{-3}. Calculate the edge length of the unit cell. *(A.I.S.B. 2001)*

Solution : Let length of each edge = a cm

$$\text{Volume of unit cell} = a^3 \text{ cm}^3$$
$$\text{Density} = 7.2 \text{ g cm}^{-3}$$
$$\text{Mass of each atom} = \frac{200}{4.12 \times 10^{24}}$$
$$= 48.54 \times 10^{-24} \text{ g}$$
$$\text{No. of atoms per unit cell} = 4 \; (fcc)$$
$$\text{Mass of unit cell} = 4 \times 48.54 \times 10^{-24}$$
$$= 194.16 \times 10^{-24} \text{ g}$$

$$\text{Now, density} = \frac{\text{Mass}}{\text{Volume}}$$

$$7.2 = \frac{194.16 \times 10^{-24}}{a}$$

$$\text{or} \quad a^3 = \frac{194.16 \times 10^{-24}}{7.2} = 26.97 \times 10^{-24}\,\text{cm}^3$$

$$\text{or} \quad a = \mathbf{2.999 \times 10^{-8}\ cm = 299.9\ pm.}$$

Example 27.

Niobium crystallizes in body centered cubic structure. If density is 8.55 g cm⁻³, calculate atomic radius of niobium given its atomic mass 93 u.

N.C.E.R.T.

Solution : Density = 8.55 g cm^{-3}

Let length of the edge = a cm

Number of atoms per unit cell, Z = 2 *(bcc)*

Atomic mass, M = 93 g mol^{-1}

$$\text{Density,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$8.55\ \text{g cm}^{-3} = \frac{2 \times (93\ \text{g mol}^{-1})}{a^3 \times (6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$\therefore \quad a^3 = \frac{2 \times (93\ \text{g mol}^{-1})}{(8.55\ \text{g cm}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$= 36.12 \times 10^{-24}\ \text{cm}^3$$

$$\text{Edge length, } a = (36.12 \times 10^{-24})^{1/3} = 3.306 \times 10^{-8}\ \text{cm}$$

$$= 3.306 \times 10^{-10}\ \text{m}$$

$$\text{Now, radius in body centred cubic, } r = \frac{\sqrt{3}}{4}\,a$$

$$= \frac{\sqrt{3} \times 3.306 \times 10^{-10}\,\text{m}}{4} = 1.431 \times 10^{-10}\,\text{m}$$

$$= \mathbf{0.143\ nm.}$$

Example 28.

KF has NaCl structure. What is the distance between K⁺ and F⁻ in KF if density is 2.48 g cm⁻³ ?

(Hr. S.B. 2005)

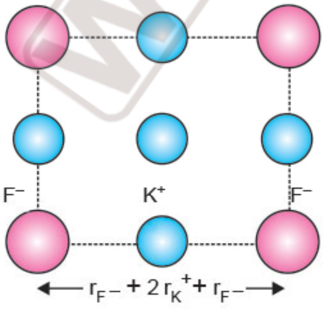
Solution : KF has NaCl (*fcc*) structure, therefore, the number of KF molecules per unit cell, Z = 4

Molar mass of KF = 58 g mol^{-1}

Let the edge of unit cell = a cm

Density, ρ = 2.48 g cm^{-3}

$$\text{Density, } \rho = \frac{Z \times M}{a^3 \times N_A}$$



$$2.48\ \text{g cm}^{-3} = \frac{4 \times 58\ \text{g mol}^{-1}}{a^3 \times (6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$a^3 = \frac{4 \times 58\ \text{g mol}^{-1}}{(2.48\ \text{g cm}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$= 155.3 \times 10^{-24}\ \text{cm}^3$$

$$\therefore \quad a = (155.3 \times 10^{-24})^{1/3}$$

$$\text{or} \quad a = 5.375 \times 10^{-10}\ \text{cm or } 537.5\ \text{pm}$$

Now, if radius of F⁻ is r_{F^-} and radius of K⁺ is r_{K^+}, then according to the figure, edge of unit cell,

$$a = r_{F^-} + 2r_{K^+} + r_{F^-}$$

$$= 2(r_{K^+} + r_{F^-})$$

$$\text{or} \quad r_{K^+} + r_{F^-} = \frac{a}{2}$$

Thus, distance between K⁺ and F⁻ ions will be half the edge length in the unit cell.

$$\text{Thus, the distance between K}^+ \text{ and F}^- \text{ ions} = \frac{537.5}{2}$$

$$= \mathbf{268.8\ pm.}$$

Example 29.

Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125 pm.

(a) What is the length of the side of unit cell?

(b) How many unit cells are there in 1.00 cm³ of Al ?

(D.S.B. 2005, A.I.S.B. 2005, Meghalaya S.B. 2018)

Solution : For a cubic close packed structure, length of the side of unit cell is related to radius.

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

$$\text{or} \quad a = r \times 2\sqrt{2}$$

$$= 125 \times 2 \times 1.414\ \text{pm} = 353.5\ \text{pm}$$

$$\text{Volume of unit cell} = (353.5 \times 10^{-10}\,\text{cm})^3 = 4.42 \times 10^{-23}\,\text{cm}^3$$

$$\text{No. of unit cells in 1 cm}^3 = \frac{1}{4.42 \times 10^{-23}}$$

$$= \mathbf{2.26 \times 10^{22}\ unit\ cells.}$$

Example 30.

Silver has atomic mass 108 a.m.u. and density 10.5 g cm⁻³. If the edge length of its unit cell is 409 pm, identify the type of unit cell. Also calculate the radius of an atom of silver.

Solution : Edge length of unit cell

$$a = 409\ \text{pm}$$

$$= 409 \times 10^{-10}\ \text{cm}$$

$$\text{Density,} \quad \rho = 10.5\ \text{g cm}^{-3}$$

Atomic mass of silver = 108 u

$$\text{Now,} \quad \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$10.5\ \text{g cm}^{-3} = \frac{Z \times (108\,\text{g mol}^{-1})}{(409 \times 10^{-10}\,\text{cm})^3 \times (6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$\text{or } Z = \frac{(10.5\,\text{g cm}^{-3}) \times (409 \times 10^{-10}\text{cm})^3 \times (6.022 \times 10^{23}\,\text{mol}^{-1})}{108\,\text{g mol}^{-1}}$$

$$Z = 4.0$$

Since the unit cell contains 4 atoms per unit cell, it is **face centred cubic** (*fcc*) unit cell.

For *fcc*, $$r = \frac{a}{2\sqrt{2}} = \frac{409\,\text{pm}}{2\times1.414} = \mathbf{144.6\,pm}$$

❑ Example 31.

Silver metal crystallises with a face centred cubic lattice. The length of the unit cell is found to be 4.077 × 10^{-8} cm. Calculate atomic radius and density of silver. (Atomic mass of Ag = 108u, N_A = 6.02 × 10^{23} mol^{-1}).

(C.B.S.E. Sample Paper 2012, H.P.S.B. 2016)

Solution : Edge length of unit cell, $a = 4.077 \times 10^{-8}$ cm

For *fcc* lattice, radius of an atom is related to edge length, a as :

$$r = \frac{a}{2\sqrt{2}} = \frac{4.077\times10^{-8}}{2\times1.414} = \mathbf{1.441 \quad 10^{-8}\ cm}$$

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$= \frac{4\times108}{(4.077\times10^{-8})^3\times(6.02\times10^{23})}$$

$(\because Z = 4 \text{ for } fcc)$

$$= \mathbf{10.58\ g\ cm^{-3}}$$

❑ Example 32.

The density of lead is 11.35 g cm^{-3} and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (At. Mass of lead = 207 g mol^{-1} and N_A = 6.02 × 10^{23} mol^{-1}) *(D.S.B. 2011)*

Solution : Let length of edge = a cm

Density = 11.35 gcm^{-3}

No. of atoms per unit cell in *fcc* lattice = 4

Atomic mass, M = 207 g mol^{-1}

Density, $$\rho = \frac{Z\times M}{a^3\times N_A}$$

$$11.35\ g\ cm^{-3} = \frac{4\times(207\ g\ mol^{-1})}{a^3\times(6.022\times10^{23}\,mol^{-1})}$$

$$a^3 = \frac{4\times(207\ g\ mol^{-1})}{(11.35\ g\ cm^{-3})\times(6.022\times10^{23}\,mol^{-1})}$$

$$= 121.14 \times 10^{-24}\ cm^3$$

Edge length, $a = (121.14)^{1/3}\times10^{-8} = 4.948 \times 10^{-8}$ cm

or = 4.948×10^{-10} m

or = 494.8×10^{-12} m = 494.8 pm

Now, radius in *fcc* $$= \frac{a}{2\sqrt{2}} = \frac{494.8\ \text{pm}}{2\times1.414} = \mathbf{174.96\ pm}$$

Practice Problems

24. An element 'X' (At. mass = 40 g mol^{-1}) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X'. (N_A = 6.022 × 10^{23} mol^{-1}) *(A.I.S.B. 2018)*

25. An element crystallizes in a f.c.c. lattice with cell edge of 400 pm. The density of the element is 7 g cm^{-3}. How many atoms are present in 280 g of the element? *(A.I.S.B. 2016)*

26. Tungsten has body centred cubic lattice. Each edge of the unit cell is 316 pm and density of the metal is 19.35 g cm^{-3}. How many atoms are present in 50 g of the element ? *(Pb.S.B. 2011)*

27. CsCl has body centred cubic lattice with the length of a side of a unit cell 412.1 pm and aluminium is face centred cubic lattice with length of the side of unit cell 405 pm. Which of the two has larger density ? (Atomic mass of Cs = 132.9, Al = 26.9, Cl = 35.5)

28. Unit cell of an element (atomic mass = 108 amu and density = 10.5 g cm^{-3}) has edge length 409 pm. Deduce the type of the crystal lattice. *(Nagaland S.B. 2016, Pb.S.B.2017)*

29. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro number. (At. mass of Fe = 55.845 u) *(A.I.S.B. 2009; D.S.B. 2009)*

30. Gold (atomic mass = 197 u, atomic radius = 0.144 nm) crystallizes in a face centred unit cell. Determine the density of gold, (N_A = 6.022 × 10^{23} mol^{-1}). *(C.B.S.E. Sample Paper 2010)*

31. An element (atomic mass = 60) having face centred cubic structure has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell ? *(Pb.S.B. 2015)*

32. An element with density 10 g cm^{-3} forms a cubic unit cell with edge length of 3 × 10^{-8} cm. What is the nature of the cubic unit cell if the atomic mass of the element is 81 g mol^{-1}? *(A.I.S.B. 2015)*

33. Lead (II) sulphide crystal has NaCl structure. What is its density ? The edge length of the unit cell of PbS crystal is 500 pm. (atomic masses : Pb = 207, S = 32) *(Pb.S.B. 2008)*

34. Formula mass of NaCl is 58.45 g mol^{-1} and density of its pure form is 2.167 g cm^{-3}. The average distance between adjacent sodium and chloride ions in the crystal is 2.814 × 10^{-8} cm. Calculate the Avogadro number.

Answers to Practice Problems

24. 4.15 g cm^{-3}, 1.505 × 10^{22}
25. 2.5 × 10^{24} atoms
26. 1.64 × 10^{23} atoms.
27. Density of CsCl = 3.995 g cm^{-3}, density of Al = 2.69 g cm^{-3}. CsCl has larger density.
28. Z = 4, *fcc*
29. 6.022 ×× 10^{23}
30. 19.41 g cm^{-3}
31. 400 pm
32. *bcc*
33. 12.7 g cm^{-3} **34.** 6.06 × 10^{23}

Hints & Solutions on page 57A

35. Copper crystallizes 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}.

36. Crystalline CsBr has a cubic structure. Calculate the unit cell edge length if the density of CsBr crystal is 4.24 g cm^{-3} (atomic masses : Cs = 133, Br = 80).

37. The unit cell of an element of atomic mass 108 and density 10.5 g cm^{-3} is a cube with edge length of 409 pm. Find the structure of the crystal lattice (simple cube, *fcc* or *bcc*). Avogadro's number = 6.023×10^{23}.

(Pb. S.B. 2014, Meghalaya S.B. 2015)

38. What is the distance between Na^+ and Cl^- ions in NaCl crystal if the density is 2.165 g cm^{-3}. Molar mass of NaCl = 58.5 g mol^{-1}, ($N_A = 6.02 \times 10^{23}$ mol^{-1}.) *(A.I.S.B. 2006)*

39. A compound AB crystallizes in bcc lattice with unit cell edge length of 380 pm. Calculate

(*i*) the distance between oppositely charged ions in the lattice.

(*ii*) radius of A^+ if radius of B^- is 175 pm.

40. Thallium chloride TlCl crystallises in either a simple cubic lattice or a face centred cubic lattice of Cl^- ions with Tl^+ ions in the holes. If the density of the solid is 7.00 g cm^{-3} and edge of the unit cell is 3.85×10^{-8} cm, what is the unit cell geometry ? (Atomic mass of Tl = 208.37 and of Cl = 35.5).

41. Cesium chloride crystallizes as cubic lattice and has a density of 4.0 g cm^{-3}. Calculate the length of the edge of the unit cell of cesium chloride. (Molar mass of CsCl = 168.5 g mol^{-1}) *(D.S.B. 2003)*

42. An element having atomic mass 107.9 u has FCC lattice. The edge length of its unit cell is 408.6 pm Calculate density of the unit cell. [Given, $N_A = 6.022 \times 10^{23}$ mol^{-1}] *(Karnataka S.B. 2018)*

43. Calculate the Avogadro number from the following data of AB when AB has NaCl type structure :

Density of AB = 2.48 g cm^{-3}, M = 58

Distance between A^+ and B^- ions in AB = 269 pm

(Hr.S.B. 2005)

44. X-ray diffraction studies show that copper crystallizes in a fcc unit cell with cell edge of 3.61×10^{-8} cm. In a separate experiment copper is determined to have a density of 8.92 g cm^{-3}. Calculate the molar mass of copper. *(H.P.S.B. 2005)*

45. Chromium crystallizes in a body centred cubic lattice whose density is 7.20 g/ cm^3. The length of the edge of unit cell is 288.4 pm. Calculate the Avogadro number (atomic mass of chromium = 52).

(Pb S.B. 2013, Meghalaya S.B. 2016)

46. An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell. *(D.S.B. 2017)*

Answers to Practice Problems

35. 8.96 g cm^{-3}

36. 436.9 pm.

37. *fcc* type

38. 282 pm

39. (*i*) 329.1 pm

(*ii*) 154.1 pm

40. Z = 1. Simple cubic.

41. 412 pm

42. 10.506 g cm^{-3}

43. 6.007×10^{23}.

44. 63.2. g mol^{-1}

45. 6.02×10^{23}

46. *bcc*

Hints & Solutions on page 57A

Advanced Levels PROBLEMS

Accelerate Your Potential (for JEE Advance)

Problem 4. Lithium borohydride ($LiBH_4$) crystallizes in an orthorhombic system having 4 molecules per unit cell. The unit cell dimensions are: $a = 6.81$ Å, $b = 4.43$ Å and $c = 7.17$ Å. Calculate the density of the crystal (At. mass of Li = 7, B = 11, H = 1u).

Solution Since orthorhombic unit cell has all the angles, $\alpha = \beta = \gamma = 90°$, then

$$\text{Volume of unit cell} = a \times b \times c$$

$$\text{Molar mass of } LiBH_4 = 7 + 11 + 4 \times 1 = 22 \text{ g mol}^{-1}.$$

$$\rho = \frac{Z \times M}{(a \times b \times c)N_A}$$

$$= \frac{4 \times (22 \text{ g mol}^{-1})}{(6.81 \times 10^{-8} \times 4.43 \times 10^{-8} \times 7.17 \times 10^{-8} \text{ cm}^3) \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= \mathbf{0.676 \text{ g cm}^{-3}}$$

Problem 5. Iron crystallizes in several forms. At 1185 K, the body centred cubic α-form of iron changes to the face centred cubic γ-form of iron. Assuming that the distance between the nearest neighbours is the same in two forms at the transition temperature, calculate the ratio of the density of α-form to that of γ-form at the transition temperature.

Solution For body centred α-form

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

No. of atoms of per unit cell, Z = 2

$$\text{Density of } \alpha\text{-form of iron} = \frac{Z \times M}{N_A \times a^3} = \frac{2 \times M}{N_A \times (4r/\sqrt{3})^3}$$

For face centred γ-form, $r = \frac{a}{2\sqrt{2}}$ or $a = 2\sqrt{2}\,r$

No. of atoms of per unit cell, Z = 4

$$\text{Density of } \gamma\text{-form of iron} = \frac{Z \times M}{N_A \times a^3} = \frac{4 \times M}{N_A \times (2\sqrt{2}\,r)^3}$$

$$\frac{\text{Density of } \alpha\text{- form of iron}}{\text{Density of } \gamma\text{- form of iron}} = \frac{2}{(4r/\sqrt{3})^3} \times \frac{(2\sqrt{2}r)^3}{4}$$

$$= \frac{2 \times 3\sqrt{3} \times 16\sqrt{2}}{64 \times 4}$$

$$= \frac{3 \times 1.732 \times 1.414}{8} = \mathbf{0.918}$$

Problem 6. **KCl and NaCl crystallize in the same form and** $\frac{r_{Na^+}}{r_{Cl^-}} = 0.52$ **and** $\frac{r_{Na^+}}{r_{K^+}} = 0.71$

Calculate

(*i*) ratio of the side of the unit cell for KCl to that for NaCl.

(*ii*) the ratio of density of KCl to that of NaCl.

Solution (*i*) Both KCl and NaCl crystallize in face centred cubic arrangement in which the face length is related to radii of cation and anion as:

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2} \quad \text{and} \quad r_{K^+} + r_{Cl^-} = \frac{a'}{2}$$

Now $\frac{r_{Na^+}}{r_{Cl^-}} = 0.52$

or $\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.52 + 1$

(adding 1 on both sides)

or $\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.52$ ...(*i*)

$$\frac{r_{Na^+}}{r_{K^+}} = 0.71$$

But $r_{Na^+} = r_{Cl^-} \times 0.52 = 0.52\, r_{Cl^-}$

∴ $\frac{0.52\, r_{Cl^-}}{r_{K^+}} = 0.71$

or $\frac{r_{K^+}}{r_{Cl^-}} = \frac{0.52}{0.71}$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = \frac{0.52}{0.71} + 1$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = \frac{0.52 + 0.71}{0.71} = \frac{1.23}{0.71} \quad \text{...}(ii)$$

Dividing eq. (*ii*) by eq. (*i*)

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.23}{0.71} \times \frac{1}{1.52}$$

or $\frac{a'/2}{a/2} = 1.14$

∴ $\frac{\text{Side of unit cell for KCl}}{\text{Side of unit cell for NaCl}} = 1.14$

(*ii*) Density $= \frac{Z \times M}{a^3 \times N_A}$

Since Z and N_A are same for both KCl and NaCl

Density $\propto \frac{M}{a^3}$

$$\therefore \quad \frac{\rho(\text{KCl})}{\rho(\text{NaCl})} = \frac{M(\text{KCl})}{M(\text{NaCl})} \times \frac{[a(\text{NaCl})]^3}{[a(\text{KCl})]^3}$$

$$= \frac{74.5}{58.5} \times \left(\frac{1}{1.14}\right)^3 \quad \left(\because \frac{a(\text{NaCl})}{a(\text{KCl})} = \frac{1}{1.14}\right)$$

$= \mathbf{0.86}$

IMPERFECTIONS IN SOLIDS

Crystalline solids are formed by regular repetition of large number of unit cells in all directions. **An ionic crystal which has the same unit cell containing the same lattice points throughout the whole of crystal** is known as **ideal crystal**. However, such ideal crystals exist only at absolute zero (0 K) temperature. At any temperature above 0 K, the crystals have some departure from complete ordered arrangement. In actual practice, it is very difficult to grow a perfect or an ideal crystal. A solid consists of a number of many small individual crystals or grains, each of which is deformed because it is highly packed among other deformed crystals. Even single crystals which are grown with all care and which appear to be perfect may contain some internal irregularities.

Any deviation from completely ordered arrangement of constituent particles in a crystal** is called **disorder or a defect.

The crystal may have additional defects due to the presence of some impurities. The term **disorder** or **imperfection** is generally used to denote departure from perfectly ordered state of the constituents of the crystals. These imperfections will not only change the properties of the crystals but also give rise to new properties.

TYPES OF DEFECTS

Broadly speaking, there are two types of defects:

(i) Point defects *(ii) Line defects*

(i) Point defects

The defects which arise due to the irregularity or deviations from ideal arrangement of atoms around a point or an atom in a crystalline substance are called **point defects or atomic imperfections.**

(ii) Line defects

The defects which arise due to irregularities or deviations from ideal arrangement in entire row of lattice points are called **line defects.**

These irregularities are called **crystal defects or crystal imperfections**. In the present unit we shall confine our discussion to point defects only.

POINT DEFECTS IN SOLIDS

The point defects arise due to any one of the following causes :

***(i)* Vacancy defect.** *When some of the lattice sites are vacant, the crystal is said* to have **vacancy defect** (Fig. 39). The unoccupied positions are called vacancies. This defect results in decrease in density of the substance. This type of defect may also develop when a substance is heated and therefore, it is also called **thermodynamic defect.**

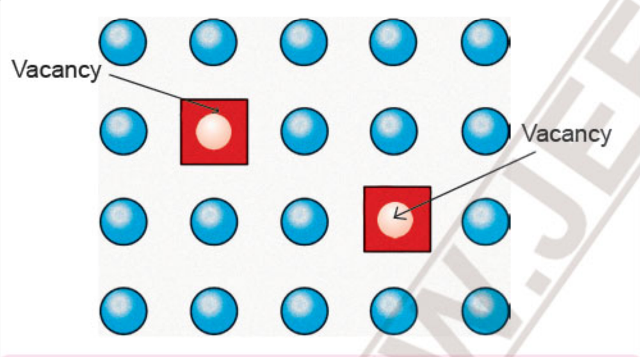


Fig. 39. Vacancy defect.

(ii)* Interstitial defect.** *When some constituent particles (atoms or molecules) occupy vacant interstitial positions, the crystal is said to have* ***interstitial defect (Fig. 40). This defect increases the density slightly.

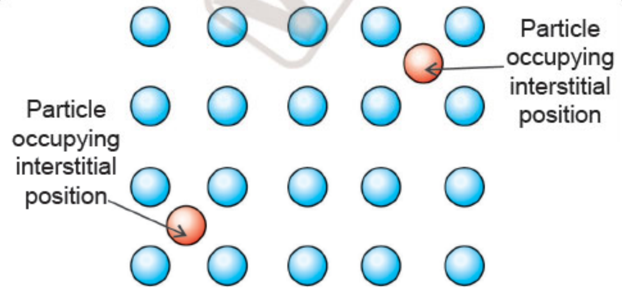


Fig. 40. Interstitial defect.

It may be noted that vacancy and interstitial defects are shown by non-ionic solids. On the otherhand, ionic solids must always maintain electrical neutrality.

The **point defects** in ionic crystals may be classified as:

A. *Defects in stoichiometric crystals.*

B. *Defects in non-stoichiometric crystals.*

C. *Impurity defects*

A. Point Defects in Stoichiometric Crystals

Stoichiometric compounds *are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae.* For simplicity, we can consider the compounds of the type AB having equal number of A^+ and B^- ions. The defects in these types of compounds are called **stoichiometric defects**. In these compounds two types of defects are generally observed. These are :

1. *Schottky defect.* 2. *Frenkel defect.*

1. Schottky defect

This defect was discovered by German scientist Schottky in 1930. *It arises if some of the atoms or ions are missing from their normal lattice sites.* The lattice sites which are unoccupied are called **lattice vacancies** or **holes.** Since the crystal is to remain electrically neutral, equal number of cations and anions are missing. The ideal AB crystal is shown in Fig. 41. The existence of two holes one due to a missing cation and the other due to a missing anion is shown in Fig. 42. This is basically a vacancy defect in ionic solids.

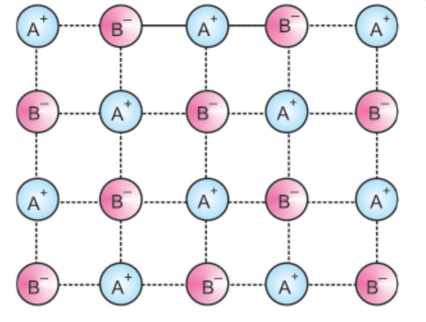


Fig. 41. An ideal crystal.

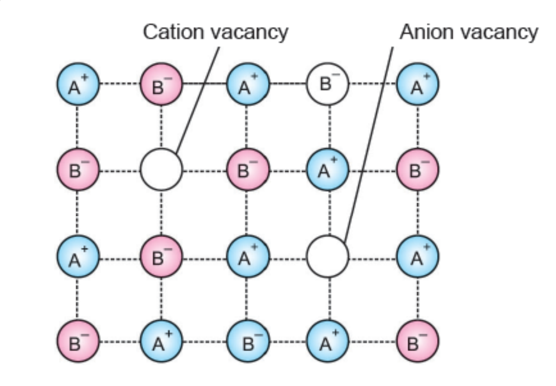


Fig. 42. The Schottky defect in crystals.

Conditions causing Schottky defects. This type of defect is usually observed in strongly ionic compounds having

(*i*) *high co-ordination number, and*

(*ii*) *ions (cations and anions) of almost similar sizes.*

For example, NaCl, KCl, KBr, CsCl and AgBr ionic solids have Schottky defects. It has been observed that in NaCl, there are about 10^6 Schottky pairs per cm^3 at room temperature. In one cm^3, there are about 10^{22} ions and this means that there will be one Schottky defect per 10^{16} ions in NaCl. Because of the presence of large number of vacancies in crystals, **its density is markedly lowered.**

2. Frenkel defect

This defect was discovered by a Russian scientist Frenkel in 1926. *It arises when an ion is missing from its normal position (causing a vacancy or a hole) and occupies an interstitial site between the lattice points.* The existence of one hole due to a missing cation from its normal position and occupying an interstitial position is shown in Fig. 43. In this case also, the crystal remains electrically neutral because the number of anions and cations remains the same.

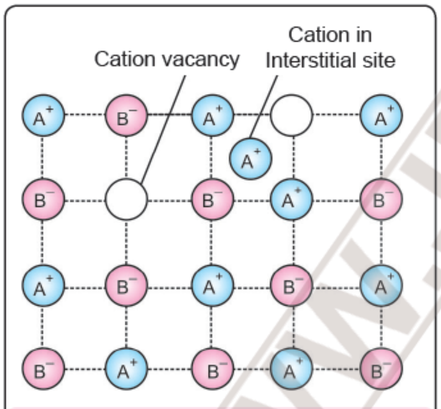


Fig. 43. A Frenkel defect.

This defect is also known as **interstitial defect.** It creates a *vacancy defect* at its original position and an *interstitial defect* in its new location.

Conditions causing Frenkel defects. This defect generally occurs in compounds in which

(*i*) *co-ordination number is low,*

(*ii*) *anions are much larger in size than the cations.*

In pure alkali metal halides, these defects are not very common because the ions cannot get into interstitial positions due to their large sizes. These defects can be found in silver halides such as AgCl, AgBr, AgI, ZnS, etc. Because of the small size of the Ag^+ ion and Zn^{2+} ion, these ions can go into the interstitial sites.

We observe that vacancies or holes are present in crystals with Schottky as well as Frenkel defect *but the former leads to decrease in the overall density of the substance but the latter does not.*

It may be noted that in addition to two basic types of defects (Schottky and Frenkel), another hybrid type of defect can also arise from a combination of the two.

Consequences of Schottky and Frenkel Defects. Schottky and Frenkel defects in crystals lead to some *interesting consequences.* These are given below :

1. Because of the presence of these defects, the electrical conductivity of crystals increases. When an electric field is applied, a nearby ion moves from its lattice site to occupy a 'hole'. This results in creating a new 'hole' and another nearby ion moves into it and so on. This process continues and a hole, thereby, moves from one end to the another end. Thus, it conducts electricity across the whole of the crystal.

2. Due to the presence of holes in the crystal, its density decreases. However, it may be noted that density decreases only for crystals having Schottky defects.

3. The presence of 'holes' also decreases *the lattice energy or the stability of the crystal*. The presence of too many holes may cause a partial collapse of the lattice.

4. The closeness of similar charges in Frenkel defects tends *to increase the dielectric constant of the crystals.*

NOTE

It may be noted that in certain ionic solids such as AgBr, both Schottky and Frenkel defects occur.

Differences between Schottky and Frenkel Defects

Schottky defect	Frenkel defect
1. It is produced because of missing atoms or ions from their normal crystal sites.	It is produced when some atoms or ions are displaced from their normal sites and occupy interstitial sites.
2. The presence of Schottky defect lowers the density of the crystal.	It does not affect the density of the crystal.
3. It is generally shown by ionic solids having high co-ordination number and in which cations and anions are of equal sizes *e.g.,* NaCl, CsCl.	It is generally exhibited by ionic solids having low co-ordination number and in which anions are larger in size than cations *e.g.,* AgCl, ZnS.

B. Point Defects in Non-Stoichiometric Crystals

The compounds in which the ratio of positive and negative ions present in the compound differs from that required by ideal chemical formula of the compound are called **non-stoichiometric compounds**. * The defects in these compounds are called **non-stoichiometric defects**. Vanadium oxide, for example has, the formula VO_x where x lies between 0.6 and 1.3. Similarly, iron (II) oxide of ideal composition FeO are difficult to obtain. Normally, we get samples of more oxygen atoms than iron atoms (composition of $Fe_{0.95}O$ but it may range from $Fe_{0.93}O$ to $Fe_{0.96}O$). ZnO usually has excess of zinc atoms than oxygen atoms, ZnO_x ($x < 1$). However, it may be noted that in each case, the electrical neutrality of the crystal is maintained. Non-stoichiometric behaviour is most commonly found for transition metal compounds. It is also found for some lanthanoids and actinoids.

These are of two types depending upon whether positive ions are in excess or negative ions are in excess. These are also known as **metal excess defects** and **metal deficiency defects** respectively. Some of these examples are given below :

(A) Metal Excess Defects

In these defects, the positive ions are in excess. These may arise due to the following two ways :

(*i*) anionic vacancies

(*ii*) presence of extra cations in interstitial sites.

(*i*) Anion vacancies. In this case, *negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality*. This is shown in Fig. 44. Evidently, there is an excess of positive (metal) ions although, the crystal as a whole is electrically neutral. This type of defect is observed in those crystals which are likely to form Schottky defects.

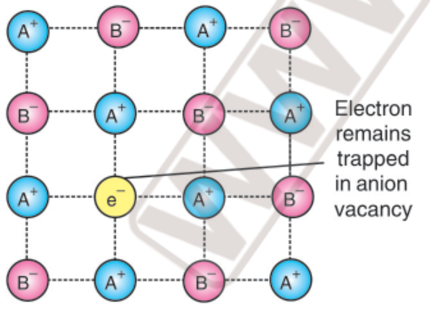


Fig. 44. Metal excess defects due to anion vacancy.

In alkali metal halides, anion vacancies are produced when alkali metal halide crystals are heated in the atmosphere of the alkali metal vapours. For example, when crystal of NaCl are heated in an atmosphere of sodium vapour, the excess of 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 the loss of electrons by sodium atoms to form Na^+ ions. The electrons, thus produced by the ionisation of the sodium atoms diffuse into the crystal and get trapped at the anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centres** (from German word *farbenzenter* meaning 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 potassium in KCl makes the crystal appear violet (or lilac), excess of lithium in LiCl makes the crystal appear pink.

NOTE

The electrons trapped in anion vacancies are called **F-centres** because they impart colour to crystals.

(*ii*) Excess cations occupying interstitial sites. In this case, *there are extra positive ions occupying interstitial sites and the electrons in another interstitial sites to maintain electrical neutrality*. This is shown in Fig. 45. The defect may be visualised as the loss of non-metal atoms which leave their electrons behind. The excess metal ions occupy interstitial positions.

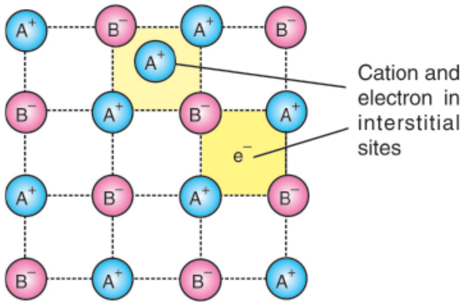


Fig. 45. Metal excess defects due to extra cation.

This type of defect is found in crystals which are likely to develop Frenkel defect. The common example is zinc oxide. Zinc oxide (ZnO) is white in colour at room temperature. On heating, it loses oxygen reversibly at high temperatures and turns yellow in colour.

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

The excess Zn^{2+} ions are trapped in interstitial sites and equal number of electrons are trapped in the neighbourhood to balance the electrical charge. These electrons give rise to enhanced electrical conductivity.

---

* Non-stoichiometric compounds are sometimes called **berthollides** after the name of French inorganic chemist Claude Louis Berthollet, who studied such compounds.

Consequences of Metal Excess Defects

1. *The crystals with metal excess defects conduct electricity due to the presence of free electrons.* However, the conductivity is very low because of the number of defects and therefore, the number of free electrons is very small. Because of low conductivity as compared to conductivity of metals, these are called semiconductors. These compounds are also called ***n*-type semi-conductors** since the current is carried by the electrons in the normal way.

2. The crystals with metal excess defects are generally coloured. For example, *non-stoichiometric sodium chloride is yellow, non-stoichiometric potassium chloride is violet.*

(B) Metal Deficient Defects

These contain less number of positive ions than negative ions. These arise due to two ways :

(*i*) *Cation vacancies*

(*ii*) *Extra anions occupying interstitial sites*

(*i*) **Cation vacancies.** In some cases, *the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one*. This is shown in Fig. 46.

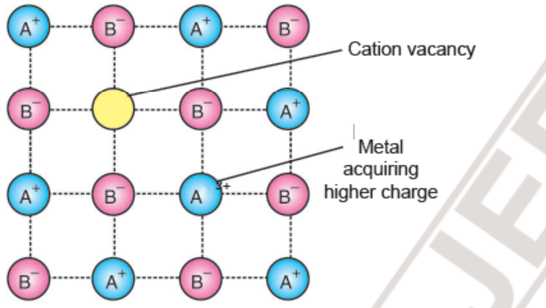


Fig. 46. Metal deficient defect due to cation vacancy.

This type of defect is possible in metals which show variable oxidation states. The common examples of compounds having this defect are ferrous oxide, ferrous sulphide, nickel oxide etc. In case of iron pyrites (FeS), for example, two out of three ferrous ions in a lattice may be converted into Fe^{3+} state and the third Fe^{2+} ion may be missing from its lattice site. Therefore, the crystal contains Fe^{2+} and Fe^{3+} ions. This gives rise to exchange of electrons from one Fe^{2+} ion to Fe^{3+} ion in which Fe^{2+} changes to Fe^{3+} and Fe^{3+} changes to Fe^{2+} ion. As a result, the crystal has metallic lustre. Because of the natural colour of iron pyrites and metallic lustre some samples of minerals shine like gold and have been nick-named as ***fool's gold***. Similarly, FeO 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+} ions are missing and the loss of positive charge is made up by presence of required number of Fe^{3+} ions. Moreover, since there is exchange of electrons, the substances become conductors.

REMEMBER

Because of metallic lustre of some minerals of iron pyrites, they shine like gold and have been nick named as **fool's gold**.

(*ii*) **Extra anions occupying interstitial sites.** In this case, *the extra anions may be occupying interstitial positions. The extra negative charge is balanced by the extra charges (oxidation of equal number of cations to higher oxidation states) on the adjacent metal ions.* This is shown in Fig. 47. Such type of defect is not common because the negative ions are usually very large and they cannot easily fit into the interstitial sites.

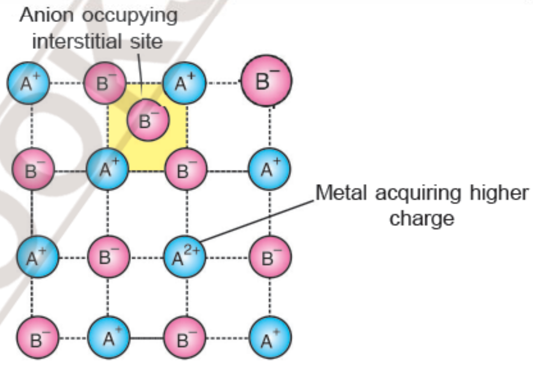


Fig. 47. Metal deficient defect due to extra anion.

Consequences of Metal Deficient Defects

Crystals with metal deficient defects are semiconductors. The conductivity is due to the movement of electron from one ion to another. For example, when an electron moves from ion A^+, it changes to A^{2+}. It is also called movement of positive hole and the substances are called ***p*-type semiconductors.**

(C) Impurity Defects

These defects in ionic crystals arise due to the presence of some impurity ions at the lattice sites (in place of host ions) or at the vacant interstitial sites. For example, if molten NaCl containing a little

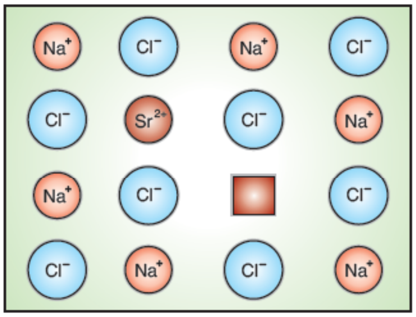


Fig. 48. Introduction of a cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}.

amount of $SrCl_2$ is allowed to crystallise, some of the sites of Na^+ ions are occupied by Sr^{2+} ions. For each Sr^{2+} ion introduced, two Na^+ ions are removed to maintain electrical neutrality. One of these lattice site is occupied by Sr^{2+} ion and the other remains vacant. This is shown in Fig. 48. Therefore, these vacancies result in increased electrical conductivity of the solid. Similar defect and behaviour is observed when $CdCl_2$ is added to AgCl.

SOLVED EXAMPLES

☐ Example 33.

If NaCl is doped with 10^{-3} mol% of $SrCl_2$, what is the concentration of cation vacancy ? **N.C.E.R.T.**

Solution : One cation of Sr^{2+} would create one cation vacancy in NaCl. Therefore, the number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.

∴ Concentration of cation vacancy on being doped with 10^{-3} mol % $SrCl_2$

$$= 10^{-3} \text{ mol\%} = \frac{10^{-3}}{100} = 10^{-5} \text{ mol}$$

$$\text{No. of } Sr^{2+} \text{ ions in } 10^{-5} \text{ mol} = 10^{-5} \times 6.023 \times 10^{23} = 6.023 \times 10^{18}\ Sr^{2+} \text{ ions}$$

$$\text{No. of cation vacancies} = \mathbf{6.023 \times 10^{18}}.$$

☐ Example 34.

Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions in given oxide?

N.C.E.R.T. *(Pb.S.B. 2018)*

Solution : $Ni_{0.98}O_{1.0.}$

Let Ni^{2+} be x so that Ni^{3+} will be $0.98 - x$. Total charge on the compound must be zero so that

$$+2x + 3(0.98 - x) - 2 = 0$$
$$2x + 2.94 - 3x - 2 = 0$$
$$-x = -0.94$$

or
$$x = 0.94$$

$$\% \text{ of } Ni^{2+} = \frac{0.94}{0.98} \times 100 = 96\%$$

$$\% \text{ of } Ni^{3+} = 4\%$$

☐ Example 35.

If Al^{3+} replaces Na^+ ion at the edge centre of NaCl lattice then calculate the vacancies in 1 mole of NaCl.

Solution : 1 mol of NaCl contains 1 mol of Na^+ ions *i.e.* 6.022×10^{23} Na^+ ions.

NaCl has *fcc* arrangement of Cl^- ions and Na^+ are present at the edge centres and body centres.

Since there are 12 edges and each edge is shared by 4 unit cells, then contribution of Cl^- ions present at the edge centres is $\frac{1}{4} \times 12 = 3$. Contribution of Na^+ ion present at the body centre = 1

Thus, for every 4 Na^+ ions, the ions present at the edge centres= 3.

∴ The Na^+ ions which have been replaced by Al^{3+} ions

$$= \frac{3}{4} \times 6.022 \times 10^{23} = 4.5165 \times 10^{23}$$

To maintain electrical neutrality, 1 Al^{3+} ion will replace 3 Na^+ ions. This means that 1 position will be occupied and remaining 2 will be vacant.

∴ No. of vacancies in 1 mole of NaCl

$$= \frac{2}{3} \times 4.5165 \times 10^{23} = \mathbf{3.011 \times 10^{23}}$$

Practice Problems

47. The composition of a sample of wustite is $Fe_{0.93}\,O_{1.00}$. What mass percentage of iron is present in the form of Fe(III) ions ?

48. Analysis shows that a metal oxide has the empirical formula $M_{0.96}\,O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal. *(C.B.S.E. Sample Paper 2007)*

Answers to Practice Problems

47. 11.5% **48.** 91.67, 8.33

Hints & Solutions on page 57A

Advanced Levels PROBLEMS

Accelerate Your Potential (for JEE Advance)

Problem 7. **A metal crystallizes in a face centred cubic unit cell with a = 0.560 nm. Calculate the density of the metal if it contains 0.1% Schottky defects. (Atomic mass of metal = 40 g mol^{-1})**

Solution Due to Schottky defect, the vacant spaces will increase resulting decrease in number of atoms per unit cell.

$$\text{In this case,} \quad Z = \left(4 - \frac{4 \times 0.1}{100}\right) = 3.996$$

$$\text{Density,} \quad \rho = \frac{Z \times M}{N_A \times a^3}$$

$$= \frac{3.996 \times (40 \text{g mol}^{-1})}{(0.560 \times 10^{-7} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= \mathbf{1.51 \text{ g cm}^{-3}}$$

Problem 8. **By X-ray diffraction method, the unit cell edge length of sodium chloride is found to be 562.6 pm. The density of NaCl is observed to be 2.158 g cm^{-3}.**

(i) Predict the type of defect present in the crystal.

(ii) Calculate the percentage of Na^+ and Cl^- ions missing.

Solution (*i*) The density can be calculated as

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$Z = 4\,(fcc)$, $M = 23 + 35.5 = 58.5 \text{ g mol}^{-1}$,
$a = 562.6 \text{ pm or} = 562.6 \times 10^{-10} \text{ cm}$, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad \rho = \frac{4 \times 58.5}{(562.6 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$= 2.182 \text{ g cm}^{-3}$$

Observed density $= 2.158 \text{ g cm}^{-3}$

Since observed density is less than theoretically calculated value, this means that some Na^+ and Cl^- ions are missing from their lattice sites *i.e.* the crystal has **Schottky defect.**

(*ii*) Actual formula units of NaCl per unit cell can be calculated as :

$$Z = \frac{a^3 \times N_A \times \rho}{M}$$

$$= \frac{(562.6 \times 10^{-10} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.158 \text{ g cm}^{-3})}{(58.5 \text{ g mol}^{-1})}$$

$$= 3.956$$

Formula units missing per unit cell

$$= 4 - 3.956 = 0.044$$

$$\therefore \quad \% \text{ missing unit cells} = \frac{0.044}{4} \times 100 = \mathbf{1.1\%}$$

PROPERTIES OF SOLIDS

There is a close relationship between the properties of a solid and its composition and structure. Some important properties of solids are discussed below :

1. Electrical Properties of Solids

Solids exhibit an interesting range of variation of electrical conductivities extending over 27 orders of magnitude ranging from 10^{-20} to 10^7 ohm^{-1} m^{-1}, which no other physical property show.

On the basis of electrical conductivity, solids can be classified into three types :

(i) conductors

(ii) insulators

(iii) semiconductors.

(*i*) **Conductors.** *The solids which allow the passage of electric current* are called **conductors.** They have conductivities in the range 10^4 to 10^7 ohm^{-1} m^{-1}. For example, metals have conductivities of the order of 10^7 ohm^{-1} m^{-1} and hence are the best conductors of electricity. Conductors are of two types : *metallic conductors or electrolytic conductors.*

(*a*) **Metallic conductors** *are those which allow the electricity to pass through them without undergoing any chemical change.* For example, copper, silver etc. Metals conduct electricity in solid as well as in molten state. In metallic conductors, the conductance is due to the movement of electrons under the influence of an applied electric potential. The streams of electrons constitute the current. *The conductivity of metals depends upon the number of valence electrons available per atom.*

(*b*) **Electrolytic conductors** *are those which allow the electricity to pass through them by undergoing chemical change.* The conduction in ionic solids is due to the migration of ions or other charged particles under the applied field. Due to strong electrostatic forces of attraction, the ionic solids do not conduct electricity. However, these conduct electricity to a good extent when they are in their molten state or in the form of their aqueous solutions. In these states, the ions of the electrolyte become free and they conduct electricity due to the movement of ions.

REMEMBER

- Metals conduct electricity through the movement of electrons.
- Electrolytes conduct electricity due to movement of ions.
- Metals conduct electricity in the solid as well as molten state.
- Electrolytes conduct electricity only in aqueous solution or molten state.

(*ii*) **Insulators.** *The solids which do not allow the passage of electric current through them* are called **insulators**. They have very very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1} m^{-1}. For example, wood, sulphur, phosphorus, rubber etc.

(*iii*) **Semiconductors.** *The solids whose conductivity lies between those of typical metallic conductors and insulators* are called **semiconductors**. The semiconductors have conductivity in the range of 10^{-6} to $10^4\ \Omega^{-1}\text{m}^{-1}$. The conductivity of semiconductors is due to the presence of impurities and defects.

REMEMBER

Range of conductivity

• Conductors	:	10^4 to 10^7 ohm^{-1}m^{-1}
• Semiconductors	:	10^{-6} to 10^4 ohm^{-1}m^{-1}
• Insulators	:	10^{-20} to 10^{-10} ohm^{-1}m^{-1}

Effect of Temperature on Conductivity

In general, with increase in temperature the conductivity of metals decreases while that of semiconductors increases. However, there is very little increase in the conductivity of an insulator as the temperature is increased.

REMEMBER

With increase in temperature electrical conductivity of
- metals decreases
- semiconductors increases.

The electrical behaviour of some typical transition metal oxides as metals (M), insulators (I) and oxides showing transition from metal to insulators behaviour (T) at a certain temperature are given below :

TiO (M)	VO (T)		MnO(I)	FeO(I)	CoO(I) NiO(I) CuO(I)
Ti_2O_3 (T)	V_2O_3 (T)	Cr_2O_3(I)	Mn_2O_3 (I)	Fe_2O_3(I)	
	VO_2 (T)	CrO_2 (M)	MnO_2 (I)		
TiO_2 (I)	V_2O_5 (I)				

Similar behaviour is exhibited by sulphides.

Learning Plus

It is very interesting to note that transition metal monoxides (MO), all of which have similar NaCl structures show very marked differences in their electrical properties.

- TiO is metallic, MnO, FeO, CuO, etc. are insulators while VO is metallic or insulator depending upon temperature.
- CrO_2 is metallic, MnO_2 is insulator while VO_2 is metallic or insulator depending upon temperature.
- ReO_3 is metallic, while VO_3 and TiO_3 are metallic or insulator depending upon temperature.

▶ Thus, transition metal oxides show marked differences in electrical properties.

To sum up

- ❒ TiO, CrO_2, ReO_3 are metallic.
- ❒ MnO, FeO, CuO, are insulators
- ❒ VO, VO_2, V_2O_3, TiO_3 etc. change from metallic to insulator at a certain temperature.
- ❒ **Rhenium oxide, ReO_3 has appearance as well as conductivity like copper.**

Mechanism of Electrical Conduction

The conduction in most of the solids is through electron movement under an electric field. However, in some ionic solids, the conduction is by ions. Therefore, in the solids where the conduction is by the movement of electrons, the electrical conductivity depends on the number of electrons available to participate in the conduction process. *The difference in electrical conductance behaviour of conductors, insulators and semiconductors* can be explained with the help of **band model.**

BAND THEORY FOR EXPLAINING THE BEHAVIOUR OF METAL CONDUCTORS, SEMICONDUCTORS AND INSULATORS

The bonding in metals can be explained by extending the simple molecular orbital theory to metals, called **band theory.** The basis of band theory is that a metal lattice has an extremely large number of atoms. The atomic orbitals of these metal atoms overlap to form a large number of molecular orbitals which are so close in energy to each other that they form **energy bands.**

Let us consider an example of lithium metal. Ignoring inner 1*s*-electrons which do not involve in bonding, 2*s*-orbitals of lithium atoms may combine to form molecular orbitals. We have learnt that in case of Li_2 (two atoms) 2*s* AOs on two lithium atoms combine to give two MOs; one bonding MO and one anti-bonding MO [Fig. 49 (*a*)]. If we have three lithium atoms, three 2*s* AOs would combine to form three MOs; one bonding, one antibonding and one non-bonding [Fig. 49 (b)].

The energy of non-bonding MO is in between the bonding and antibonding MO, exactly at the same level as the energy of the AOs. Similarly, in case of four lithium atoms, four 2*s* AOs would combine to form four MOs; two bonding and two antibonding MOs [Fig. 49 (*c*)]. Similarly, if we have N atoms of lithium (N is Avogadro number, 6.02×10^{23} atoms), 2*s* AOs of N atoms would combine to give N MOs. As the number of molecular orbitals is large, the energy levels of MOs are so close together, that they may almost be treated as continuous. Such a group of energy levels is known as **energy band** and is responsible for the name **band model for metals.**

The energy levels in a band is equal to the number of atoms in the metal. The formation of an energy band depends upon :

(*i*) the close proximity of large number of atoms.

(*ii*) the energy difference between the pure atomic orbitals.

Thus, 2*s*-atomic orbitals give rise to one energy band, the 2*p*-atomic orbitals also form a band of closely spaced energy levels. The various energy bands from different atomic orbitals may overlap or be separated from each other depending upon the relative energies of the atomic energy levels.

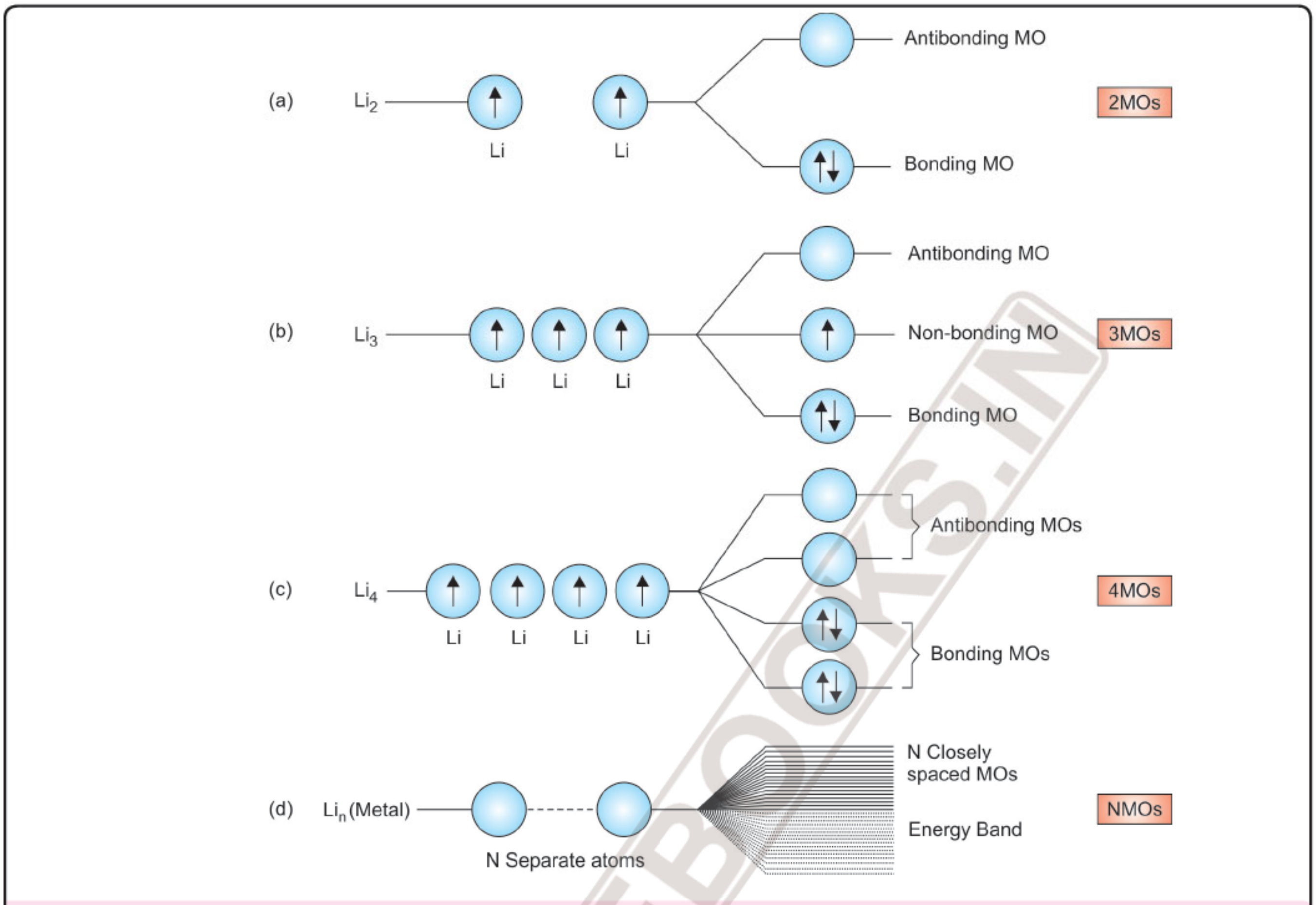


Fig. 49. Formation of molecular orbitals from 2, 3, 4 and N lithium atoms.

The energy bands formed by the overlap of 1*s*, 2*s* and 2*p* AOs of lithium metal are shown in Fig. 50.

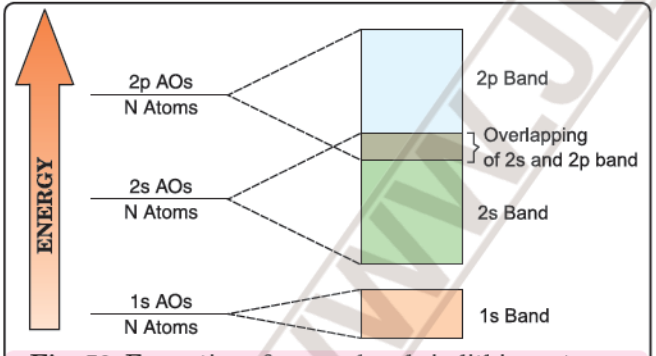


Fig. 50. Formation of energy bands in lithium atoms.

The arrangement of electrons in different energy bands determine the characteristics of a metal. Now, in the case of Li atom, the electronic configuration is $1s^2\ 2s^1$. The 1*s* energy band will be completely filled. These electrons do not contribute towards bonding and may be ignored. As already learnt, in case of Li_2, there will be 2 valence electrons and there are two MOs. Since each MO can accommodate two electrons (Pauli's exclusion principle), only bonding molecular orbital will be completely filled. Similarly, in case of Li_4, the four valence electrons would occupy only the two lowest bonding MOs.

Thus, in these cases, half of the molecular orbitals remain unoccupied. Similarly, N 2*s* atomic orbitals give N 2*s* molecular orbitals (energy band). Since Li atom has only one valence electron, only half of the molecular orbitals will be filled. In other words, only one half of the 2*s* band, will be filled in the lithium metal. This is shown in Fig. 51. (It may be noted that the bands are displaced laterally for clarity). Thus, there are many empty levels into which electrons can move. This movement of electrons from one level to another *constitutes an electric current.*

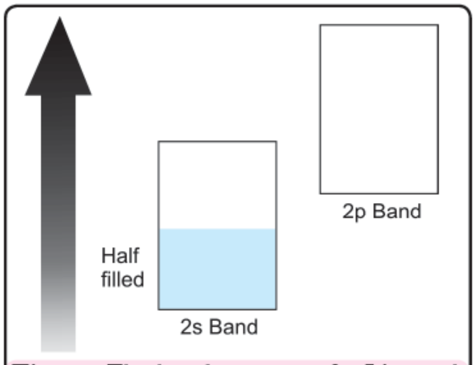


Fig. 51. The band structure for Li metal.

Thus, lithium is good conductor. At the same time, if we heat one end of metal, electrons at that end gain energy and move to empty energy bands where they can travel easily to another part of the metal. This accounts for thermal conduction of metals.

We can apply the same arguments to beryllium. In beryllium, there are two valence electrons and therefore, N atoms of beryllium will have 2N electrons from 2*s* AOs. Therefore, in beryllium metal, the 2*s* band will be completely filled (Fig 52) There are no empty orbitals in 2*s* energy band into which electrons can move. However, 2*p* energy band is completely empty and it overlaps the 2*s* energy band. When some electric field is applied, the electrons can move into the empty band.

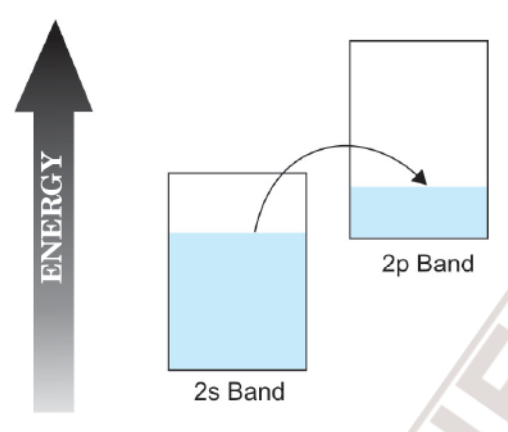


Fig. 52. The band structure for Be metal.

Thus, if the band is partially filled or it overlaps with a higher energy unoccupied band, then electrons can easily flow under an applied electric field and metal shows conductivity. For example, a partially filled band is shown in Fig. 53. (*a*) and overlapping bands are shown in Fig. 53(*b*) found in metals. Therefore, when some electric field is applied electrons can easily move within partially filled band or empty overlapping band and this movement is responsible for electrical conductance of the substance. This type of behaviour is shown by metals.

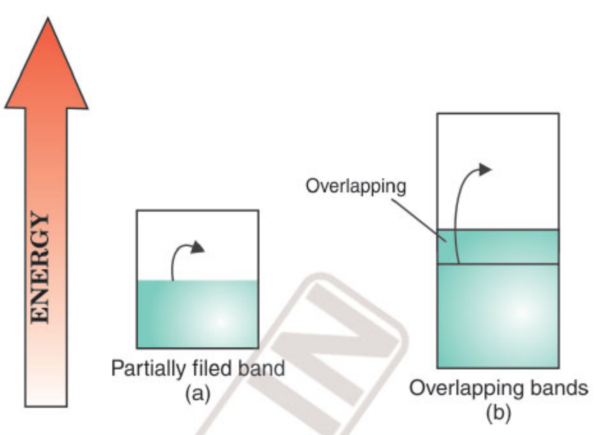


Fig. 53. Partially filled and overlapping bands.

In general, the electrical conductance of solids depends upon the energy gap between the filled valence bands and next higher vacant energy band.

- The *outermost filled energy band is called* **valence band** *and*
- *the next (lowest lying) empty band in which electrons can move is called* **conduction band.**

The spaces between valence band and conduction band represent energies forbidden to electrons and are called **energy gaps** or **forbidden zone.** The valence band and conduction bands for metals, semi-conductors and insulators are shown in Fig. 54.

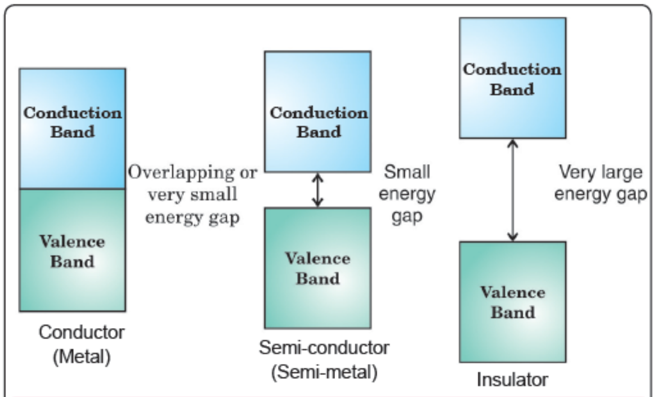


Fig. 54. Valence and conductance bands in metals, semi-conductors and insulators.

(*i*) In **metals**, the *conduction band is close to valence band* and, therefore, the electrons can easily go into the conduction band. Therefore, metals are good **conductors**.

(*ii*) In **insulators**, *the energy gap between valence band and conduction band is very large.* Therefore, the electrons from valence band cannot jump into the conduction band. Hence, the insulators have extremely low conductivity.

(*iii*) Several solids have properties intermediate between metals and insulators. These are called **semi-metals** or **semiconductors**. They have only small difference in energy between the filled valence band and empty conduction band. Therefore, some electrons may jump to conduction band and hence they show some conductivity. *Electrical conductivity of semi-conductors increases with rise in temperature because more electrons can jump to the conduction band.* Substances like silicon and germanium show this type of behaviour.

Conduction of Electricity in Semiconductors

Germanium and silicon are the most important commercial examples of semiconductors. Atoms of both germanium and silicon have four electrons in the outermost shell. Therefore, each atom is covalently bonded with four neighbouring atoms. There are no free electrons in this structure and therefore for practical purposes, the conductivities of pure germanium and silicon are very low and they behave as insulators. The energy gap between valence band and conduction band for Ge and Si are 68 kJ mol^{-1} and 106 kJ mol^{-1} respectively at room temperature.

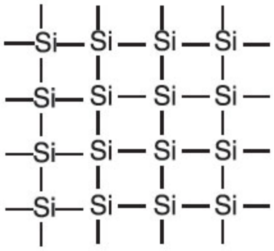
These can behave as semi-conductors in two types :

(*i*) *Intrinsic conduction*

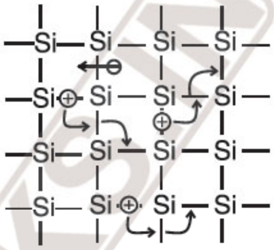
(*ii*) *Extrinsic conduction*

(*i*) Intrinsic conduction

Pure silicon or germanium are poor conductors because they have network or lattice of four strong covalent bonds. [Fig. 55 (*a*)] When a sufficient amount of energy by increasing temperature is supplied to the crystal, some covalent bonds may break due to thermal vibrations and electrons are released. When the crystal is connected to the elecric current, these electrons move leaving behind a positive charge or a ‘positive hole’ at the site of missing electron. The crystal will now be able to conduct electricity because when electric field is applied, the electrons move in one direction and the ‘positive holes’ move in the other direction. The electrons move through the interstices of the lattice and the positive holes jump from one bond to another as shown in Fig. 55 (*b*). This is known as **intrinsic semiconductivity of the crystal.** The intrinstic semiconductor contains equal number of current carrying holes and electrons.



(*a*) Network of pure silicon



(*b*) Intrinsic semi-conduction in silicon

Fig. 55. (*a*) Pure silicon (*b*) Silicon showing positive holes and negative electrons.

(*ii*) Extrinsic semi-conduction

The conductivity of the 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**. The conductivity of silicon and germanium increases drastically by doping it with certain other elements.

The impurities are of two types :

(*i*) Electron rich (or donor) impurities and

(*ii*) Electron deficient (or acceptor) impurities.

(*i*) Electron rich (or donor) impurities. The electron rich (or donor) impurities provide electrons in the following way:

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons. In their crystals each atom forms four covalent bonds (as discussed above) with its neighbours (Fig. 55).

Let us consider that some atoms with five valence electrons (of group 15) such as arsenic (As) are added to the silicon crystal. As a result, silicon atoms at some lattice sites are replaced by As atoms with five electrons in their outermost shell. As a Si atom is substituted by an atom of As, four of the electrons in arsenic form covalent bonds with surrounding Si atoms and the fifth electron remains free. Hence, an extra electron, over and above the number required for forming the four covalent bonds, gets introduced in the crystal. This extra electron which is not needed for bonding becomes delocalised and can serve to conduct electricity and therefore, silicon containing traces of arsenic (or arsenic doped silicon) exhibits high electrical conductivity. This type of conduction is known as ***n*-type semi-conduction** where '*n*' stands for negative because electrons are responsible for semiconducting behaviour. This is shown in Fig. 56. Doping of a germanium or silicon semiconductor with other group-15 elements such as P, Sb or Bi also give *n*-type semiconductors.

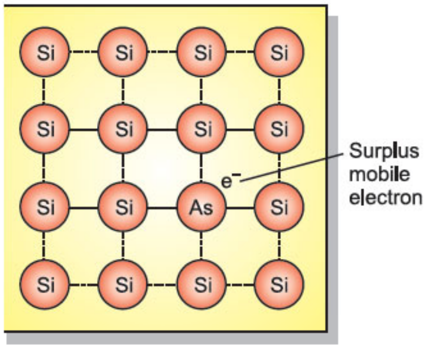


Fig. 56. Arsenic doped silicon semi-conductor.

***(ii)* Electron deficient or Acceptor Impurities.** An electron deficient or Acceptor impurity helps in conduction in the following way :

Suppose some atoms of silicon are doped with acceptor atoms having only three outer shell electrons such as indium (of Group 13). As a result, silicon atoms at some sites are replaced by indium atoms with three electrons in their outermost shell. Each indium atom uses its three electrons to form three bonds in the lattice and some sites normally occupied by electrons will be left empty and gives rise to electron deficiencies. The electron deficient sites are called **electron vacancies** or **electron holes**. An electron from neighbouring atom can jump to fill up this electron hole, but in doing so it would create an electron hole at its original position. As it continues, it would appear as if the electron hole has moved in the direction opposite to that of electron which filled it. When an electric field is applied, the electrons move towards the positively charged plate through electron holes and electron holes move towards the negatively charged plate as if they carry positive charge. This type of semiconductors are called ***p*-type semiconductors** because holes (positive in charge) appear to be responsible for the semiconducting properties. Doping of silicon or germanium with other group-13 elements such as B, Al or Ga also give *p*-type semiconductors. This is shown in Fig. 57.

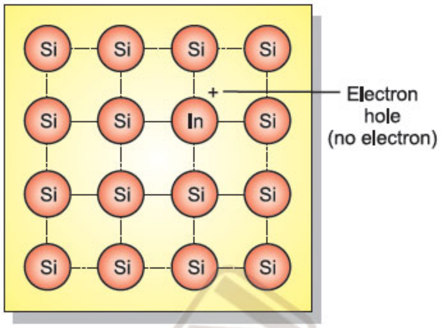


Fig. 57. Indium doped silicon semiconductor.

Thus, doping of germanium or silicon with traces of arsenic (or other group-15 element) gives rise to *n*-type semi-conductor and that with indium (or other group 13 element) gives rise to *p*-type semiconductor. Both *n*-type and *p*-type semiconductors are electrically neutral because each atom of impurity added is neutral in itself containing equal number of protons and electrons.

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

n-type and *p*-type of semiconductors are shown in Fig. 58. Various combinations of *n*-type and *p*-type semiconductors are possible which are used to make electronic components. For example,

- A **diode** is a combination of *n*-type and *p*-type semi-conductors and is used as a rectifier.
- Transistors which are *p-n-p* or *n-p-n* 'sandwich' semi-conductors are used to detect or amplify radio or audio signals.

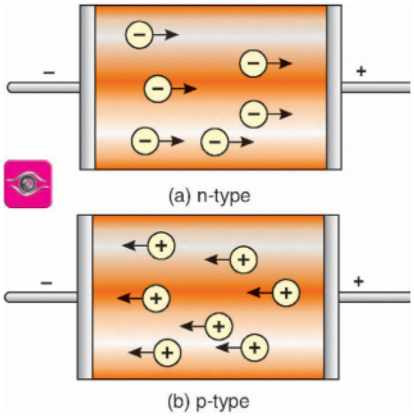


Fig. 58. Conduction in *n*-type and *p*-type of semiconductors.

- A solar cell is a photo diode used for converting radiant energy (of light) into electrical energy.
- Now, a large variety of solid materials have been prepared by combination of elements

of group-13 and 15 or 12 and 16 which have average valence of 4 as in Ge or Si. Typical examples of group 13–15 compounds are AlP, GaAs or InSb. Gallium arsenide (GaAs) semiconductors have gained much response and have revolutionised the design of semiconductor devices. The examples of group 12–16 compounds are ZnS, CdS, CdSe and HgTe. In these compounds, the bonds are not perfectly covalent and the ionic character depends upon the electronegativity differences between the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, VO, CrO_2 and ReO_3 behave like typical metals. Rhenium oxide, ReO_3 behaves metallic like copper in conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending upon temperature.

Competition Plus

Superconducting materials are those which offer no resistance to the passage of electricity. For detail, refer **Competition File** (Page 78A).

2. Magnetic Properties of Solids

The microscopic (observable) magnetic properties of materials are due to the magnetic moments associated with individual electron. Each electron in an atom has magnetic moment which originates from two sources :

(i) Orbital motion around the nucleus.

(ii) Spin of electron around its own axis.

A moving electron may be regarded as a small current loop generating a small magnetic field and having a magnetic moment along its axis of rotation as shown in Fig. 59 (*a*). The magnetic moment which originates from electron spin is directed along the spin axis. The spin magnetic moments are generally shown by up and down direction as shown in Fig. 59 (*b*). Thus, each electron in an atom may be regarded as a small magnet having permanent orbital and spin magnetic moments. The fundamental magnetic moment is the **Bohr magneton** μ_B which is equal to 9.27×10^{-24} A m^2. For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ depending upon the two possibilities of the spin. The contribution of the orbital magnetic moment is equal to $m_l \mu_B$ where m_l is the **magnetic quantum number** of the electron.

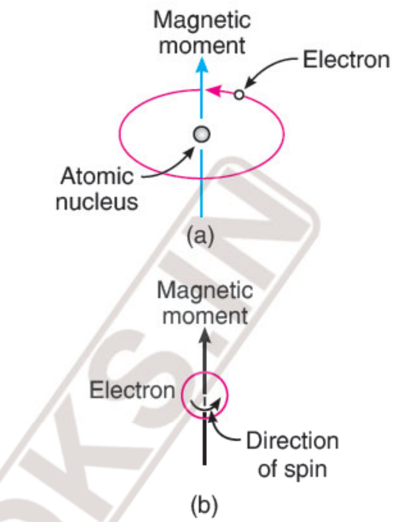


Fig. 59. (*a*) An orbiting electron.
(*b*) A spinning electron.

The magnetic properties of solids are also related to their electronic structures. Materials can be divided into the following types depending upon their response to magnetic field :

***(i)* Diamagnetic materials.** *The substances which are weakly repelled by the magnetic field* are known as **diamagnetic substances**. For example, NaCl, water, benzene, etc. are diamagnetic substances. The property thus exhibited is called **diamagnetism**. Diamagnetism arises when all the electrons are paired. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

***(ii)* Paramagnetic materials.** *The substances which have permanent magnetic dipoles and are attracted by the magnetic field are known* as **paramagnetic substances**. These consist of atoms, ions or molecules having one or more unpaired electrons. The common examples are Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2, TiO, Ti_2O_3, VO_2, CuO, etc. They lose their magnetism in the absence of magnetic field. Solids like TiO_2 which are expected to be diamagnetic often show paramagnetism due to the presence of slight non-stoichiometry.

***(iii)* Ferromagnetic substances.** *The substances which are strongly attracted by the magnetic field and show permanent magnetism even when the magnetic field is removed* are known as

ferromagnetic substances. Once such a material is magnetised, it remains magnetised permanently. Iron is the most common example. Other examples are cobalt, nickel, gadolinium (Gd), CrO_2, etc. at room temperature. These substances are very important in technology. For example, CrO_2 is the oxide used to make magnetic tapes for use in cassette recorders.

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 unmagnetized piece of 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 magnetic field. Depending upon the alignment of magnetic moments of domains in ferromagnetic substances, these are divided into three types :

(*a*) *When there is spontaneous alignment of magnetic moments of domains in the same direction, we get* **ferromagnetism** [Fig. 60 (*a*)]. These have strong magnetic effect. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.


(a) Ferromagnet


(b) Anti-ferromagnet


(c) Ferrimagnet

Fig. 60. Alignment of magnetic moments in (*a*) Ferromagnet (*b*) Anti-ferromagnet (*c*) Ferrimagnet.

(*b*) *If the alignment of magnetic moments of domains is in a compensatory way so as to give zero net magnetic moment because of cancellation of the individual magnetic moments then we get* **anti-ferromagnetism** in the material. The common example is MnO. A pattern of alignment of magnetic domains in anti-ferromagnetic substance is shown in Fig. 60 (*b*).

(*c*) *When the magnetic moments of domains are aligned in parallel and anti-parallel directions in unequal numbers resulting in net magnetic moment, we get* **ferrimagnetism**. This is shown in Fig. 60 (*c*). They are weakly attracted by magnetic field as compared to ferromagnetic substances. For example, Fe_3O_4 (magnetite) and ferrites of formula $M^{2+}Fe_2O_4$; M = Mg, Cu, Zn, etc show ferrimagnetism. These substances also lose ferrimagnetism on heating and become paramagnetic.

It may be noted that all the magnetically ordered solids (ferromagnetic, anti-ferromagnetic and ferrimagnetic) transform to paramagnetic state at a higher temperature due to randomisation of their spins. For example,

(*i*) V_2O_3 transforms from anti-ferromagnetic state to paramagnetic state at 150 K.

(*ii*) Fe_3O_4 becomes paramagnetic from ferrimagnetic at 850 K.

Magnetic properties of some transition metal oxides are shown below (where p = paramagnetic, af = anti-ferromagnetic, fe = ferrimagnetic, f = ferromagnetic and d = diamagnetic)

TiO (p)	VO (p)		MnO (af)	FeO (af)	CoO (p)	NiO (p)	CuO (p)
Ti_2O_3 (p)	V_2O_3 (af)	Cr_2O_3 (af)	Mn_2O_3 (af)	Fe_2O_3 (af)			
TiO_2 (d)	VO_2 (p)	CrO_2 (f)	MnO_2 (af)	Fe_3O_4 (fe)	Co_3O_4 (af)		
	V_2O_5 (d)						

REMEMBER

It may be noted that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie temperature.**

Competition Plus

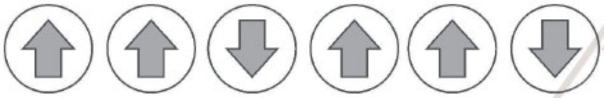
Solids have dielectric properties.For detail, refer **Competition File** (Page 78A).

add on Conceptual Questions 2A

Q.1. Analysis shows that FeO has a non-stoichiometric composition with molecular formula $Fe_{0.95}O$. Give reason. ***(A.I. S.B. 2018)***

Ans. It shows metal deficiency defect. In FeO, some Fe^{2+} ions are replaced by Fe^{3+} ions. Three Fe^{2+} ions are replaced by two Fe^{3+} ions to maintain electrical neutrality.

Q.2. Following is the schematic alignment of magnetic moments:



Identify the type of magnetism. What happens when these substances are heated ? ***(CBSE Sample Paper 2017-18)***

Ans. Ferrimagnetism. These substances lose ferrimagnetism on heating and become paramagnetic.

Q.3. Name any one solid in which both Frenkel and Schottky defects occur.

Ans. Silver bromide, AgBr has both Frenkel and Schottky defects.

Q.4. What is the effect of temperature on the conductivity of metals and semi-metals ?

Ans. In general, with increase in temperature, the conductivity of metals decreases and that of semi-metals increases.

Q.5. What is photovoltaic cell ?

Ans. The process in which electricity is produced by shining sunlight on certain substances. Amorphous silicon acts as a typical photovoltaic cell.

Q.6. Why is Frenkel defect not found in pure alkali metal halides ?

Ans. Frenkel defect is not found in alkali metal halides because the ions cannot get into the interstitial sites due to their larger size.

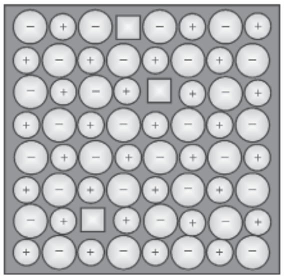
Q.7. What is the effect of presence of Schottky defects on the density of the crystal ?

Ans. The overall density of a crystalline substance decreases due to Schottky defects.

Q.8. What is the difference in the semi-conductors obtained by doping silicon with As or with Ga?

Ans. Semi-conductor produced by doping silicon with As is *n-type semiconductor* in which flow of current is due to electrons while silicon doped with Ga is *p*-type *semiconductor* in which flow of current is due to positive holes.

Q.9. Identify the type of defect shows in the following figure:
What type of substances show this defect ? ***(CBSE Sample Paper 2017-18)***



Ans. Schottky defect.

This type of defect is shown by ionic compounds in which

(*i*) the ions have high coordination number and

(*ii*) ions (cations and anions) are of almost similar sizes.

Q.10. Classify each of the following as being either a *p*-type or *n*-type semiconductor :

(*i*) Ge doped with In.

(*ii*) Si doped with B. ***(CBSE Sample Paper 2011)***

Ans. (*i*) Ge belongs to group 14 and In belongs to group 13.

Therefore, an electron deficient hole is created and it is a ***p*-type semiconductor.**

(*ii*) B belongs to group 13 and Si belongs to group 14. Therefore, an electron deficient hole is created and it is a ***p*-type semiconductor.**

Q.11. Name a salt which is added to AgCl so as to produce cation vacancies.

(A.I.S.B. 2003, D.S.B. 2004)

Ans. $CdCl_2$.

Q.12. Which point defect lowers the density of a crystal ? ***(A.I.S.B. 2004)***

Ans. Schottky defect.

Q.13. How does the electrical conductivity of semi-conductors vary with temperature ? ***(Pb.S.B. 2006)***

Ans. The electrical conductivity of semi-conductors increases with increase in temperature.

Q.14. Name the non-stoichiometric point defect responsible for colour in alkali metal halides. ***(A.I.S.B. 2006)***

Ans. Metal excess non-stoichiometric point defects.

Q.15. $CaCl_2$ will introduce Schottky defect when added to AgCl crystal. Explain. ***(Pb.S.B. 2003)***

Ans. $CaCl_2$ on adding to AgCl introduces impurity defect. The addition of one Ca^{2+} ion will replace two Ag^+ ions to maintain electrical conductivity. One of the position of Ag^+ will be occupied by Ca^{2+} ion and other will be left as a hole. Thus, a hole is created similar to Schottky defect.

Q.16. Why does ZnO appear golden yellow at high temperature? Explain. ***(Meghalaya S.B. 2013, Kerala S.B. 2018))***

Ans. When ZnO is heated it loses oxygen as :

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

The Zn^{2+} ions are entrapped in the interstitial sites and electrons are entrapped in the neighbouring interstitial sites to maintain electrical neutrality. This results in metal excess defect. Due to the presence of electrons in the interstitial void, the colour is yellow.

Q.17. The electrical conductivity of metals decreases with rise in temperature while that of a semiconductor increases. Explain. ***(H.P.S.B. 2003)***

Ans. In case of metals, with increase in temperature, the kernels start vibrating and therefore, they offer resistance to the flow of electrons. Hence, conductivity of metals decreases with rise in temperature. On the other hand, in case of semi-conductors, the conducitivity is due to the presence of impurities and defects. As the number of defects (such as holes) increases with rise in temperature, the conductivity increases.

Q.18. Why does zinc oxide exhibit enhanced electrical conductivity on heating ? ***(D.S.B. 2005 C)***

Ans. On heating, zinc oxide loses oxygen as :

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

The zinc ions thus formed are entrapped into the interstitial sites while the electrons are entrapped in the neighbouring interstitial sites. The entrapped electrons enhance the electrical conductivity of ZnO.

Q.19. Give reason :

(a) Why is Frenkel defect found in AgCl ?

(b) What is the difference between phosphorus doped and gallium doped silicon semi-conductors ? ***(CBSE Sample Paper 2011)***

Ans. (a) Due to small size of Ag^+ ion, it can fit into interstitial sites.

(b) Phosphorus doped silicon are *n*-type semiconductors while gallium doped silicon are *p*-type semiconductors.

Q.20. Why does LiCl acquire pink colour when heated in Li vapours ? ***(CBSE Sample Paper 2011)***

Ans. On heating LiCl in Li vapours, the excess of Li atoms deposit on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Li atoms to form LiCl. The electrons produced by ionisation of Li atoms diffuse into the crystal and get trapped at anion vacancies called F-centres. These absorb energy from visible light and radiate pink colour.

Solution File

Hints & Solutions for Practice Problems

☐ **1.** As Y atoms are at the corners of the cube and contribution of each = 1/8, therefore, no. of Y atoms/unit cell = $8 \times \frac{1}{8} = 1$. There can be only one X atom at the body centre.
Hence, formula = **XY.**

☐ **2.** There are only 8 corners so, no. of atoms per unit cell = $8 \times \frac{1}{8} = 1$

☐ **3.** No. of A atoms at the corners = 8
No. of A atoms missing from corners = 2
No. of A atoms present = 8 – 2 = 6

No. of A atoms per unit cell = $\frac{6}{8} = 3/4$

No. of B atoms per unit cell = $6 \times \frac{1}{2} = 3$

$\therefore$ Formula = $A_{3/4}B_3$ = $\mathbf{AB_4}$.

☐ **4.** There are 8 Y atoms at the corners and contribution of each is 1/8.

$\therefore$ No. of Y atoms per unit cell = $8 \times \frac{1}{8} = 1$

There can be only two X atoms at alternate faces and contribution of each of them is 1/2.

$\therefore$ No. of X atoms per unit cell = $2 \times \frac{1}{2} = 1$

Hence, formula is **XY.**

☐ **5.** 1 mole of gold = 197 g = 6.02×10^{23} atoms
No. of atoms in 2×10^{-3} g of gold

$$= \frac{6.02\times10^{23}}{197}\times 2\times10^{-3}$$

$$= 6.11 \times 10^{18}$$

Since face centred cubic unit cell contains 4 atoms, therefore, number of unit cells present

$$= \frac{6.11\times10^{18}}{4} = \mathbf{1.528 \times 10^{18}} \text{ unit cells}$$

☐ **6.** Distance between nearest neighbour.

$$d = \frac{a}{\sqrt{2}} = \frac{620}{\sqrt{2}} = 438.5 \text{ pm}$$

$$r = \frac{d}{2} = \mathbf{219.25\ pm}$$

☐ **7.** For *bcc* crystal, $r = \frac{\sqrt{3}}{4}a$

$$= \frac{1.732\times 352}{4} = \mathbf{152.416\ pm}$$

☐ **8.** For *fcc* unit cell, radius

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

$$r = \frac{4.086\times10^{-10}\text{ m}}{2\times1.414} = \mathbf{1.44 \times 10^{-10}\ m.}$$

☐ **9.** No. of W atoms = 8 × 1/8 = 1

No. of O atoms = $12\times\frac{1}{4} = 3$

No. of Na atoms= 1

Formula = $\mathbf{NaWO_3}$

☐ **10.** We assume that the closest Cs^+ to Cl^- ion distance is the sum of ionic radii of Cs^+ and Cl^- ions.

Nearest neighbour distance = 1.69 + 1.81 = 3.50Å

This distance is one half of the body diagonal of the cube

Body diagonal = $\sqrt{3}a$

$$\therefore \quad \frac{\sqrt{3}a}{2} = 3.50$$

$$\text{or} \quad a = \frac{3.50\times2}{\sqrt{3}} = \mathbf{4.04\text{Å}.}$$

☐ **11.** 1 mol of tungsten = 184g = 6.022×10^{23} atoms

No. of atoms in 1.5g of tungsten = $\frac{6.022\times10^{23}}{184}\times1.5$
$= 4.909 \times 10^{21}$

A bcc unit cell contains 2 atoms per unit cell.

$\therefore$ No. of unit cells = $\frac{4.909\times10^{21}}{2} = \mathbf{2.45 \times 10^{21}}$

☐ **12.** 1 mol of sodium = 23 g = 6.022×10^{23} atoms
No. of atoms present in 9.2 g of sodium

$$= \frac{6.022\times10^{23}}{23} \times 9.2 = 2.4088 \times 10^{23}$$

A *bcc* unit cell contains 2 atoms,

$\therefore$ No. of unit cells present = $\frac{2.4088\times10^{23}}{2}$
$= \mathbf{1.2044 \times 10^{23}}$

☐ **13.** For face centred unit cell, radius of atom

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

$$\text{or} \quad a = 2\sqrt{2}.r$$

$$r = 0.144 \text{ nm}$$

$$\therefore \quad a = 2 \times 1.414 \times 0.144$$

$$= \mathbf{0.407\ nm.}$$

☐ **14.** No. of atoms of A at corners = 7 (because one A is missing).

Contribution of atoms A in a unit cell = $7\times\frac{1}{8} = \frac{7}{8}$

No. of atoms of B at face centres = 6

$\therefore$ Contribution of atoms B in a unit cell $= 6 \times \frac{1}{2} = 3$

$A : B = \frac{7}{8} : 3$ or $7 : 24$

$\therefore$ Simplest formula = $\mathbf{A_7B_{24}}$

❑ **15.** $$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{1.69Å}{1.81Å} = 0.934$$

Since the radius ratio lies between 0.732 to 1, the coordination number of Cs^+ is 8 and the geometry of CsCl is cubic.

❑ **16.** $$r_{B^-} = \frac{r_{A^+}}{0.414} \text{ to } \frac{r_{A^+}}{0.732}$$

$$= \mathbf{241.6 \text{ to } 136.6 \text{ pm}}$$

❑ **17.** For a cation to fit into a tetrahedral hole

$$\frac{r_+}{r_-} < 0.414$$

or $$r_+ < 0.414 \times r_-$$

$$< 0.414 \times 0.182 \text{ nm}$$

$\therefore$ $$r_+ < 7.53 \times 10^{-2} \text{ nm}$$

❑ **18.** For each X atom, there are one octahedral and two tetrahedral sites.

No. of Y atoms in octahedral sites = 1 per X atom

Since alternative (*i.e.,* half) tetrahedral sites are occupied,

No. of Y atoms in tetrahedral sites = 1 per X atom

Total Y atoms = 2 per X atom

$\therefore$ Formula = $\mathbf{XY_2}$.

❑ **19.** Suppose number of atoms of Y in *ccp* = N

No. of octahedral voids = N

No. of atoms of X = N

Formula : **XY**

❑ **20.** Since N forms *ccp* arrangement, it will have 4 atoms in a unit cell.

Number of N atoms in unit cell = 4

For each atom, there are two tetrahedral voids so that there are 8 tetrahedral voids per unit cell.

$$\text{No. of M atoms} = \frac{1}{3} \times 8 = \frac{8}{3}$$

$$\text{Formula} = M_{8/3}N_4$$

or $$= \mathbf{M_2N_3}.$$

❑ **21.** Suppose the number of anions Y = N

No. of octahedral voids = N

No. of tetrahedral voids = 2 N

Since octahedral and tetrahedral voids are equally occupied by cations X and all the octahedral voids are occupied (as given) then N cations X are present in octahedral voids and N cations X are present in tetrahedral voids. Therefore,

No. of cations present = N + N = 2N

Ratio of cations X and anions Y = 2N : N

or 2 : 1

Thus, the formula of the compound will be $\mathbf{X_2Y}$.

❑ **22.** Suppose the number of oxide ions = N

No. of octahedral voids = N

No. of tetrahedral voids = 2 N

No. of cations P present $= \frac{1}{6} \times 2N = \frac{1}{3}N$

No. of cations Q present $= \frac{1}{3} \times N = \frac{N}{3}$

Ratio P : Q : O^{2-}

$$\frac{N}{3} : \frac{N}{3} : N \quad \text{or} \quad 1 : 1 : 3$$

Formula of compound = $\mathbf{PQO_3}$.

❑ **23.** In *hcp* arrangement, there is one octahedral void corresponding to each atom in the close packing. Since $\frac{2}{3}$ of the octahedral voids are occupied by aluminium ions, therefore, for each oxide ion there will be $\frac{2}{3}$ aluminium ions.

Therefore, ratio between aluminium ion and oxide ion is :

$$\frac{2}{3} : 1 \quad \text{or} \quad 2 : 3$$

Formula of corrundum = $\mathbf{Al_2O_3}$.

❑ **24.** $$d = \frac{Z \times M}{a^3 \times N_A}$$

$$= \frac{4 \times 40}{(400 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$$

$$= \mathbf{4.15 \text{ g cm}^{-3}}$$

40 g of element = 6.022×10^{23} atoms

4 g of element $= \frac{6.022 \times 10^{23}}{40} \times 4$

$= 6.022 \times 10^{22}$ atoms

For fcc, Z = 4

1 unit cell = 4 atoms

No. of unit cells in 4g $= \frac{6.022 \times 10^{22}}{4}$

$$= \mathbf{1.505 \times 10^{22}}$$

❑ **25.** Edge length = 400 pm = 400×10^{-10} cm

Volume of unit cell = $(400 \times 10^{-10})^3 = 64 \times 10^{-24}$ cm^3

Volume of 280 g of element $= \frac{280 \text{ g}}{7\text{g cm}^{-3}} = 40$ cm^3

Number of unit cells in this volume

$$= \frac{40}{64 \times 10^{-24}} = 6.25 \times 10^{23}$$

For *fcc*, number of atoms per unit cell = 4

$\therefore$ No. of atoms in 280 g of element = $6.25 \times 10^{23} \times 4$

$$= \mathbf{2.5 \times 10^{24} \text{ atoms}}$$

Solution File

❑ **26.** Volume of 50 g of element $= \dfrac{50}{19.35}$

$= 2.59\ \text{cm}^3$

Volume of unit cell $= (3.16 \times 10^{-8})^3$

$= 31.6 \times 10^{-24}\ \text{cm}^3$

No. of unit cells in this volume $= \dfrac{2.59}{31.6 \times 10^{-24}}$

$= 8.2 \times 10^{22}$

Since *bcc* arrangement has 2 atoms per unit cell,

Total no. of atoms $= 2 \times 8.2 \times 10^{22} = \mathbf{1.64 \times 10^{23}}$**.**

❑ **27.** Volume of unit cell of CsCl $= (4.121 \times 10^{-8})^3$

$= 69.99 \times 10^{-24}\ \text{cm}^3$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

Z = 1 (for *bcc*)

Formula mass = 132.9 + 35.5 = 168.4

The unit cell contains one Cs^+ ion and one Cl^- ion *i.e.,* one formula unit of CsCl.

$$\text{Density (CsCl)} = \frac{1 \times 168.4}{(412.1 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$= \mathbf{3.995\ g\ cm^{-3}}$$

For Al, Z = 4

$$\text{Density (Al)} = \frac{4 \times 26.9}{(405 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$= \mathbf{2.690\ g\ cm^{-3}}.$$

CsCl has larger density.

❑ **28.** $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$a = 409\ \text{pm} = 409 \times 10^{-10}\ \text{cm}$

$$10.5 = \frac{Z \times 108}{\left(409 \times 10^{-10}\right)^3 \times \left(6.022 \times 10^{23}\right)}$$

$$\therefore Z = \frac{10.5 \times \left(409 \times 10^{-10}\right)^3 \times \left(6.022 \times 10^{23}\right)}{108} = 4.0$$

∴ ***fcc* type structure**

❑ **29.** Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$a = 286.65 \times 10^{-10}$ cm, Z = 2 (for *bcc*)

M = 55.845 u, $\rho = 7.874\ \text{g cm}^{-3}$

$$7.874 = \frac{2 \times 55.845}{(286.65 \times 10^{-10})^3 \times N_A}$$

$$\text{or } N_A = \frac{2 \times 55.845}{(286.65 \times 10^{-10})^3 \times 7.874} = \mathbf{6.022 \times 10^{23}}$$

❑ **30.** Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

For *fcc* unit cell, $r = \dfrac{a}{2\sqrt{2}}$

$a = 2\sqrt{2}r = 2 \times 1.414 \times 0.144$

$= 0.407\ \text{nm} = 0.407 \times 10^{-7}\ \text{cm}$

$$\rho = \frac{4 \times (197\ \text{g mol}^{-1})}{(0.407 \times 10^{-7}\ \text{cm})^3 \times (6.022 \times 10^{23}\ \text{mol}^{-1})}$$

$$= \mathbf{19.41\ g\ cm^{-3}}$$

❑ **31.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

Z = 4 (for *fcc*)

$$6.23 = \frac{4 \times 60}{a^3 \times 6.022 \times 10^{23}}$$

$$a^3 = \frac{4 \times 60}{6.23 \times 6.022 \times 10^{23}}$$

$= 64 \times 10^{-24}$

$a = 4 \times 10^{-8}$ cm

$= \mathbf{4 \times 10^{-10}\ m = 400\ pm.}$

❑ **32.** Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$\rho = 10\ \text{g cm}^{-3}$, $M = 81\ \text{g mol}^{-1}$

$a = 3 \times 10^{-8}$ cm, $N_A = 6.022 \times 10^{23}$

$$\therefore \quad 10 = \frac{Z \times 81}{(3 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$\text{or} \quad Z = \frac{10 \times (3 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{81} = 2.0$$

∴ Nature of cubic unit cell is ***bcc***.

❑ **33.** $\text{Density} = \dfrac{Z \times M}{a^3 \times N_A}$

M = 207 + 32 = 239

$$= \frac{4 \times 239}{(500 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$= \mathbf{12.70\ g\ cm^{-3}}$$

❑ **34.** Edge of unit cell $= 2 \times 2.814 \times 10^{-8}$ cm

$= 5.628 \times 10^{-8}$ cm

Z = 4

If N_A is Avogadro number,

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

M = 202 + 37 = 239

$$2.167 = \frac{4 \times 58.5}{(5.628 \times 10^{-8})^3 \times N_A}$$

$$N_A = \frac{4 \times 58.5}{(5.628 \times 10^{-8})^3 \times 2.167}$$

$$= \mathbf{6.06 \times 10^{23}}$$

❑ **35.** $$\text{Density} = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times (6.022 \times 10^{23})}$$

$$= \mathbf{8.96\ g\ cm^{-3}}$$

Solution File

☐ **36.** Molecular mass of CsBr = 133 + 80 = 213

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$Z = 1$$

$$4.24 = \frac{1\times 213}{a^3\times 6.022\times 10^{23}}$$

$$\therefore \quad a^3 = \frac{1\times 213}{6.022\times 10^{23}\times 4.24}$$

$$= 8.34\times 10^{-23}$$

$$\therefore \quad a = 4.369\times 10^{-8}\text{ cm} = \mathbf{436.9\ pm}$$

☐ **37.**

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$10.5 = \frac{Z\times 108}{(409\times 10^{-10})^3\times 6.022\times 10^{23}}$$

$$Z = \frac{10.5\times(409\times 10^{-10})^3\times 6.022\times 10^{23}}{108}$$

$$= \mathbf{4.0}$$

∴ ***fcc*** type structure.

☐ **38.**

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$2.165 = \frac{4\times 58.5}{a^3\times 6.022\times 10^{23}}$$

$$a^3 = \frac{4\times 58.5}{2.165\times 6.022\times 10^{23}}$$

$$a^3 = 179.48\times 10^{-24}\text{ cm}^3$$

$$\text{or} \quad a = 5.64\times 10^{-8}\text{ cm}$$

In NaCl structure, $a = 2\,(r_{Na^+} + r_{Cl^-})$

∴ Distance between Na^+ and Cl^- ion,

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2} = 2.82\times 10^{-8}\text{ cm} = \mathbf{282\ pm}$$

☐ **39.** In a *bcc* lattice,

body diagonal $= \sqrt{3}a$

Now, $\quad 2\,(r_{A^+} + r_{B^-}) = \sqrt{3}a$

$$r_{A^+} + r_{B^-} = \frac{\sqrt{3}}{2}\times a = \frac{1.732\times 380}{2}\text{ pm} = \mathbf{329.1\ pm}$$

$$r_{A^+} = 329.1 - r_{B^-} = \mathbf{154.1\ pm}$$

☐ **40.** Formula unit mass of TlCl = 208.37 + 35.5 = 243.87

$$Z = ?$$

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$7.00 = \frac{Z\times 243.87}{(3.85\times 10^{-8})^3\times(6.022\times 10^{23})}$$

$$\text{or} \quad Z = \frac{7.00\times(3.85\times 10^{-8})^3\times(6.022\times 10^{23})}{243.87}$$

$$= 0.99 \quad \text{or} \quad 1$$

∴ A unit cell of TlCl contains one formula unit of TlCl.

∴ It is a simple cubic arrangement.

☐ **41.**

$$\text{Density} = 4.0\text{ g cm}^{-3}$$

$$Z = 1\text{ (for cubic lattice)}$$

$$4.00 = \frac{1\times 168.5}{a^3\times 6.022\times 10^{23}}$$

$$\text{or} \quad a^3 = \frac{168.5}{4.00\times 6.022\times 10^{23}}$$

$$= 69.9\times 10^{-24}\text{ cm}^3$$

$$\therefore \quad a = 4.12\times 10^{-8}\text{ cm} = \mathbf{412\ pm}$$

☐ **42.** For *fcc*, $Z = 4$

$$a = 408.6\text{ pm} = 408.6\times 10^{-10}\text{ cm}$$

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$= \frac{4\times(107.9)}{(408.6\times 10^{-10}\text{ cm})^3\times 6.022\times 10^{23}}$$

$$= \mathbf{10.506\ g\ cm^{-3}}$$

☐ **43.** If N_A is Avogadro number,

$$Z = 4\text{ (for } fcc)$$

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

Edge of unit cell = 2 × 269 = 538 pm

= 538×10^{-10} cm

$$\therefore \quad 2.48 = \frac{4\times 58}{(538\times 10^{-10})^3\times N_A}$$

$$N_A = \frac{4\times 58}{(538\times 10^{-10})^3\times 2.48}$$

$$= \mathbf{6.007\times 10^{23}}$$

☐ **44.** If M is the molar mass of copper,

$$\text{Density} = \frac{Z\times M}{a^3\times N_A}$$

$$Z = 4\text{ (for } fcc)$$

Cell edge, $a = 3.61\times 10^{-8}$ cm, $N_A = 6.022\times 10^{23}$

$$8.92 = \frac{4\times M}{(3.61\times 10^{-8})^3\times 6.022\times 10^{23}}$$

$$\text{or } M = \frac{8.92\times 6.022\times 10^{23}\times(3.61\times 10^{-8})^3}{4} = \mathbf{63.2\ g\ mol^{-1}}.$$

Solution File

☐ **45.** If N_A is Avogadro number

$$\text{Edge of unit cell} = 288.4 \text{ pm} = 288.4 \times 10^{-10} \text{ cm}$$

$$Z = 2 \text{ for } bcc$$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A}$$

$$\therefore \quad 7.20 = \frac{2 \times 52}{(288.4 \times 10^{-10})^3 \times N_A}$$

$$\text{or} \quad N_A = \frac{2 \times 52}{7.20 \times (288.4 \times 10^{-10})^3}$$

$$= \mathbf{6.02 \times 10^{23}}$$

☐ **46.** $$\rho = \frac{Z \times M}{a^3 \times N_A}$$

$a = 300 \text{ pm} = 300 \times 10^{-12} \text{ m} = 3 \times 10^{-8} \text{ cm}$

$M = 93 \text{ g mol}^{-1}$, $\rho = 11.5 \text{ g cm}^{-3}$

$$\therefore \quad 11.5 \text{ g cm}^{-3} = \frac{Z \times 93 \text{ g mol}^{-1}}{(3 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$\text{or } Z = \frac{(11.5 \text{ g cm}^{-3}) \times (3 \times 10^{-8} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(93 \text{ g mol}^{-1})}$$

$$= 2.01$$

$\therefore$ It is ***bcc*** type

☐ **47.** $Fe_{0.93}\,O_{1.0}$ is non-stoichiometric and is a mixture of Fe^{2+} and Fe^{3+} ions. Let x atoms of Fe^{3+} ions are present in the compound. This means that x Fe^{3+} ions have been replaced by Fe^{2+} ions.

No. of Fe^{2+} ions $= 0.93 - x$

For electrical neutrality, positive charge on the compound = Negative charge on the compound

$$2(0.93 - x) + 3x = 2$$

$$1.86 + x = 2$$

$$\text{or} \quad x = 0.14$$

$\therefore$ Fraction of $Fe^{3+} = 0.14$, $Fe^{2+} = 0.93 - 0.14 = 0.79$

Thus, the given formula may be represented as

$$Fe^{2+}_{0.79}\,Fe^{3+}_{0.14}\,O^{2-}_{1.0}$$

Total molar mass $= 0.93 \times 56 + 1 \times 16 = 68.08$g

$$\%\text{ of iron present as Fe(III)} = \frac{0.14 \times 56}{68.08} \times 100 = \mathbf{11.5\%}$$

☐ **48.** Let M^{2+} ions in the crystal be x so that M^{3+} ions in the crystal will be $0.96 - x$. Total charge on the compound must be zero, so that

$$+2 \times x + 3\,(0.96 - x) - 2 = 0$$

$$2x - 2.88 - 3x - 2 = 0$$

$$\text{or} \quad x = 0.88$$

$$\therefore \quad \%\text{ of } M^{2+} = \frac{0.88}{0.96} \times 100 = \mathbf{91.67}$$

$$\%\text{ of } M^{3+} = 100 - 91.67 = \mathbf{8.33.}$$

Chapter Summary

Key Terms

- **Isotropic substances.** The substances which show same physical properties (electrical conductivity, thermal conductivity, refractive index etc.) in all directions are called **isotropic substances**.
- **Anisotropic substances.** The substances which show different physical properties (electrical conductivity, thermal conductivity, refractive index, etc.) in different directions are called **anisotropic substances**.
- **Crystal lattice or space lattice.** It is the regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.
- **Unit cell.** It is the the smallest three dimensional repeating portion of a space lattice which when repeated over and again in different directions produces the complete crystal lattice.
- **Close packing.** The arrangement in which maximum available space is occupied leaving minimum available space.
- **Interstitial voids or sites.** The holes or voids in the crystal lattice are called **interstitial voids** or **sites**.
- **Coordination number.** It is the number of nearest (or closest) neighbours of any constituent particle in the crystal lattice.
- **Radius ratio.** The ratio of the radius of the cation to the radius of the anion (*i.e.* r_+/r_-) is called **radius ratio**.
- **Disorder or defect.** Any deviation from completely ordered arrangement of constituent particles in a crystal is called disorder or defect.
- **Schottky defect.** The defect in ionic solids in which equal number of cations and anions are missing from their normal sites.
- **Frenkel defect.** The defect in ionic solids in which some cations are missing from normal lattice sites and occupy interstitial sites.

QUICK CHAPTER ROUND UP

SOLIDS

Crystalline Solids
- Constituent particles have definite geometric arrangement
- long range order
- ➢ NaCl, Cu, Fe, S

Amorphous Solids
- Constituent particles do not have regular arrangement
- short range order
- ➢ glass, rubber, plastics

- ■ Crystalline solids are **anisotropic** (different properties in different directions)
- ■ Amorphous solids are **isotropic** (same properties in all directions)

MOLECULAR

Non polar
- Dispersion forces
  - ▸ Ar, I_2, H_2, solid CO_2

Polar
- Dipole-dipole forces
  - ▸ HCl, SO_2

Hydrogen bonded
- Hydrogen bonding
  - ▸ Ice (H_2O)

IONIC
- Constituents: +ve and –ve ions
- Strong electrostatic forces
  - ▸ NaCl, MgO, CaF_2

METALLIC
- +ve ions in a sea of electrons
- Metallic bonding
  - ▸ Cu, Ag, Fe, Mg

COVALENT OR NETWORK
- Atoms
- Covalent bonds
  - ▸ SiC, quartz, (SiO_2) diamond, graphite, AlN

7 crystal systems ← **CRYSTAL SYSTEMS** → **14 Bravais lattices**

Cubic	Orthorhombic	Tetragonal	Monoclinic	Triclinic	Hexagonal	Rhombohedral
$a = b = c$	$a \neq b \neq c$	$a = b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a = b \neq c$	$a = b = c$
$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	$\alpha \neq \beta \neq \gamma \neq 90°$	$\alpha = \beta = 90°$ $\gamma = 120°$	$\alpha = \beta = \gamma \neq 90°$
P, F, B	**P, F, B, E**	**P, B**	**P, E**	**P**	**P**	**P**
③	④	②	②	①	①	①

No. of atoms per cubic unit cell

Simple = 1
Body centred = 2
Face centred = 4
End centred = 2

No. of atoms in hcp = 6

Relationship between nearest distance (*d*) and radius of atom (*r*)

Simple cubic	$d = a$	$r = a/2$
Face centred cubic	$d = \frac{a}{\sqrt{2}}$	$r = \frac{a}{2\sqrt{2}}$
Body centred cubic	$d = \frac{\sqrt{3}}{2}a$	$r = \frac{\sqrt{3}}{4}a$

No. of tetrahedral sites = 2 per atom
No. of octahedral sites = 1 per atom

CLOSE PACKING

Cubic close or face centred cubic
- ABCABCA .....

Hexagonal close packing
- ABABA ....

PACKING EFFICIENCY

Percentage of total space filled by particles

ccp	*hcp*	*bcc*	simple cubic
74%	74%	68%	52.4%

The limiting radius ratio (r_c / r_a) and the coordination numbers in different crystals

r_c / r_a	Coordination No.	Arrangement	
0.155 – 0.225	3	Planar triangular	(*e.g.*, B_2O_3)
0.225 – 0.414	4	Tetrahedral	(*e.g.*, ZnS)
0.414 – 0.732	6	Octahedral	(*e.g.*, NaCl)
0.732 – 1	8	Body centred cubic	(*e.g.*, CsCl)

Mass of atoms of unit cell = No. of atoms in unit cell (Z) × Mass of atom

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

$$\text{Density of unit cell} = \frac{Z \times M}{a^3 \times N_A}$$

Z for
fcc = 4
bcc = 2
simple cubic = 1

DEFECTS IN CRYSTALS

Stoichiometric

Frenkel defect
- cations missing from normal sites and occupy interstitial sites
- does not cause change in density
  - ▸ AgCl, AgBr, AgI, ZnS

Schottky defect
- equal number of cations and anions missing from normal sites
- density decreases
  - ▸ NaCl, KCl, CsBr, AgBr

Non-stoichiometric

Metal excess type
- anion vacancies or interstitial cations
- *n*-type semiconductors

Metal deficient type
- cations vacancies or interstitial anions
- *p*-type semiconductors

In AgBr, both Frenkel and Schottky defects occur

SOLIDS ON THE BASIS OF ELECTRICAL PROPERTIES

Conductors
Electrical conductivity:
10^4 to 10^7 ohm^{-1}m^{-1}

Semiconductors
Electrical conductivity:
10^{-6} to 10^4 ohm^{-1} m^{-1}

Insulators
Electrical conductivity:
10^{-20} to 10^{-10} ohm^{-1} m^{-1}

- ***n*-type semiconductors:** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
- ***p*-type semiconductors:** Group 14 elements doped with group 13 elements, presence of holes increase conductivity.

MAGNETIC PROPERTIES OF SOLID

Paramagnetic
permanent magnetic dipoles and attracted by magnetic field
▸ O_2, Cu^{2+}, Fe^{3+}, TiO
Cuo, TiO_3, VO

Diamagnetic
weakly repelled by magnetic field
▸ benzene, NaCl, TiO_2, V_2O_3

Ferromagnetic
remain permanently, magnetised even in the absence of magnetic field ▸ Fe, CO, Ni, CrO_2

Anti-ferromagnetic
zero magnetic moment due to equal number of magnetic moments in opposite directions.
▸ MnO, FeO, Cr_2O_3

Ferrimagnetic
magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers giving net small magnetic moment .
▸ $MgFe_2O_4$

- **Curie temperature:** Temperature above which ferromagnetism is not observed.

- **Bragg's equation:** $n\lambda = 2\,d\,\sin\theta$

NCERT FILE Solved

NCERT In-text Question

Q.1. Why are solids rigid ?

Ans. In solids, the particles are closely packed and the empty spaces between the particles are very small. Therefore, solids are incompressible and they maintain their own shape when subjected to outside force. Hence, solids are rigid.

Q.2. Why do solids have a definite volume ?

Ans. The intermolecular forces between the particles in the solid state are very strong. Therefore, they are strongly held at fixed positions and particles cannot separate from one another. Hence, solids have a definite volume.

Q.3. Classify the following as amorphous or crystalline solids :

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinylchloride, fibre glass, copper.

Ans. *Refer Solved Example 1 (Page 7).*

Q.4. Why is glass considered a super cooled liquid ?

Ans. Glass is an amorphous solid. Like liquids, it has a tendency to flow, though very slowly. Moreover, glass is obtained when molten silicates are allowed to cool rapidly. Therefore, glass is considered as a super cooled liquid.

Q.5. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property ?

Ans. Since refractive index of the solid has same value in all directions *i.e.,* isotropic, it is an **amorphous solid.** It will not show cleavage property. When cut with a sharp edged tool (knife) it will cut into two pieces with irregular surfaces.

Q.6. Classify the following solids in different categories based on the nature of intermolecular forces operating in them :

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

Ans. Potassium sulphate : ionic solid, tin : metallic solid, benzene : molecular solid, urea : molecular solid, ammonia : molecular solid, water : molecular solid, zinc sulphide : ionic solid, graphite : covalent solid, rubidium : metallic solid, argon : molecular solid, silicon carbide : covalent solid.

Q.7. Solid A is very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it ?

Ans. Covalent or network solid like quartz (SiO_2), SiC or C (diamond).

Q.8. Ionic solids conduct electricity in molten state but not in solid state. Explain.

Ans. In solid state, the ions are present in fixed positions in the crystal lattice and cannot move when electric field is applied. However, when melted, the well ordered arrangement of the ions in the crystal is destroyed and the ions are in a position to move about when an electric current is applied. Hence, ionic solids conduct electricity in molten state.

Q.9. What type of solids are electrical conductors, malleable and ductile ?

Ans. Metallic solids.

Q.10 Give the significance of lattice point.

Ans. Lattice points represent the positions of the constituent particles (atoms, molecules or ions) in a crystal lattice.

Q.11. Name the parameters that characterize a unit cell.

Ans. A unit cell is characterized by the two types of parameters:

(*i*) Dimensions along the three edges represented as a, b and c.

(*ii*) Angles between edges α (between b and c), β (between a and c) and γ (between a and b).

Hence a unit cell is represented by six parameters a, b, c, α, β, and γ.

Q.12. Distinguish between :

(*i*) Hexagonal and monoclinic unit cell

(*ii*) Face centred and end centred unit cell

Ans. (*i*) Hexagonal unit cell has two edges of equal length ($a = b \neq c$) while monoclinic unit cell has all the three edges of unequal length ($a \neq b \neq c$).

In hexagonal two angles are of 90° and one angle of 120° ($\alpha = \beta = 90$, $\gamma = 120$). In monoclinic, two angles are of 90° but one is not of 90° ($\alpha = \gamma = 90°$, $\beta \neq 90°$).

(*ii*) Face centred unit cell has points at the corners as well as at the centre of each face. It has 4 atoms per unit cell.

End centred unit cell has points at all the corners and at the centre of any two opposite faces. It has 2 atoms per unit cell.

Q.13. Explain how much portion of an atom located at :

(*i*) corner and (*ii*) body centre of a cubic unit cell is part of its neighbouring unit cell ?

Ans. (*i*) 1/8 part of an atom located at corner belongs to neighbouring unit cell

(*ii*) No part.

Q.14. What is the two dimensional coordination number of a molecule in square close packed layer ?

Ans. 4.

Q.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 ?

Ans. An atom in hcp structure has three voids, one octahedral and two tetrahedral

$$\text{No. of atoms in 0.5 mol} = 0.5 \times 6.022 \times 10^{23}$$
$$= 3.011 \times 10^{23}$$

$$\text{Total number of voids} = 3 \times 3.011 \times 10^{23} = 9.033 \times 10^{23}$$

$$\text{Number of tetrahedral voids} = 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$$

Q. 16. A compound is formed by two elements M and N. The element N forms ccp and M atoms occupy 1/3 of tetrahedral voids. What is the formula of the compound ?

Ans. Since N forms *ccp* arrangement, it will have 4 atoms in a unit cell.

Number of N atoms in unit cell = 4

For each atom, there are two tetrahedral voids so that there are 8 tetrahedral voids per unit cell.

$$\text{No. of M atoms} = \frac{1}{3} \times 8 = \frac{8}{3}$$

$$\text{Formula} = M_{8/3}N_4$$

$$\text{or} \quad = M_2N_3.$$

Q. 17. Which of the following lattices has the highest packing efficiency (*i*) simple cubic (*ii*) body centred cubic and (*iii*) hexagonal close packed lattice ?

Ans. The packing efficiencies are :

simple cubic = 52.4%

body centred cubic = 68%

hexagonal close packed = 74%

∴ Hexagonal close packed lattice has highest packing efficiency.

Q.18. An element with molar mass 2.7 × 10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If the density is 2.7 × 10^3 kg m^{-3}. What is the nature of the cubic unit cell ?

Ans. Edge length = 405 pm = 405 × 10^{-12} m

Density of the cell = 2.7 × 10^3 kgm^{-3}

Molar mass = 2.7 × 10^{-2} kg mol^{-1}

$$\text{Now, density} = \frac{Z \times M}{a^3 \times N_A}$$

Z = ?

$$2.7 \times 10^3 \text{ kg m}^{-3} = \frac{Z \times 2.7 \times 10^{-2} \text{kg mol}^{-1}}{(405 \times 10^{-12} \text{m})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$\therefore Z = \frac{(2.7 \times 10^3 \text{kg m}^{-3}) \times (405 \times 10^{-12} \text{m})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}{2.7 \times 10^{-2} \text{kg mol}^{-1}}$$

$$= 4.0$$

Since the unit cell contains 4 atoms, it is **cubic close packed structure, *ccp*.**

Q.19. What type of defect can arise when a solid is heated ? Which physical property is affected by it and in what way ?

Ans. Electronic imperfections.

These defects affect electrical conductivity. It increases with rise in temperature.

Q.20. What type of stoichiometric defect is shown by:

(*i*) ZnS (*ii*) AgBr

Ans. (*i*) ZnS : Frenkel defect.

(*ii*) AgBr : Frenkel defect as well as Schottky defect.

Q.21. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it ?

Ans. When a cation of higher valence is added to an ionic solid, it results into impurity defect and cationic vacancies are introduced to maintain electrical neutrality. For example, when molten NaCl is allowed to crystallise in the presence of $SrCl_2$, some of the Na^+ ions are replaced by Sr^{2+} ions. Each Sr^{2+} ion replaces two Na^+ ions to maintain electrical neutrality. One of the site is occupied by Sr^{2+} ion and the other site remains vacant. Hence, cationic vacancies are produced equal to the number of Sr^{2+} ions.

Q.22. Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of a suitable example.

Ans. When crystals of alkali metal halides such as NaCl are heated in the atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface and combine with sodium atoms to form NaCl. This happens by the loss of electrons by Na atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result, the structure has an excess of sodium.

The crystals acquire yellow colour because when visible light falls on the crystals, they absorb energy from the visible region to excite the electrons. Hence, they are coloured. Similarly, excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet.

Q.23. A group 14 element is to be converted into *n*-type semiconductor by doping with a suitable impurity. To which group should this impurity belong ?

Ans. Group 15

e.g., P, As.

Q.24. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic ? Justify your answer.

Ans. Ferromagnetic substances. When the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field.

NCERT Textbook Exercises

Q.1. Define the term 'amorphous'. Give a few examples of amorphous solids.

Ans. A solid is said to be amorphous if the constituent particles are not arranged in any regular fashion. They may have short range order. For example, glass, plastics, amorphous silica.

Q.2. What makes a glass different from a solid such as quartz ? Under what conditions could quartz be converted into glass ?

Ans. Quartz is a crystalline solid in which SiO_4 tetrahedral units are arranged in an orderly arrangement. Glass is a supercooled liquid and is an amorphous solid.

In which SiO_4 tetrahedral units are not arranged in any regular order.

Quartz can be converted into glass by melting the quartz and then cooling it rapidly.

Q.3. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(*a*) Tetra phosphorus decoxide (P_4O_{10})

(*b*) Graphite (*c*) Brass

(*d*) Ammonium phosphate $(NH_4)_3PO_4$

(*e*) SiC (*f*) Rb (*g*) I_2 (*h*) LiBr (*i*) P_4

(*j*) Si (*k*) Plastic

Ans. *Refer Solved Example 2 (Page 8).*

Q.4. (*a*) What is meant by term 'coordination number' ?

(*b*) What is the coordination number of atoms :

(*i*) in a cubic close packed structure

(*ii*) in a body centred cubic structure.

Ans. (*a*) Coordination number gives the number of nearest neighbours with which a given atom is in contact. In case of ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that ion.

(*b*) (*i*) 12 (*ii*) 8

Q.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.

Ans. *Refer Text ; page 35.*

$$\text{Atomic mass, M} = \frac{\rho \times a^3 \times N_A}{Z}$$

Q.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 inter-molecular forces between these molecules ?

Ans. The melting point of a crystal depends upon the magnitude of forces holding the constituent particles together, which determine the stability. Higher the melting point, greater are the forces holding the constituent particles together and hence greater is the stability. For example, ionic crystals such as NaCl, KNO_3, etc. have very high melting points and are stable. On the other hand, molecular solids such as naphthalene, iodine, etc. are less stable because they have low values of melting points.

The melting points of some compounds are :

Water = 273 K, ethyl alcohol = 155.8 K, diethyl ether = 156.8 K and methane = 90.5 K.

The intermolecular forces in water and ethyl alcohol are mainly hydrogen bonding. The higher melting point of water than ethyl alcohol indicates that the hydrogen bonding in water is stronger than in ethyl alcohol. Diethyl ether is a polar molecule and, therefore, the intermolecular forces in diethyl ether are dipole-dipole interactions. On the other hand, methane is a non-polar molecule and the only forces present in them are the weak van der Waals forces (London dispersion forces). These are weaker than dipole-dipole interactions and hence methane has very low melting point than diethyl ether.

Q.7. How will you distinguish between the following pair of terms :

(*i*) Hexagonal close packing and cubic close packing

(*ii*) Crystal lattice and unit cell.

(*iii*) Tetrahedral void and octahedral void.

Ans. (*i*)

Hexagonal close packing	Cubic close packing
(*i*) In *hcp*, the spheres of the third layer are exactly aligned with those of the first layer. This arrangement is represented as AB AB........... type.	(*i*) In *ccp*, the spheres of the third layer are not aligned with those of the first layer or second layer. The layers of fourth layer are aligned with those of the first layer. This pattern is represented as ABCABC ....
(*ii*) In *hcp*, the tetrahedral voids of the second layer may be covered by the spheres of the third layer.	(*ii*) In *ccp*, the third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.

(*ii*) The three dimensional arrangement of constituent particles of a substance (atoms, ions or molecules) is called crystal lattice.

The smallest repeating pattern in a crystal lattice which when repeated in three dimensions gives the crystal is called unit cell.

(*iii*) A void surrounded by four spheres is called a tetrahedral void while a void surrounded by six spheres is called an octahedral void.

Q.8. How many lattice points are there in one unit cell of each of the following lattice ?

(*a*) face centred cubic (*b*) face centred tetragonal (*c*) body centred.

Ans. (*a*) In face centred cubic arrangement, number of lattice points are :

8 (at corners) + 6 (at face centres)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(*b*) In face centred tetragonal, number of lattice points are:

= 8 (at corners) + 6 (at face centres)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(*c*) In body centred cubic arrangement number of lattice points are :

= 8 (at corners) + 1 (at body center)

$$\text{Lattice points per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

Q.9. Explain : (*a*) The basis of similarities and differences between metallic and ionic crystals.

(*b*) Ionic solids are hard and brittle.

Ans. (*a*) Basis of similarities

(*i*) Both ionic and metallic crystals have electrostatic forces of attraction. In ionic crystals, these are between the oppositely charged ions while in metals, these are among the valence electrons and the kernels. That is why both ionic and metallic crystals have high melting points.

(*ii*) In both cases, the bond is non-directional.

Basis of differences

(*i*) In ionic crystals, the ions are not free to move and therefore, they do not conduct electricity in the solid state. They conduct electricity in the molten state or in their aqueous solution. However, in metals, the valence electrons are free to move and hence they conduct electricity in the solid state.

(*ii*) Ionic bond in ionic crystals is strong due to electrostatic forces of attraction. However, metallic bond may be weak or strong depending upon the number of valence electrons and the size of the kernels.

(*b*) Ionic crystals are hard because there are strong electrostatic forces of attraction among the oppositely charged ions. They are brittle because the ionic bond is non-directional.

Q.10. Calculate the efficiency of packing in case of a metal crystal for

(*a*) simple cubic (*b*) body centered cubic (*c*) face centered cubic

(with the assumptions that atoms are touching each other).

Ans. *Refer Text ; page 22–24.*

Q.11. Silver crystallizes in *fcc* lattice. If edge length of the cell is 4.077×10^{-8} cm and density is 10.5 g cm^{-3}. Calculate the atomic mass of silver.

(*A.I.S.B. 2008, Uttarakhand S.B. 2015*)

Ans. Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

or $M = \dfrac{\rho \times a^3 \times N_A}{Z}$

$Z = 4$ (*fcc* lattice), $\rho = 10.5$ g cm^{-3}, $N_A = 6.022 \times 10^{23}$, ($a = 4.077 \times 10^{-8}$ cm)

$$\therefore \quad M = \frac{10.5 \times (4.077 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4}$$

$$= 107.12 \text{ g mol}^{-1}.$$

Q.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 ?

Ans. As atoms Q are present at the 8 corners of the cube, therefore, number of atoms of Q in the unit cell = $8 \times \frac{1}{8} = 1$

As atoms P are present at the body centre, therefore, number of atoms P in the unit cell = 1

∴ Formula of the compound = PQ

Coordination number of each P and Q = 8

Q.13. Niobium crystallizes in body centered cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.

Ans. *Refer Solved Example 27* (*Page 38*).

Q.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.

Ans. *Refer Text ; page 24–25.*

Q.15. Copper crystallizes into a *fcc* latice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.29 g cm^{-3}.

Ans. Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

For *fcc* lattice, Z = 4

Atomic mass, M of copper = 63.5

$a = 3.61 \times 10^{-8}$ cm

$$\therefore \quad \rho = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}} = \mathbf{8.96\,g\,cm^{-3}}$$

This value is close to measured value.

Q.16. Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions ?

Ans. *Refer Solved Example 34* (*Page 46*).

Q.17. What is a semiconductor ? Describe the two main types of semiconductors and contrast their conduction mechanism.

Ans. The substances whose conductance lies between that of conductors (metals) and insulators are called semiconductors. They have conductivity values ranging from 10^{-6} to $10^4 \Omega^{-1} m^{-1}$. Two main types of semi-conductors are *n*-type and *p*-type. *For details Refer Text, page 51-52.*

Q.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 semi-conductor ?

Ans. Since the ratio of Cu : O in Cu_2O is less than 2 : 1, therefore, Cu_2O is non-stoichiometric crystal. This means that some Cu^+ ions have been replaced by Cu^{2+} ions. To maintain electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion thereby creating a hole. Since the conduction will be due to the presence of these positive holes, it is a *p*-types semi-conductor.

Q.19. Ferric oxide crystallizes 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.

Ans. In a close packed arrangement, there is one octahedral site corresponding to each atom constituting the lattice.

No. of oxide ions per unit cell in *hcp* arrangement = 6

No. of octahedral holes = 6

No. of ferric ions = $6 \times \frac{2}{3} = 4$

Formula of the compound Fe_4O_6 or Fe_2O_3.

Q.20. Classify each of the following as being either a *p*-type or a *n*-type semiconductor :

(*i*) Ge doped with In (*ii*) B doped with Si

Ans. (*i*) Ge belongs to group 14 and In belongs to group 13.

Therefore, an electron deficient hole is created and its is a ***p*-type semiconductor.**

(*ii*) B belongs to group 13 and Si belongs to group 14. Therefore, there will be a free electron and it is a ***n*-type semi conductor.**

Q.21. Gold (atomic radius = 0.144 nm) crystallizes in a face centered unit cell. What is the length of a side of the cell.

Ans. For face centred unit cell, radius of atom

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

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

$$r = 0.144 \text{ nm}$$

$$\therefore \quad a = 2 \times 0.144 \times 1.414 = \mathbf{0.407\ nm.}$$

Q.22. In terms of band theory, what is the difference (*i*) between a conductor and an insulator (*ii*) between a conductor and a semi-conductor ?

Ans. (*i*) The energy gap between the valence band and the conduction band in an insulator is very large. As a result, under an applied electric field, the electrons cannot jump from valence band to conduction band and therefore, such a substance has very small conductivity and behaves as an insulator. On the other hand, in a conductor the energy gap is either very small or there is overlapping between valence band and conduction band. Therefore, under an applied electric field, the electron can jump from valence band to insulator band and the substance shows conductivity.

(*ii*) In a conductor, the energy gap between valence band and conductance band is very small or there is overlapping between valence band and conduction band. But in a semiconductor, there is always a small energy gap between them. (*see Fig. 54 on page 50*).

Q.23. Explain the following terms with suitable examples :

(*i*) Schottky defect (*ii*) Frenkel defect

(*iii*) Interstitials (*iv*) F-centres

Ans. *Refer Text pages 42, 43, 44.*

Q.24. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125 pm.

(*a*) What is the length of the side of the unit cell ?

(*b*) How many unit cells are there in 1.00 cm^3 of aluminium ?

Ans. *Refer Solved Example 29 (Page 38).*

Q.25. If NaCl is doped with 10^{-3} mol% of $SrCl_2$. What is the concentration of cation vacancies ?

Ans. *Refer Solved Example 33 (Page 46).*

Q.26. Explain the following with suitable examples :

(*a*) ferromagnetism (*b*) paramagnetism

(*c*) ferrimagnetism (*d*) antiferromagnetism

(*e*) 12–16 and 13–15 group compounds.

Ans. *Refer Text page 53-54 [for (a) to (d)].*

(*e*) The solid binary compounds prepared by combining elements of group 12 and 16 are called 12 – 16 compounds. For example, CdS, ZnS, etc. The compounds prepared by combining elements of group 13 and 15 are called 13–15 compounds. For example, AlP, GaAs, etc. These compounds are used as semiconductors.

NCERT Exemplar Problems

Subjective Questions

Objective Questions from Exemplar Problems are given in Competition File, page 90.

Short Answer Type Questions

1. Why are liquids and gases categorised as fluids?

Ans. The liquids and gases have a property to flow i.e. the molecules of liquids and gases can easily move past and tumble over one another freely. Because of their tendency to flow, these have been categorised as fluids.

2. Why are solids incompressible?

Ans. The internuclear distances between the constituent particles (atoms, molecules or ions) in solids are very less. On bringing them further closer, there will be large repulsive forces between electron clouds of these particles. Therefore, solids cannot be compressed.

3. Inspite of long range order in the arrangement of particles why are the crystals usually not perfect?

Ans. During the crystallisation process, some deviations from the ideal ordered arrangement may occur. As a result, crystals are usually not perfect.

4. Why does table salt, NaCl, some times appear yellow in colour?

Ans. The yellow colour of sodium chloride crystals is due to metal excess defect. In this defect, the unpaired electrons get trapped in anion vacancies. These sites are called F-centres. The yellow colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

5. Why is FeO(*s*) not formed in stoichiometric composition?

Ans. In the crystals of FeO, some of the Fe^{2+} cations are replaced by Fe^{3+} ions. To balance the charge, three Fe^{2+} ions are replaced by two Fe^{3+} ions to make up for the loss of positive charge. As a result, there would be less amount of metal as compared to stoichiometric proportion.

6. Why does white ZnO (s) becomes yellow upon heating?

Ans. When ZnO is heated it loses oxygen as :

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

The Zn^{2+} ions are entrapped in the interstitial sites and electrons are entrapped in the neighbouring interstitial sites to maintain electrical neutrality. This results in metal excess defect and F-centres are created. Due to the presence of electrons in the interstitial voids, the colour is yellow.

7. Why does the electrical conductivity of semiconductors increase with rise in temperature?

Ans. According to band model, the gap between conduction band and valence band is small in semiconductors as shown in Fig. 54 (Page 51).

Therefore, electrons from the valence band can jump to the conduction band on increasing temperature. Thus, they become more conducting as the temperature increases.

8. Explain why does conductivity of germanium crystals increase on doping with gallium.

Ans. On doping germanium with gallium, some of the positions of lattice of germanium are occupied by gallium. Gallium atom has only three valence electrons. Therefore, fourth valency of nearby germanium atom is not satisfied and this site remains vacant. This place is deficient of electrons and is called electron hole or electron vacancy. Electron from neighbouring atom moves to fill the gap, thereby creating a hole in its original position. Under the influence of electric field, electrons move towards positively charged plates through these holes and conduct electricity. The holes appear to move towards negatively charged plates. The movement of electrons (or electron holes) results in increase in conductivity of germanium.

9. In a compound, nitrogen atoms (N) make cubic close packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids present. Determine the formula of the compound formed by M and N?

Ans. N atoms make up ccp arrangement and there are two tetrahedral sites per atom of N.

No. of N atoms per unit cell = 4

No. of tetrahedral sites = 4 × 2 = 8

No. of sites occupied by M = $\frac{1}{3} \times 8 = \frac{8}{3}$

$\therefore$ No. of M atoms per unit cell = $\frac{8}{3}$

Formula $M_{8/3}N_4$ or M_8N_{12} or M_2N_3

10. Under which situations can an amorphous substance change to crystalline form?

Ans. On heating, amorphous solids become crystalline at some temperature. For example, some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.

QUICK MEMORY TEST

A. Say True or False

1. Tetragonal and orthorhombic crystal systems have same axial angles.
2. In a *fcc* unit cell, the distance along one of the faces of the unit cell is 2.828 times the radius of the atoms.
3. In a face centred cubic system, number of atoms at faces is 4.
4. Copper crystallises in a *fcc* lattice. If radius of copper atom is 130 pm, then the edge length of the unit cell will be 450.32 pm.
5. The percentage of vacant space in *bcc* unit cell and simple cubic unit cell are 26% and 32% respectively.
6. Number of atoms per unit cell in *fcc* and *bcc* unit cells are 4 and 2 respectively.
7. For *bcc* metallic unit cell, the edge length (a) and radius (r) of atom are related as : $a = \frac{4}{\sqrt{3}} r$.
8. The volume of a *fcc* unit cell with atomic radius of atom 100 pm is 2.26×10^{-29} m^3.
9. The two ions A^+ and B^- have radii 90 and 200 pm respectively. In close packed crystal of a compound AB, the coordination number of A^+ is 4.
10. Number of Na^+ and Cl^- ions in a unit cell are 6 and 6 respectively.
11. Schottky defect results in the decrease in the density of the crystal.
12. Number of octahedral voids in 1 mole of a compound having *ccp* and *bcc* arrangement are 24.08×10^{23} and 12.04×10^{23} respectively.
13. The edge length of an ionic crystal XY having sodium chloride type structure is the sum of the radius of P and Q.
14. *hcp* arrangement has 6 atoms per unit cell.
15. Ferromagnetic and antiferromagnetic solids change into paramagnetic at high temperature.

B. Complete the missing links

1. The number of atoms for primitive unit cell is ...., for body centred cubic unit cell is .... and for face centred cubic unit cell is ....
2. The electrical conductivity of metals .... with decrease in temperature.
3. The substances which are strongly attracted by the magnetic field and show permanent magnetism even when magnetic field is removed are called .... substances.
4. The formula of a compound is .... in which atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids.
5. A group 14 element is to be converted in to *n*-type semiconductor by doping it with a suitable impurity belonging to group .... of the periodic table.
6. If electrical conductivity is found to be same in all directions through a solid, the substance is .... and this property is called ....
7. The coordination number of each sphere in hcp is ...., in *ccp* is .... and in *bcc* packing is ....
8. The packing fraction of a simple unit cell is ....
9. The empty space in *hcp* is .... and that in *bcc* packing is ....
10. In a body centred cubic crystal, the nearest neighbour distance is .... times the edge of the crystal and in a face centred cubic crystal, the nearest neighbour distance is .... times the edge of the crystal.
11. An octahedral void is .... times larger than a tetrahedral void.
12. In a body centred cubic arrangement .... atoms along the body diagonal touch each other.

13. The compound showing both Frenkel and Schottky defects is ....

14. If there is a large energy gap between the filled valence band and empty conduction band, the substance acts as ....

15. In a body centred cubic crystal of an element, the ratio of edge of the unit cell to the radius of the atom is ....

16. NaCl crystals have yellow colour due to the presence of ....

C. Choose the correct alternative

1. Lithium, sodium, potassium and rubidium crystallize in the *bcc / fcc* structure.

2. Most unsymmetrical crystal system is *monoclinic / triclinic*.

3. Orthorhombic has *4 / 3* types of lattices.

4. Total number of tetrahedral and octahedral voids in *hcp* arrangement are *12 / 18*.

5. In a crystalline solid, anions B are arranged in a ccp. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, the formula of the compound is A_2B / A_3B.

6. In a body centred cubic unit cell of elements, the radius of an atom is *0.433 / 0.354* times the edge length of the unit cell.

7. For a hcp unit cell, the number of atoms per unit cell is *6 / 4*.

8. $CdCl_2$ added to AgCl crystal will introduce *Schottky defect / Frenkel defect*.

9. MnO_2 is *antiferromagnetic / ferromagnetic* substance.

10. *Ferrimagnetism / ferromagnetism* arises due to unequal number of domains in opposite direction resulting in net magnetic moment.

11. The substance showing both Schottky defect and Frenkel defect is *AgBr / ZnS*.

12. When silicon is doped with arsenic, *n-type/p-type* semiconductor is produced.

Answers QUICK MEMORY TEST

A. Say True or False

1. True. Both have axial angles $\alpha = \beta = \gamma = 90°$.

2. True. In *fcc* unit cell, the face diagonal is

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

or

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

$$= 2 \times 1.414\,r = 2.828\,r$$

3. False. No. of atoms at faces = 3

4. False. Edge length $(a) = 2\sqrt{2}\,r$

$$= 2 \times 1.414 \times 130 = 367.64 \text{ pm}$$

5. False. In *bcc* vacant space = 32% and in simple cubic unit cell vacant space = 48%.

6. True. **7. True.**

8. True. For *fcc* arrangement, $r = \frac{a}{2\sqrt{2}}$

$$a = 2\sqrt{2}\,.\,r = 2 \times 1.414 \times 100 \times 10^{-12} \text{ m}$$

$$= 2.828 \times 10^{-10} \text{ m}$$

$\therefore$ Volume of unit cell $= a^3 = (2.828 \times 10^{-10} \text{ m})^3$

$$= 2.26 \times 10^{-29} \text{ m}^3$$

9. False. $$\frac{r(A^+)}{r(B^-)} = \frac{90 \text{ pm}}{200 \text{ pm}} = 0.45$$

Since it lies in the range of 0.414 to 0.732, the coordination number of A^+ will be 6.

10. False. No. of Na^+ ions = 4, No. of Cl^- ions = 4.

11. True.

12. False. 1 mole of compound in *ccp* or *bcc* arrangement has 6.02×10^{23} atoms.

No. of octahedral voids in *ccp* or *bcc* arrangement $= 6.023 \times 10^{23}$

13. False. $d(XY) = 2(r_{X^+} + r_{Y^-})$

14. True. **15. True.**

B. Complete the missing links

1. 1, 2, 4

2. increases

3. ferromagnetic

4. A_4B_3

5. 15

6. amorphous, isotropy

7. 12, 12, 8

8. 52.4%

9. 26%, 32%

10. $\frac{\sqrt{3}}{2}(0.866)$, $\frac{1}{\sqrt{2}}(0.707)$

11. 0.414/0.225 = 1.84

12. three

13. AgBr

14. insulator

15. $\frac{a}{\sqrt{3}\,a/4} = \frac{4}{\sqrt{3}} = (2.309)$

16. F-centres

C. Choose the correct alternative

1. *bcc*

2. triclinic

3. 4

4. 18

5. A_2B

6. 0.433

7. 6

8. Schottky defect

9. antiferromagnetic

10. ferrimagnetism

11. AgBr

12. *n*-type

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Diamond and solid rhombic sulphur both are covalent solids but the latter has very low melting point than the former. Explain why ?

Ans. Diamond is a three dimensional network covalent solid having very strong interatomic forces while, rhombic sulphur is a molecular solid consisting of puckered eight membered rings (S_8) held together by weak van der Waals' forces.

Q.2. Why does the window glasses of the old buildings look milky ?

Ans. Due to heating during the day and cooling at night (*i.e.*, annealing) over a number of years, glass acquires some crystalline character and hence looks milky.

Q.3. Can cubic lattice have end-centred unit cell ?

Ans. No, because a cubic unit cell must have all the faces to be same.

Q.4. Silver iodide crystallizes in the cubic close packed zinc sulphide structure. Assuming that ions occupy the lattice points, what fraction of the tetrahedral sites is occupied by Ag^+ ions ?

Ans. To maintain stoichiometry, Ag^+ ions occupy half the tetrahedral sites because there are two tetrahedral sites occupied for each I^- ion.

$\therefore$ 50% tetrahedral sites are occupied.

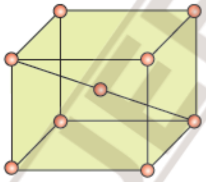
Q.5. An element 'X' has *bcc* lattice as shown below : The unit cell length, *a* is 306 pm.

(*a*) What is the distance between nearest neighbours ?

(*b*) What is the distance between next nearest neighbours ?

(*c*) How many nearest neighbours does each X atom have ?

(*d*) How many next nearest neighbours does each X have ?



Ans. (*a*) The body diagonal is $\sqrt{3}\,.\,a = 1.732 \times 306 = 530$ pm

Nearest neighbours along body diagonal are half the body diagonal.

$\therefore$ Distance between nearest neighbours $= \dfrac{530}{2} = 265$ pm

(*b*) The next nearest neighbours are along the edge.

$\therefore$ Distance between next nearest neighbour = 306 pm

(*c*) 8, because the body centre is next to 8 corners.

(*d*) 6, because each corner has neighbours along each edge.

Q.6. For a cubic crystal, the face diagonal is 4.25Å. Calculate its face length.

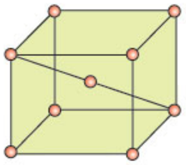
Ans. If *a* is the length of the face, then

$$\text{face diagonal} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore \text{Face length,} \quad a = \frac{\text{Face diagonal}}{\sqrt{2}} = \frac{4.25}{1.414} = \mathbf{3.01Å}$$

Q.7. What fraction of edge is not covered by atoms in *bcc* arrangement ?

Ans. If *a* is the edge length of *bcc* unit cell and *r* is the radius of atom, then



$$\text{edge not covered by atoms} = a - 2r$$

$$\text{In bcc, body diagonal} = \sqrt{3}\,a$$

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

$$\therefore \text{Edge not covered by atoms} = \frac{a - 2 \times \frac{\sqrt{3}}{4}a}{a}$$

$$= \frac{a\left(\frac{2-\sqrt{3}}{2}\right)}{a} = \frac{2-1.732}{2} = \mathbf{0.134\%}$$

Q.8. A face centred cubic lattice of a single type of atoms has same defects and its one corner and one face centre is left unoccupied per unit cell. Calculate the packing fraction of such solid.

Ans. Suppose the edge length of unit cell is *a* and radius of each atom is *r*.

$$\text{No. of atoms per unit cell} = 7 \times \frac{1}{8} + 5 \times \frac{1}{2} = \frac{27}{8}$$

$$\text{For face centred unit cell,} \quad a = 2\sqrt{2}\,r$$

$$\text{Volume of unit cell,} \quad a^3 = (2\sqrt{2}\,r)^3 = 16\sqrt{2}\,r^3$$

$$\text{Total volume of } \frac{27}{8} \text{ atoms} = \frac{27}{8} \times \frac{4}{3}\pi r^3 = \frac{9}{2}\pi r^3$$

$$\text{Packing fraction} = \frac{\frac{9}{2}\pi r^3}{16\sqrt{2}\,r^3}$$

$$= \frac{9\pi}{32\sqrt{2}} = \frac{9 \times 3.142}{32 \times 1.414}$$

$$= \mathbf{0.625}$$

Q.9. The CsCl has cubic structure of Cl^- ions in which Cs^+ ion is present in the body centre of the cube. Its density is 3.99 g cm^{-3}.

(*i*) Calculate the length of the edge of unit cell.

(*ii*) What is the distance between Cs^+ and Cl^- ions ?

(*iii*) What is the radius of Cs^+ ion if the radius of Cl^- ion is 180 pm ?

Ans. The unit cell of CsCl has cubic arrangement of Cl^- ions and Cs^+ ion is present in the body centre of the cube. Therefore, the unit cell contains one Cs^+ and one Cl^- ion or one CsCl unit, *i.e.*, Z = 1

Molar mass of CsCl, M = 133 + 35.5 = 168.5 g mol^{-1}

$$\text{Density, } \rho = \frac{Z \times M}{a^3 \times N_A}$$

$$3.99 \text{ g cm}^{-3} = \frac{1 \times (168.5 \text{ g mol}^{-1})}{a^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$a^3 = \frac{1 \times (168.5 \text{ g mol}^{-1})}{(3.99 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{mol}^{-1})}$$

$$= 7.02 \times 10^{-23} \text{ cm}^3$$

(*i*) Let length of the edge of unit cell $= a$

$$a^3 = 7.02 \times 10^{-23}\ \text{cm}^3 = 70.2 \times 10^{-24}\ \text{cm}^3$$

$$a = (70.2 \times 10^{-24}\ \text{cm})^{1/3}$$

$$= 4.12 \times 10^{-8}\ \text{cm} = \mathbf{412\ pm}$$

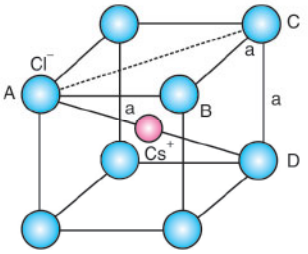
(*ii*) As shown in the figure, Cs^+ ion is present in the centre of unit cell and is in contact with 8 Cl^- ions at the corners. It is clear that the length of the body diagonal is equal to twice the distance between centre of Cs^+ and centre of Cl^- ion. The body diagonal can also be calculated as :

If length of unit cell edge is a, then face diagonal AC, is

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}\,a$$

The body diagonal AD is :

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}\,a$$



Now,

$$2\,(\text{Distance between } Cs^+ \text{ and } Cl^-) = \sqrt{3}\,a$$

or $$\text{Distance between } Cs^+ \text{ and } Cl^- = \frac{\sqrt{3}}{2}a$$

$$= \frac{\sqrt{3}}{2} \times 412\ \text{pm} = 1.732 \times 206\ \text{pm}$$

$$= \mathbf{356.8\ pm.}$$

(*iii*) Let the radius of Cl^- be $r(Cl^-)$ so that

$$r(Cs^+) + r(Cl^-) = 356.8\ \text{pm}$$

$$r(Cl^-) = 356.8 - 180 = \mathbf{176.8\ pm.}$$

Q.10. A metal crystallizes into two cubic phases, face centred cubic (*fcc*) and body centred cubic (*bcc*), whose unit cell lengths are 3.5 Å and 3.0 Å respectively. Calculate the ratio of densities of *fcc* and *bcc*.

Ans. Density of a crystal is

$$d = \frac{Z \times \text{Formula mass of substance}}{N_A \times a^3}$$

Now, for *fcc*, Z = 4 and for *bcc*, Z = 2

$$\therefore \quad d(fcc) = \frac{Z \times \text{Formula mass of substance}}{N_A \times (305\ \text{Å})^3}$$

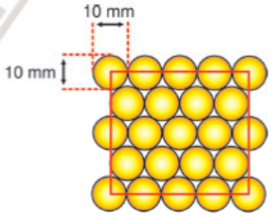
$$d(bcc) = \frac{2 \times \text{Atomic mass of metal}}{N_A \times (3.0\ \text{Å})^3}$$

$$\therefore \quad \frac{d(fcc)}{d(bcc)} = \frac{4}{2} \times \frac{(3.0)^3}{(3.5)^3} = \mathbf{1.26.}$$

Q.11. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangement of marbles in a plane so that maximum number of marbles can be placed inside the area ? Sketch the diagram and derive an expression for the number of molecules per unit area. *(I.I.T. 2003)*

Ans. Area of square = 40 × 40 = 1600 mm^2

To have maximum number of spheres, packing must be *hcp*. As shown in the figure, the maximum number of spheres of diameter 10 mm are = 18



Area = 1600 mm^2 = 16 cm^2

∴ No. of spheres per cm^2

$$= \frac{18}{16} = \mathbf{1.125}$$

Q.12. A compound AB has rock salt type structure. The formula weight of AB is 6.023 Y amu and the closest A—B distance is $Y^{1/3}$ nm, where Y is an arbitrary number.

***(a)* Find the density of the lattice.**

(b)* If the density of lattice is found to be 20 kg m^{-3}, predict the type of defect. *(I.I.T. 2004)

Ans. (*a*) Density of a crystal is

$$d = \frac{Z \times \text{Formula mass of substance}}{N_A \times a^3}$$

Now AB has rock salt type structure *i.e.*, *fcc* so that

Z = 4

Formula mass = $6.023\,Y \times 10^{-3}$ kg, $a = 2Y^{1/3}$ nm $= 2Y^{1/3} \times 10^{-9}$ m

$$\therefore \quad \text{Density} = \frac{4 \times 6.023\ Y \times 10^{-3}\text{kg}}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9}\text{m})^3}$$

$$= \mathbf{5.0\ kg\ m^{-3}.}$$

(*b*) Since the observed density (20 kg m^{-3}) is higher than the calculated value (5 kg m^{-3}), the compound must has either interstitial impurity defect or substitutional impurity defect.

Revision Exercises

Very Short Answer Questions *Carrying 1 mark*

1. Crystalline solids are anisotropic in nature. What does this statement mean? *(D.S.B. 2011)*
2. Define a unit cell. How many atoms are present in a simple cubic unit cell ?
3. In a close packed arrangement of N spheres, how many (*i*) tetrahedral and (*ii*) octahedral sites are present ?
4. Why is Frenkel defect not found in pure alkali metal halides ?
5. What is the coordination number of *hcp* and *ccp* structures ? *(Jammu S.B. 2015)*
6. State the type of crystal defects shown by AgBr. *(Meghalaya S.B. 2017)*
7. What is meant by point defects in crystals? *(Jharkhand S.B. 2011)*

8. What is meant by 'doping' in a semiconductor ? (*D.S.B. 2012*)

9. What is the radius ratio (r^+/r^-) for an ion to occupy tetrahedral site ?

10. Explain the nature of crystal defect produced when sodium crystal is doped with $MgCl_2$?

11. What is the effect of Frenkel structural defect on the electrical conductivity of a crystalline solid?

12. Why does Frenkel defect not change the density of AgCl crystals?

13. What makes alkali metal halides sometimes coloured, which are otherwise colourless ? (*D.S.B. 2004*)

14. What is meant by coordination number? (*Uttarakhand S.B. 2014*)

15. How does temperature influence the conductivity of a semi-conductor ? (*Pb.S.B. 2007*)

16. What type of substances exhibit anti-ferromagnetism? (*D.S.B. 2008*)

17. Name an element with which silicon should be doped to given *n*-type of semiconductor. (*D.S.B. 2008C*)

18. How does electrical conductivity vary in metals with temperature? (*Pb.S.B. 2008*)

19. What is the relationship between the edge length (a) of the unit cell and the radius (r) of an atom in a face-centred unit cell? (*Meghalaya S.B. 2013*)

20. Which point defect in crystals of a solid does not change the density of the solid ?(*D.S.B. 2009, 2010*)

21. How does ferromagnetism arise ? (*Pb.S.B. 2011*)

22. A compound forms *hcp* structure. Calculate the total number of voids in 0.5 mol of it. (*Assam S.B. 2017*)

23. Write a point of distinction between a metallic solid and an ionic solid other than metallic lustre. (*D.S.B. 2012*)

24. How many lattice points are there in one unit cell of each of the following lattices?
   (*i*) Face centred cubic lattice
   (*ii*) Body centred cubic lattice. (*Pb.S.B. 2012*)

25. Identify each of the following as being either a *p*-type or *n*-type semiconductor:
   (*i*) Ge doped with In
   (*ii*) Si doped with As. (*Pb.S.B. 2012*)

26. How many atoms are there in a unit cell of a metal crystallizing in *fcc* structure ?
(*D.S.B. 2013, Meghalaya S.B. 2015, Tripura S.B. 2016*)

27. What type of stoichiometric defect is shown by AgCl? (*D.S.B. 2013*)

28. What type of substances would make better permanent magnets: ferromagnetic or ferrimagnetic? (*D.S.B. 2013*)

29. What is the formula of a compound in which the element *Y* forms *ccp* lattice and atoms of *X* occupy 1/3 of tetrahedral voids ? (*D.S.B. 2015*)

30. What are the coordination number of Na^+ and Cl^- ions in NaCl? (*Nagaland S.B. 2016*)

31. What is Frenkel defect? How does it affect density of the solid? (*Karnataka S.B. 2018*)

32. What is the coordination number of particles present in fcc crystal structure? (*Kerala S.B. 2018*)

33. Which point defect in crystals lowers the density of a crystal? (*A.I.S.B. 2009, Assam S.B. 2013, 2015*)

34. What type of semiconductor is obtained when silicon is doped with arsenic ? (*A.I.S.B. 2010*)

35. What type of interactions hold the molecules together in a polar molecular solid ? (*A.I.S.B. 2010*)

36. Which stoichiometric defect in crystals increases the density of a solid ? (*D.S.B. 2011, A.I.S.B. 2012*)

37. How the conductivity of an intrinsic semiconductor be increased ? (*A.I.S.B. 2012*)

38. What is the formula of a compound in which the element Y forms *hcp* lattice and atoms X occupy 2/3rd of tetrahedral voids ? (*A.I.S.B. 2015*)

39. Analysis shows that FeO has a non-stoichiometric composition with molecular formula $Fe_{0.95}O$. Give reason. (*A.I.S.B. 2018*)

Short Answer Questions *Carrying 2 or 3 marks*

1. How are the solids classified on the basis of bonding in them? Give the constituents and one example of each type. (*J.K.S.B. 2011*)

2. What do you understand by the terms 'space lattice' and 'unit cell' ? (*Pb.S.B. 2015*)

3. Explain with the help of diagrams the structural differences between three types of cubic crystals. (*J.K.S.B. 2011*)

4. What are crystalline solids? Give two examples. (*Hr.S.B. 2017*)

5. What are crystalline and amorphous solids? Give four important differences between crystalline and amorphous solids. (*H.P.S.B. 2005, Pb. S.B. 2013*)

6. Explain :
   (*a*) Zinc oxide is white but it turns yellow on heating and becomes highly conducting.
   (*b*) $CdCl_2$ will induce Schottky defect if added to AgCl crystal.

7. If the radius of an octahedral void is *r* and the radius of atoms in close-packed arrangement is R, derive the relationship between *r* and R.

8. What is meant by coordination number ? What is the coordination number of atoms in a
   (*a*) cubic close packed structure
   (*b*) body centred cubic structure.

9. What is the radius ratio (r^+/r^-) for an ion to occupy :
   (*i*) tetrahedral void. (*ii*) octahedral void ?

10. What are the differences between Schottky and Frenkel defects ?(*Pb.S.B. 2013, H.P.S.B. 2013, Hr. S.B. 2013*)

11. Explain the Schottky defects in stoichiometric crystals. What are the important consequences of Schottky and Frenkel defects? (*Uttarakhand S.B. 2012*)

12. Differentiate between *n*-type and *p*-type extrinsic semiconductors.

13. Account for electrical conductivity in ionic compounds having
   (*i*) metal excess defects (*ii*) metal deficient defects.

14. Name the types of semiconductors produced when germanium (Ge) is doped separately with boron (B) and arsenic (As). Which one will be a better semiconductor and why ? *(Manipur S.B. 2014)*

15. (*i*) Explain Schottky defect in sodium chloride crystal.
(*ii*) Explain electric properties of semiconductors on the basis of band theory.
(Uttarakhand S.B. 2014)

16. (*a*) Calculate the packing efficiency in simple cubic lattice. *(Karnataka S.B. 2018)*
(*b*) What is Frenkel defect ? Give an example.
(Karnataka S.B. 2014)

17. In terms of band theory, what is the difference between
(*a*) a conductor and an insulator
(*b*) a conductor and a semiconductor.

18. Explain the following :
(*i*) Why is Frenkel defect not found in pure alkali metal halides ? *(Meghalaya S.B.2014)*
(*ii*) Anti-ferromagnetic substances have unpaired electrons but their dipole moment is zero.
(Hr. S.B. 2006)

19. What are semiconductors? How does electrical conductivity of semiconductors vary with temperature? Give one example of intrinsic semiconductor.

Or

What are paramagnetism and ferromagnetism? What type of substances would make better permanent magnets—ferromagnetic or ferrimagnetic?
(Assam S.B. 2018)

20. Write two differences between ferromagnetic substances and antiferromagnetic substances.
(Pb.S.B. 2009, 2014)

21. Explain the following terms :
(*i*) Schottky defects
(*ii*) Frenkel defects
(Uttarakhand S.B. 2015, Jammu S.B. 2016)

22. Explain the following terms with examples :
(*i*) Metal excess defects
(*ii*) Metal deficiency defects *(Hr. S.B. 2011)*

23. (*a*) What are imperfections in solids ?
(*b*) What are F-centres ? *(H.P.S.B. 2011)*

24. (*a*) Define ferromagnetism and ferrimagnetism.
(*b*) Differentiate between metals, insulators and semiconductors on the basis of band theory.
(Hr.S.B. 2012)

25. (*a*) Why does Frenkel defect not change the density of AgCl crystals ?
(*b*) Why does electrical conductivity of a semiconductor increases with rise in temperature ? *(Pb.S.B. 2012)*

26. (*i*) What is a semiconductor? Mention two main types of semiconductors.
(*ii*) Sodium crystallizes in a body centred cubic (*bcc*) unit cell. Calculate the approximate number of unit cells in 9.2g of sodium. (Atomic mass of Na = 23*u*) *(Assam S.B. 2013)*

27. (*a*) Give two differences between ferromagnetic and anti-ferromagnetic substances.
(*b*) Tungsten crystallizes in body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten. (At. mass of tungsten = 184*u*)
(Pb. S.B. 2013)

28. (*a*) A unit cell of sodium chloride has four formula units (number of atoms per unit cell). The edge length of unit cell is 0.564 nm. Find out the density of sodium chloride.
(*b*) Define Frenkel defect and Schottky defect. What is the difference between these two?
(Uttarakhand S.B. 2013)

29. (*a*) NaCl has fcc structure. Calculate the number of NaCl units in a unit cell of NaCl.
(*b*) Calculate the density of NaCl if edge length of NaCl unit cell is 564 pm. (Molar mass of NaCl = 58.5 g mol^{-1}) *(Kerala S.B. 2013)*

30. (*a*) What type of semiconductor is obtained when silicon is doped with boron?
(*b*) What type of magnetism is shown in the following alignment of magnetic moments?
↑ ↑ ↑ ↑ ↑ ↑
(*c*) What type of point defect is produced when AgCl is doped with $CdCl_2$? *(D.S.B. 2013)*

31. Examine the given defective crystal

A^+	B^-	A^+	B^-	A^+
B^-	O	B^-	A^+	B^-
A^+	B^-	A^+	O	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:
(*i*) What type of stoichiometric defect is shown by the crystal?
(*ii*) How is the density of the crystal affected by this defect ?
(*iii*) What type of ionic substances show such defect ?
(D.S.B. 2014)

32. Explain the following
(*i*) F-centres
(*ii*) Doping *(H.P.S.B. 2015)*

33. Write any two differences between crystalline and amorphous solids. *(H.P.S.B. 2015, D.S.B. 2017)*

34. Distinguish between crystal lattice and unit cell.
(Hr.S.B. 2015)

35. (*a*) Briefly discuss Schottky defect and give examples.
(*b*) Calculate the density of copper crystal which crystallises in *fcc* arrangement with edge length of 3.61×10^{-8} cm. *(Hr.S.B. 2015)*

36. Define ferromagnetism and ferrimagnetism.
(Pb.S.B. 2015)

37. Unit cells can be divided into two categories, primitive and centred unit cells.
(*a*) Differentiate between unit cell and crystal lattice.
(*b*) Calculate the number of atoms per unit cell in the following:
(*i*) body centred cubic unit cell (*bcc*)
(*ii*) face centred cubic unit cell (*fcc*)
(Kerala S.B. 2015)

38. Calculate packing effciency in simple cubic lattice.
(Karnataka S.B. 2018)

39. Explain
(*i*) radius ratio (*ii*) unit cells
(*iii*) Ferromagnetism (*iv*) Ferrimagnetism
(*v*) F-centre (*vi*) Doping
(H.P.S.B. 2018)

40. (*a*) Defince the following terms:

(*i*) F-centre

(*ii*) Unit cell (*Hr. S.B. 2018*)

(*b*) Explain Schottky defect with an example (*Hr. S.B. 2018*)

41. Differentiate between Schottky and Frenkel defects. (*Pb S.B. 2016*)

42. Differentiate between crystalline and amorphous solids. (*Pb S.B. 2016*)

43. What is Schottky defect? Find out the packing efficiency in a simple cubic lattice. (*Kolkata S.B. 2016*)

44. (*a*) Which of the following is a molecular solid?

(*i*) Diamond (*ii*) Graphite

(*iii*) Ice (*iv*) Quartz

(*b*) Unit cells can be classified into primitive and centred unit cells. Differentiate between primitive and centred unit cells.

(*c*) Presence of excess sodium makes NaCl crystal coloured. Explain on the basis of crystal defects. (*Kerala S.B. 2016*)

45. Write short notes on the following :

(*i*) Schottky defect

(*ii*) Ferromagnetic substances. (*H.P.S.B. 2017*)

46. (a) Based on the nature of intermolecular forces, classify the following solids?

(*i*) SiO_2 (*ii*) Ice

(b) ZnO turns yellow an heating. Why ? (*Kerala S.B. 2018*)

47. Assign reasons for the following :

(*i*) Phosphorus doped silicon is a semiconductor

(*ii*) Schottky defect lowers the density of a solid

(*iii*) Some of the very old objects appear slightly milky instead of being transparent. (*A.I.S.B. 2007*)

48. Explain the following properties with suitable examples:

(*i*) ferromagnetism (*ii*) paramagnetism

(*iii*) ferrimagnetism (*A.I.S.B. 2008*)

49. How do metallic and ionic substances differ in conducting electricity ? (*A.I.S.B. 2009*)

50. Explain how you can determine the atomic mass of an unknown metal if you know its mass, density and the dimensions of unit cell of its crystal. (*A.I.S.B. 2011, Manipur S.B. 2012*)

51. Calculate the packing efficiency of a metal crystal for a simple cubic lattice. (*A.I.S.B.2011*)

52. Account for the following:

(*b*) Schottky defects lower the density of related solids.

(*c*) Conductivity of silicon increases on doping it with phosphorus. (*A.I.S.B. 2013*)

53. (*a*) What change occurs when AgCl is doped with $CdCl_2$?

(*b*) What type of semiconductor is produced when silicon is doped with boron? (*A.I.S.B. 2013*)

54. (*i*) What type of non-stoichiometric point defect is responsible for the pink colour of LiCl ?

(*ii*) What type of stoichiometric defect is shown by NaCl?

Or

How will you distinguish between the following pairs of terms :

(*i*) Tetrahedral and octahedral voids

(*ii*) Crystal lattice and unit cell (*A.I.S.B. 2014*)

55. (*i*) Write the type of magnetism observed when the magnetic moments are oppositely aligned and cancel out each other.

(*ii*) Which stoichiometric defect does not change the density of the crystal ? (*A.I.S.B. 2014*)

56. (*a*) Based on the nature of intermolecular forces, classify the following solids: Benzene, silver.

(*b*) AgCl shows Frenkel defect while NaCl does not. Give reason.

(*c*) What type of semiconductor is formed when Ge is doped with Al ? (*A.I.S.B. 2017*)

57. An element 'X' (At. mass = 40 g mol^{-1}) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X'. ($N_A = 6.022 \times 10^{23}$ mol^{-1}) (*A.I.S.B. 2018*)

Long Answer Questions *Carrying 5 marks*

1. What do you understand by imperfections in solids? Explain stoichiometric defects in solids.

2. Discuss briefly the following properties of solids:

(*i*) electrical properties (*ii*) magnetic properties

3. (*a*) An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(*b*) Write any two differences between amorphous solids and crystalline solids.

OR

(*a*) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1})

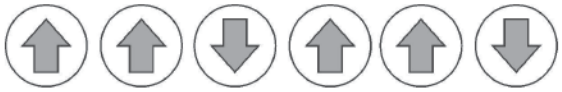
(*b*) Give reasons :

(*i*) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

(*ii*) Silicon on doping with phosphorus forms *n*-type semiconductor.

(*iii*) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. (*D.S.B. 2017*)

4. (*i*) Following is the schematic alignment of magnetic moments:



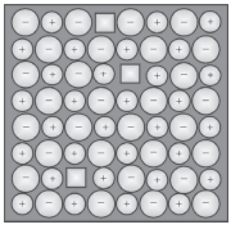
Identify the type of magnetism. What happens when these substances are heated ?

(*ii*) If the radius of the octahedral void is '*r*' and radius of the atoms in close packing is 'R'. What is the relation between '*r*' and 'R'.

(*iii*) Tungsten crystallizes in body centred cubic unit cell. If the edge length of the unit cell is 315.5 pm, what is the radius of tungsten atom?

OR

(*i*) Identify the type of defect shown in the following figure:



What type of substances show this defect ?

(*ii*) A metal crystallizes in a body centred cubic structure. If '*a*' is the edge length of its unit cell, '*r*' is the radius of the sphere. What is the relationship between '*r*' and '*a*' ?

(*iii*) An element with molar mass 63 g / mol forms a cubic unit cell with edge length of 360.8 p.m. If its density is 8.92 g/ cm^3. What is the nature of the cubic unit cell ? (*CBSE Sample Paper 2017-18*)

NUMERICAL PROBLEMS

1. Potassium iodide has cubic unit cell with cell edge of 705 pm. The density of KI is 3.12 g cm^{-3}. How many K^+ and I^- ions are contained in the unit cell ? [**Ans.** $4K^+$ and $4I^-$]
2. The unit of an element of atomic mass 96 and density 10.3 g cm^{-3} is a cube with edge length of 314 pm. Find the structure of the crystal lattice (simple cubic, FCC or BCC) (Avogadro's constant, $N_0 = 6.023 \times 10^{23}$ mol^{-1}) [**Ans.** BCC]
3. KCl and NaCl have fcc lattice. Calculate the ratio of density of NaCl to that of KCl if the ratio of edge of NaCl to that of KCl is 0.875. [**Ans.** 1.172]
4. Lithium metal has a body centred cubic structure. Its density is 0.53 g cm^{-3} and its molar mass is 6.94 g mol^{-1}. Calculate the volume of a unit cell of lithium metal. [**Ans.** 4.35×10^{-23} cm^3]
5. Iron has body centred cubic unit cell edge of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number (At. mass of iron = 56 g mol^{-1}) (*D.S.B. 2010*)
6. An element crystallizes in a structure having *fcc* unit cell of an edge 300 pm. Calculate its density if 180 g of this element contains 3.708×10^{24} atoms. (*Pb.S.B. 2012*)
7. An element (density 7.2 g cm^{-3}) crystallizes in a body centred cubic structure having its unit celll edge length 2.88 Å. Calculate the number of atoms present in 156 g of the element. (*Tripura Board 2016*)
8. Silver crystallizes in a fcc lattice. The edge length of its unit cell is 4.07×10^{-8} cm and its density is 10.48 g cm^{-3}. Calculate the relative atomic mass of silver ($N_A = 6.022 \times 10^{23}$ mol^{-1}). (*Kolkata S.B. 2016*)
9. Calculate the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 g cm^{-3}. (Molar mass of NaCl = 58.5 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}). (*A.I.S.B. 2006*)
10. Iron has a body centred cubic unit cell with a cell edge of 286.65 pm. The density of iron is 7.85 g cm^{-3}. Use this information to calculate Avogadro's number. (*A.I.S.B. 2009*)
11. Silver crystallizes with face centred cubic unit cells. Each side of the unit cell has a length of 409 pm. What is the radius of an atom of silver ? (Assume that each face atom is touching four corner atoms).(*A.I.S.B.2009*)
12. Tungsten crystallizes in a body centred cubic lattice. Calculate the number of unit cells in 1.5 g of tungsten. Atomic mass of tungsten = 184 u. (*A.I.S.B. 2009*)
13. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a *fcc* lattice. The F^- ions fill all the tetrahedral holes in the face centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro's number (Molar mass of CaF_2 = 78.08 g mol^{-1}). (*A.I.S.B. 2010, D.S.B. 2010*)
14. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom be 127.8 pm, is the copper unit cell simple cubic, body-centred cubic or face-centred cubic ? (Given : atomic mass of Cu = 63.54 g mol^{-1} and $N_A = 6.022 \times 10^{23}$ mol^{-1}) (*A.I.S.B. 2010, D.S.B. 2010*)
15. Copper crystallises with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. (Atomic mass of Cu = 63.55 u and Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1}) (*A.I.S.B. 2012*)
16. Aluminium crystallizes in an *fcc* structure. Atomic radius of the metal is 125 pm. What is length of the side of the unit cell of metal ? (*A.I.S.B. 2013*) [**Ans.** 353.3 pm]
17. An element with density 10 g cm^{-3} forms a cubic unit cell with edge length of 3×10^{-8} cm. What is the nature of the cubic unit cell if the atomic mass of the element is 81 g mol^{-1} ? (*A.I.S.B. 2015*) [**Ans.** *bcc*]
18. An element crystallizes in *fcc* lattice with cell edge of 400 pm. The density of the element in 7 g cm^{-3}. How many atoms are present in 280 g of the element? (*A.I.S.B. 2016*)

Hints & Answers *for* Revision Exercises

Very Short Answer Questions

2. 1
3. (*i*) 2N (*ii*) N
5. 12, 12
6. Schottky and Frenkel defects
9. 0.225 – 0.414
11. Electrical conductance increases.
13. Metal excess defect due to anion vacancies.
15. Conductivity of a semi-conductor increases with temperature.
17. P
18. Conductivity of metals decreases with increase in temperature.

19. $a = 2\sqrt{2}\,r$

22. 1 mol

24. (*i*) 4 (*ii*) 2

25. (*i*) *p*-type (*ii*) *n*-type

26. 4

27. Frenkel defect

28. ferromagnetic

29. X_2Y_3

30. $Na^+ = 6$, $Cl^- = 6$

32. six

33. Schottky defect

34. *n*-type

35. Dipole-dipole forces

36. Interstitial defect

38. X_4Y_3

Numerical Problems

• **1.** Density$=\dfrac{Z\times M}{a^3\times N_A}$

$$M = 39 + 127 = 166$$

$$Z = \text{No. of formula units}$$

$$\therefore \quad 3.12 = \frac{Z\times 166}{(705\times10^{-10})^3\times(6.022\times10^{23})}$$

$$Z = \frac{3.12\times(705\times10^{-10})^3\times(6.022\times10^{23})}{166}$$

$$= 3.96 \text{ or } 4$$

∴ **4 K^+ and 4 I^-** ions per unit cell.

• **2.** $\text{Density} = \dfrac{Z\times M}{a^3\times N_A}$

$$10.3 = \frac{Z\times 96}{(314\times10^{-10}\,\text{cm})^3\times(6.022\times10^{23})}$$

$$Z = \frac{10.3\times(314\times10^{-10})^3\times6.022\times10^{23}}{96} = \mathbf{2.0}$$

∴ *bcc* structure

• **3.**

$$d(\text{NaCl}) = \frac{\dfrac{M(\text{KCl})}{N_A}}{\dfrac{a^3(\text{KCl})}{M(\text{KCl})}}\times 4$$

$$d(\text{KCl}) = \frac{N_A}{a^3(\text{KCl})}\times 4$$

$$\frac{d(\text{NaCl})}{d(\text{KCl})} = \frac{M(\text{NaCl})}{M(\text{KCl})}\times\left[\frac{a\,(\text{KCl})}{a\,(\text{NaCl})}\right]^3$$

$$= \frac{58.5}{74.5}\times\left(\frac{1}{0.875}\right)^3 = \mathbf{1.172}$$

• **4.** $\text{Density} = \dfrac{Z\times M}{a^3\times N_A}$

For *bcc*, $Z = 2$

$$0.53 = \frac{2\times6.94}{a^3\times6.022\times10^{23}}$$

$$a^3 = \frac{2\times6.94}{0.53\times6.022\times10^{23}} = 4.35\times10^{-23}\ \text{cm}^3$$

Volume $= a^3 = \mathbf{4.35\times10^{-23}\ cm^3}$

• **5.** For *bcc* arrangement, $Z = 2$, $\rho = 7.87\ \text{g cm}^{-3}$, $M = 56\ \text{g mol}^{-1}$

Edge length, $a = 286.65\times10^{-12}\ \text{m} = 286.65\times10^{-10}\ \text{cm}$

$$\rho = \frac{Z\times M}{a^3\times N_A}$$

or

$$N_A = \frac{Z\times M}{\rho^3\times a^3}$$

$$= \frac{2\times(56\ \text{g mol}^{-1})}{(7.87\ \text{g cm}^{-3})\times(286.65\times10^{-10}\ \text{cm})^3}$$

$$= \mathbf{6.04\times10^{23}\ mol^{-1}}.$$

• **6.** $\text{Mass of unit cell} = \dfrac{180}{3.708\times10^{24}}\times4 = 194.17\times10^{-24}$

$$\text{Density} = \frac{194.17\times10^{-24}}{(300\times10^{-10})^3} = 7.19\ \text{g cm}^{-3}$$

• **7.** Volume of unit cell $= (2.88\times10^{-8}\ \text{cm})^3$

$$= 23.89\times10^{-24}\ \text{cm}^3.$$

$$\text{Volume of 156 g of element} = \frac{156\ \text{g}}{7.2\ \text{g cm}^{-3}} = 21.67\ \text{cm}^3$$

$$\text{No. of unit cells in this volume} = \frac{21.67}{23.89\times10^{-24}}$$

$$= 0.907\times10^{24}$$

For *bcc*, number of atoms per unit cell = 2

∴ No. of atoms in 156 g of element $= 0.907\times10^{24}\times2$

$$= \mathbf{1.814\times10^{24}}$$

• **8.** *Refer Solved Example 31 (page 39).*

• **9.** *Refer Solution of Practice Problem 38 (page 60).*

• **10.** *Refer Solution of Practice Problem 29 (page 59).*

• **11.** For fcc unit cell, radius , $r = \dfrac{a}{2\sqrt{2}}$

$$= \frac{409}{2\times1.414}$$

$$= \mathbf{144.6pm}$$

• **12.** 1 mol of tungsten = 184 g = 6.022×10^{23} atoms

$$\text{No. of atoms in 1.5 g of tungsten} = \frac{6.023\times10^{23}}{184}\times1.5$$

A body centred cubic cell contains 2 atoms.

$$\text{No. of unit cells present} = \frac{6.023\times10^{23}\times1.5}{184\times2}$$

$$= \mathbf{2.45\times10^{21}}$$

• **13.** $\text{Density} = \dfrac{Z\times M}{a^3\times N_A}$

$$3.18\ \text{g cm}^{-3} = \frac{4\times78.08\ \text{g mol}^{-1}}{(5.46\times10^{-8}\,\text{cm})^3\times N_A}$$

$$\therefore \quad N_A = \mathbf{6.02\times10^{23}}$$

• **14.** Assuming *fcc* lattice for copper,

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

$$= 2\times1.414\times127.8\times10^{-8}\ \text{cm}$$

$$= 3.614\times10^{-8}\ \text{cm}$$

$$\text{Density,}\quad \rho = \frac{4\times63.54}{(3.614\times10^{-8}\ \text{cm})^3\times(6.02\times10^{23})}$$

$$\therefore \quad = 8.94\ \text{g cm}^{-3}$$

Since the density is same as observed, the lattice is ***fcc*** lattice.

• **15.** *Refer Solved Example 15 (page 35).*

• **16.** *Refer Solved Example 7 (page 17).*

• **17.** *Refer Solution of Practice Problem 32 (page 59).*

• **18.** *Refer Solution of Practice Problem 24 (page 58).*

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

X-RAYS DIFFRACTION STUDIES

X-rays studies have helped to know the arrangement of atoms, ions or molecules in crystals. The phenomenon of X-rays by the crystals was studied by W.L. Bragg and W.H. Bragg. By analysing the diffraction patterns, Bragg deduced a simple relationship between the distance between the planes of constituent particles in the crystal (d), the wavelength of X-rays used (λ) and the angle of diffraction (θ). This relation is known as Bragg equation and is given as:

$$n\lambda = 2d \sin \theta,$$

where 2θ = angle made by a diffracted X-ray beam with the direction of incident beam.

n = positive integer (1, 2, 3.... etc,) which stands for serial order of diffracted beams.

Using Bragg's law, we can calculate the distance between rows of constituent particles in a crystal. These distances are characteristic of a crystal and depend upon the size and geometry or arrangement of these particles.

LAW OF CONSTANCY OF INTERFACIAL ANGLES

Crystals are bound by plane faces. The angle between any two faces is called an **interfacial angle.** It is measured by an instrument known as **goniometer.** The **law of constancy of interfacial angles** states that

irrespective of the size and shape of the crystals (which depend upon the conditions of their formation), the angles between any two corresponding faces of the crystal of a particular substance are always the same.

This is also known as **Steno's law.**

STRUCTURE OF METALS

The crystal structures adopted by some metallic elements at 25°C and 1 bar pressure are :

Crystal structure	Elements
hcp	Be, Cd, Co, Mg, Ca, Ti, Zn
fcc	Ag, Al, Au, Ca, Cu, Ni, Pb, Pt
bcc	Ba, Cr, Fe, Ir, Alkali metals
Primitive cubic	Po

PACKING IN OXIDES OF IRON

The packing in oxides of iron such as FeO and Fe_3O_4 is very interesting.

Structure of Iron oxide (FeO)

Iron oxide (FeO) has rock salt (NaCl) structure. In this case O^{2-} ions adopt face centred cubic arrangement (*fcc*) and Fe^{2+} ions occupy octahedral sites. This is the ideal arrangement. However, this oxide is always non-stoichiometic *i.e.,* the composition of Fe^{2+} and O^{2-} ions is not 1 : 1. It has been found to be generally $Fe_{0.95}O$ (wustite). This composition can be obtained if a small number of Fe^{3+} ions are replaced by two-third as many Fe^{2+} ions in octahedral sites.

Structure of Magnetite (Fe_3O_4)

Magnetite may be considered as having the composition FeO. Fe_2O_3. This composition can be obtained if we convert 2/3 of Fe^{2+} ions in FeO into Fe^{3+} ions (for every three Fe^{2+} ions two Fe^{3+} ions). In Fe_3O_4, the oxide ions are arranged in cubic close packing arrangement. Fe^{2+} ions occupy octahedral sites and the Fe^{3+} ions are equally distributed between octahedral and tetrahedral sites. This structure is known as **inverse spinel structure**. Fe_3O_4 is the load stone used by ancient travellers to find the direction. Another example of this structure is $MgFe_2O_4$ in which Fe^{2+} ions of Fe_3O_4 are replaced by Mg^{2+} ions.

Normal Spinel Structure

A spinel is an important class of oxides consisting of two types of metal ions with the oxide ions. The general formula of the compounds adopting spinel structure is AB_2O_4 such as $MgAl_2O_4$ and ferrites such as Zn Fe_2O_4. In this case, the oxide ions are arranged in cubic close packing arrangement, the divalent cations (Mg^{2+} or Fe^{2+}) are in tetrahedral sites and trivalent ions (Fe^{3+}, Al^{3+}) are in octahedral sites. In normal spinel structure, one-eighth of the tetrahedral holes are occupied by divalent metal ions and one-half of the octahedral holes are occupied by trivalent metal ions. Many of the ferrites which have spinel type structures are important magnetic materials used in telephones or memory loops in computers.

DIELECTRIC PROPERTIES OF SOLIDS

Depending upon the alignment of dipoles, the crystals have the following dielectric properties:

(*a*) **Piezoelectricity** in which the dipoles align themselves in an ordered manner such that there is a net dipole moment in the crystal, *e.g.,* titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), quartz.

(*b*) **Ferroelectricity** in which the dipoles are permanently aligned up even in the absence of electric field and the direction of polarization can be changed by applying an electric field. *e.g.,* barium titanate ($BaTiO_3$), sodium potassium tartarate (Rochelle salt), potassium dihydrogen phosphate (KH_2PO_4), etc.

(*c*) **Pyroelectricity.** Some polar crystals when heated produce small electric current called **pyroelectricity**.

(*d*) **Anti-ferroelectricity.** There is no net dipole moment in some crystals inspite of small dipoles because of alignment of dipoles in opposite directions and therefore they donot show ferroelectric character, *e.g.,* lead zirconate ($PbZrO_3$).

SUPERCONDUCTING MATERIALS

Ordinary metals conduct electricity and their conductivity is of order of 10^5 ohm^{-1} m^{-1}. **Superconducting materials** are those which offer no resistance to the passage of electricity. In this state, the materials become diamagnetic and are repelled by the magnets. Most metals become superconducting at very low temperatures (2–5 K). The highest temperature at which superconductivity was known till recently was 23 K in alloys of niobium (*e.g.,* Nb_3Ge). Some organic compounds also become superconducting at temperatures below 5 K.

The common examples of some superconducting materials along with their temperatures at which they become superconducting are given below :

Material	Temperature
Alloys of niobium	23 K
$Ba_{0.7}K_{0.3}BiO_3$	30 K
$La_{1.8}Sr_{0.2}CuO_4$	40 K
$Bi_2Ca_2Sr_2Cu_3O_{10}$	105 K
$Tl_2Ca_2Ba_2Cu_3O_{10}$	125 K

The important possible uses of super conducting materials are in electronics, building magnets, levitation, transportation, power transmission, etc.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions
M. C. Q.

A Topicwise MULTIPLE CHOICE QUESTIONS with only one correct answer

Select the Correct Answer :

Space Lattice, Unit Cell and Crystal Systems

A1. The crystal system of a compound with unit cell dimensions, $a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is

(a) cubic (b) hexagonal
(c) orthorhombic (d) rhombohedral

A2. In which of the following pair, both the crystals are not of the same type

(a) Ice, solid CO_2 (b) NaCl, BaO
(c) SiC, diamond (d) Mg, Ar

A3. Which of the following statements is not true about crystalline solids?

(a) Polar molecular solids have higher enthalpies of vaporisation than those of non-polar molecular solids.
(b) Graphite, though covalent solid is a good conductor of electricity.
(c) Ionic solids are conductors in molten state.
(d) Non-polar molecular solids have London forces between the constituents and have higher melting points than polar molecular solids.

A4. The most unsymmetrical and symmetrical systems are respectively

(a) tetragonal, cubic
(b) triclinic, cubic
(c) rhombohedral, hexagonal
(d) orthorhombic, cubic

A5. The packing fraction for a body centred cube is

(a) 0.42 (b) 0.54 (c) 0.68 (d) 0.74

A6. The number of atoms in *bcc* and *fcc* arrangement are respectively :

(a) 1, 2 (b) 2, 4 (c) 4, 2 (d) 2, 1

A7. The co-ordination number in *ccp* and *hcp* arrangement of metal atoms are respectively

(a) 6, 6 (b) 12, 6
(c) 8, 6 (d) 12, 12

A8. A metal crystallizes in a *ccp* structure. Its metallic radius is 141.5 pm. The number of unit cells in 64 cm^3 of the metal are

(a) 2×10^{32} (b) 1.5×10^{23}
(c) 1×10^{24} (d) 1.5×10^{22}

A9. The portion of edge length not occupied by atoms for simple cubic, *fcc* and *bcc* are respectively (*a* is edge length)

(a) $0 \; ; \; a\left(1-\frac{\sqrt{3}}{2}\right) \; ; \; a\left(1-\frac{1}{\sqrt{2}}\right)$

(b) $a\left(1-\frac{\sqrt{3}}{2}\right) ; 0 \; ; \; a\left(2-\frac{1}{\sqrt{2}}\right)$

(c) $0 \; ; \; a\left(1-\frac{1}{\sqrt{2}}\right) \; ; \; a\left(1-\frac{\sqrt{3}}{2}\right)$

(d) $a \; ; \; 2\sqrt{2}\,a \; ; \; \frac{\sqrt{3}}{2}a$

A10. Total volume of atoms present in face centred cubic unit cell of metal is (*r* is atomic radius)

(a) $\frac{24}{3}\pi r^3$ (b) $\frac{12}{3}\pi r^3$
(c) $\frac{16}{3}\pi r^3$ (d) $\frac{20}{3}\pi r^3$

A11. In a face centred cubic unit cell of close packed atoms, the radius of atom (*r*) is related to the edge length (*a*) of the unit cell by the expression

(a) $r = \frac{a}{\sqrt{2}}$ (b) $r = \frac{a}{2}$
(c) $r = \frac{a}{2\sqrt{2}}$ (d) $r = \frac{\sqrt{3}a}{4}$

A12. The number of atoms present in a hexagonal close packed unit cell is

(a) 4 (b) 6 (c) 8 (d) 12

Answers

A1. (b) **A2.** (d) **A3.** (d) **A4.** (b) **A5.** (c) **A6.** (b) **A7.** (d) **A8.** (c) **A9.** (c) **A10.** (c)
A11. (c) **A12.** (b)

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A13. In a *hcp* arrangement, each atom at the corner contributes to the unit cell equal to

(*a*) 1/2 (*b*) 1/8 (*c*) 1/6 (*d*) 1/4

A14. A metal crystallizes in *bcc* lattice. The percentage of edge length not covered by atoms is

(*a*) 12.4% (*b*) 13.4%
(*c*) 87.6% (*d*) 50.0%

A15. A metal crystallizes in *fcc* lattice and edge of the unit cell is 620 pm. The radius of metal atom is

(*a*) 265.5 pm (*b*) 310 pm
(*c*) 219.2 pm (*d*) 438.6 pm

A16. How many unit cells are present in a cubic shaped ideal crystal of NaCl of mass 1.0 g ?

(*a*) 2.57×10^{21} (*b*) 1.28×10^{21}
(*c*) 1.71×10^{21} (*d*) 5.14×10^{21}

Interstitial Voids, Structure and Density of Ionic solids

A17. For tetrahedral co-ordination, the radius ratio (r_+/r_-) should be :

(*a*) 0.155 – 0.225 (*b*) 0.225 – 0.414
(*c*) 0.414 – 0.732 (*d*) 0.732 – 1

A18. A compound formed by elements A and B crystallises in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face centre. The formula of the compound is :

(*a*) AB_3 (*b*) A_2B (*c*) AB_2 (*d*) A_2B_3.

A19. The number of second nearest Na^+ ions neighbour of a Na^+ ion in NaCl structure is

(*a*) 12 (*b*) 6 (*c*) 8 (*d*) 4

A20. The cubic unit cell of Al (molar mass = 27 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g cm^{-3}. The cubic unit cell is

(*a*) body centred (*b*) primitive
(*c*) edge centred (*d*) face centred

A21. In magnetite, O^{2-} have *ccp* arrangement with Fe^{2+} ions in 1/8th tetrahedral voids and Fe^{3+} ions in 1/4th octahedral and 1/8th tetrahedral voids. The formula of magnetite is

(*a*) Fe_3O_4 (*b*) Fe_2O_3
(*c*) FeO (*d*) Fe_3O_8

A22. An alloy of Cu, Au and Ag is found to have Cu constituting the *ccp* lattice. If Ag atoms occupy edge centres and Au is present at body centres, the alloy has formula :

(*a*) $Cu_4 Ag_2 Au$ (*b*) $Cu_4 Ag_4 Au$
(*c*) $Cu_4 Ag_3 Au$ (*d*) Cu Ag Au

A23. In spinel structure, O^{2-} ions are cubic-closed packed, whereas 1/8th of the tetrahedral holes are occupied by A^{2+} cations and 1/2 of the octahedral holes are occupied by cations B^{3+}. The general formula of this compound is

(*a*) A_2BO_4 (*b*) AB_2O_4
(*c*) A_2B_4O (*d*) A_4B_2O

A24. A crystalline solid has a cubic structure in which tungsten (W) atoms are located at the cubic corners of the unit cell, oxygen atoms at the edges of the cube and sodium atoms at the cube centre. The molecular formula of the compound is

(*a*) Na_2WO_3 (*b*) $NaWO_4$
(*c*) $NaWO_3$ (*d*) Na_2WO_4

A25. A mineral of titanium (perovskite) is found to contain calcium ions at the corners, oxygen atoms at the face centres and titanium atoms at the centre of the cube. The oxidation state of titanium in the mineral is

(*a*) + 1 (*b*) + 3 (*c*) + 4 (*d*) + 2

A26. The number of tetrahedral and octahedral holes in a hexagonal primitive unit cell are

(*a*) 8, 4 (*b*) 6, 12 (*c*) 2, 1 (*d*) 12, 6

A27. In which of the following structures, the anion has maximum co-ordination number ?

(*a*) NaCl (*b*) ZnS (*c*) CaF_2 (*d*) Na_2O

A28. In a *fcc* arrangement of P and Q atoms, where P atoms are at the corners of the unit cell, Q atoms at the face centres and two atoms are missing from two corners in each unit cell, then the formula of the compound is

(*a*) P_2Q_3 (*b*) P_4Q (*c*) P_4Q_5 (*d*) PQ_4

A29. The pyknometer density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of the unoccupied sites in sodium chloride crystal is

(*a*) 5.96 (*b*) 5.96×10^{-2}
(*c*) 5.96×10^{-1} (*d*) 5.96×10^{-3}

A30. Three elements A, B and C crystallise into a cubic solid lattice. Atoms A occupy the corners, B occupy the cube centres and C occupy the edges. The formula of the compound is

(*a*) ABC (*b*) ABC_2
(*c*) ABC_3 (*d*) ABC_4

A31. A element cystallizes in *fcc* lattice and edge length of unit cell is 400 pm. If density of unit cell is 11.2 g cm^{-3}, then atomic mass of the element is

(*a*) 215.6 (*b*) 431.2
(*c*) 107.8 (*d*) 98.6

A32. An element (atomic mass = 60 g mol^{-1}) having fcc unit cell has density 6.23 g cm^{-3}. The edge length of the unit cell is ($N_A = 6.02 \times 10^{23}$)

(*a*) 300 pm (*b*) 250 pm
(*c*) 400 pm (*d*) 160 pm

Answers

A13.	(*c*)	**A14.**	(*b*)	**A15.**	(*c*)	**A16.**	(*a*)	**A17.**	(*b*)	**A18.**	(*a*)
A19.	(*a*)	**A20.**	(*d*)	**A21.**	(*a*)	**A22.**	(*c*)				
A23.	(*b*)	**A24.**	(*c*)	**A25.**	(*c*)	**A26.**	(*d*)	**A27.**	(*d*)	**A28.**	(*d*)
A29.	(*d*)	**A30.**	(*c*)	**A31.**	(*c*)	**A32.**	(*c*)				

A33. The cell edge of a fcc crystal is 100 pm and its density is 10.0 g cm^{-3}. The number of atoms in 100 g of this crystal is

(*a*) 1×10^{25} (*b*) 2×10^{25}

(*c*) 3×10^{25} (*d*) 4×10^{25}

A34. Copper crystallizes in a cubic lattice structure. Atomic radius of copper is 128 pm and its atomic mass is 63.5. The density of copper is

(*a*) 10.71 g cm^{-3} (*b*) 4.93 g cm^{-3}

(*c*) 8.9 g cm^{-3} (*d*) 11.2 g cm^{-3}

Defects in Crystal Structures, Magnetic and Electrical Properties

A35. Which of the following is not an example of 13–15 compound?

(*a*) InSb (*b*) GaAs

(*c*) CdSe (*d*) AlP.

A36. If the alignment of magnetic moments in a substance is in a compensatory way so as to give zero net magnetic moment, then the substance is said to be

(*a*) ferromagnetism (*b*) anti-ferromagnetism

(*c*) ferrimagnetism (*d*) diamagnetism.

A37. Fe_3O_4 is ferrimagnetic at room temperature but at 850 K it becomes :

(*a*) diamagnetic (*b*) ferromagnetic

(*c*) non-magnetic (*d*) paramagnetic

A38. Iron (II) oxide has cubic structure and each unit cell has side 5Å. If the density of the compound is 4 g cm^{-3}, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell. (molar mass of FeO = 72 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1})

(*a*) 1 (*b*) 2

(*c*) 4 (*d*) 6

A39. The appearance of colour in solid alkali metal halides is generally due to

(*a*) Schottky defect (*b*) Frenkel defect

(*c*) Interstitial position (*d*) F-centres

(*C.B.S.E PMT. 2006*)

A40. An example of a ferromagnetic oxide is

(*a*) CrO_2 (*b*) TiO_2

(*c*) Fe_3O_4 (*d*) Mn_2O_7

Answers

A33. (*d*) **A34.** (*c*) **A35.** (*c*) **A36.** (*b*) **A37.** (*d*) **A38.** (*c*) **A39.** (*d*) **A40.** (*a*)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.02 \times 10^{23}$ mol^{-1})

(*a*) 6.02×10^{16} mol^{-1} (*b*) 6.02×10^{17} mol^{-1}

(*c*) 6.02×10^{14} mol^{-1} (*d*) 6.02×10^{15} mol^{-1}

(*C.B.S.E. PMT. 2007*)

B2. The fraction of total volume occupied by the atoms present in a simple cube is

(*a*) $\frac{\pi}{3\sqrt{2}}$ (*b*) $\frac{\pi}{4\sqrt{2}}$

(*c*) $\frac{\pi}{4}$ (*d*) $\frac{\pi}{6}$ (*C.B.S.E.P.M.T.2007*)

B3. If '*a*' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of the radii of the spheres in these systems will be respectively :

(*a*) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (*b*) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

(*c*) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (*d*) $1a : \sqrt{3}a : \sqrt{2}a$

(*C.B.S.E. PMT 2008*)

B4. Lithium metal crytallises in a body centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of the lithium will be :

(*a*) 151.8 pm (*b*) 75.5 pm

(*c*) 300.5 pm (*d*) 240.8 pm

(*C.B.S.E. PMT 2009*)

B5. A metal crystallises with a face-centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is

(*a*) 288 pm (*b*) 408 pm

(*c*) 144 pm (*d*) 204 pm (*A.I.P.M.T. 2012*)

B6. A metal has a *fcc* lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3}. The molar mass of the metal is:

(Avogadro's constant, $N_A = 6.02 \times 10^{23}$ mol^{-1})

(*a*) 27 g mol^{-1} (*b*) 20 g mol^{-1}

(*c*) 40 g mol^{-1} (*d*) 30 g mol^{-1}(*NEET 2013*)

B7. The number of carbon atoms per unit cell of diamond unit cell is

(*a*) 6 (*b*) 1

(*c*) 4 (*d*) 8 (*NEET 2013*)

Answers

B1. (*b*) **B2.** (*d*) **B3.** (*a*) **B4.** (*a*) **B5.** (*a*) **B6.** (*a*) **B7.** (*d*)

Competition File

B8. If a is the length of the side of a cube, the distance between the body centered atom and *one* corner atom in the cube will be

(*a*) $\frac{2}{\sqrt{3}}a$ (*b*) $\frac{4}{\sqrt{3}}a$

(*c*) $\frac{\sqrt{3}}{4}a$ (*d*) $\frac{\sqrt{3}}{2}a$ (*AIPMT 2014*)

B9. The vacant space in *bcc* lattice unit cell is :

(*a*) 23% (*b*) 32%

(*c*) 26% (*d*) 48% (*AIPMT 2015*)

B10. The correct statement regarding defects in crystalline solids is :

(*a*) Frenkel defect is a dislocation defect.

(*b*) Frenkel defect is found in halides of alkaline earth metals.

(*c*) Schottky defects have no effect on the density of crystalline solids.

(*d*) Frenkel defects decrease the density of crystalline solids. (*AIPMT 2015*)

B11. A given metal crystallises out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom ?

(*a*) 80 pm (*b*) 108 pm

(*c*) 40 pm (*d*) 127 pm (*AIPMT 2015*)

B12. Lithium has a *bcc* structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal. (N_A = 6.02×10^{23} mol^{-1})

(*a*) 527 pm (*b*) 264 pm

(*c*) 154 pm (*d*) 352 pm (*NEET 2016*)

B13. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is

(*a*) 8 (*b*) 2

(*c*) 6 (*d*) 4 (*NEET 2016*)

B14. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are

(*a*) 4 and 2 (*b*) 6 and 6

(*c*) 8 and 4 (*d*) 4 and 8 (*NEET 2016*)

B15. Which is the incorrect statement ?

(*a*) Density decreases in case of crystals with Schottky defect.

(*b*) NaCl(*s*) is insulator, silicon is semiconductor, silver is conductor, quartz is piezoelectric crystal.

(*c*) Frenkel defect is favoured in those ionic compounds in which sizes of cations and anions are almost equal.

(*d*) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect. (*NEET 2017*)

B16. Iron exhibits bcc structure at room temperature. Above 900 °C, it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900 °C (assuming molar mass and atomic radii of iron remain constant with temperature) is

(*a*) $\frac{\sqrt{3}}{\sqrt{2}}$ (*b*) $\frac{4\sqrt{3}}{3\sqrt{2}}$

(*c*) $\frac{3\sqrt{3}}{4\sqrt{2}}$ (*d*) $\frac{1}{2}$ (*NEET 2018*)

B17. Total number of tetrahedral and octahedral voids in 0.5 mol of a compound forming *hcp* structure are :

(*a*) 6.022×10^{23} (*b*) 3.011×10^{23}

(*c*) 9.033×10^{23} (*d*) 4.516×10^{23}

(*A.M.U Med. 2010*)

B18. Which one of the following compound exhibits both Schottky and Frenkel defects ?

(*a*) NaCl (*b*) AgCl

(*c*) AgBr (*d*) AgI

(*A.M.U. Med. 2010*)

B19. The mass percentage of iron present as Fe(III) in $Fe_{0.93}O_{1.0}$ is

(*a*) 8.3% (*b*) 9.6%

(*c*) 11.5% (*d*) 17.7% (*A.M.U. Med. 2013*)

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B20. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be

(*a*) X_3Y_4 (*b*) X_4Y_3

(*c*) X_2Y_3 (*d*) X_2Y (*A.I.E.E.E. 2008*)

B21. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :

(*a*) 618 pm (*b*) 144 pm

(*c*) 288 pm (*d*) 398 pm

(*A.I.E.E.E. 2010*)

B22. Percentage of free space in cubic close packed structure and in body centred packed structure are respectively :

(*a*) 32 % and 48 % (*b*) 48 % and 26%

(*c*) 30 % and 26 % (*d*) 26% and 32%

(*A.I.E.E.E. 2010*)

Answers

B8. (*d*) **B9.** (*b*) **B10.** (*a*) **B11.** (*d*) **B12.** (*d*) **B13.** (*c*) **B14.** (*c*) **B15.** (*c,d*) **B16.** (*c*) **B17.** (*c*)
B18. (*c*) **B19.** (*c*) **B20.** (*b*) **B21.** (*b*) **B22.** (*d*)

Competition File

B23. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is

(*a*) A_2B (*b*) AB_2

(*c*) A_2B_3 (*d*) A_2B_5 (*AIEEE 2011*)

B24. Copper crystallises in *fcc* lattice with a unit cell edge of 361 pm. The radius of copper atom is :

(*a*) 108 pm (*b*) 128 pm

(*c*) 157 pm (*d*) 181 pm (*AIEEE 2011*)

B25. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be

(*a*) 300 pm (*b*) 240 pm

(*c*) 152 pm (*d*) 75 pm (*A.I.E.E.E. 2012*)

B26. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

(*a*) 5.08% (*b*) 7.01%

(*c*) 4.08% (*d*) 6.05%

(*JEE Main 2013*)

B27. CsCl crystallises in body-centred cubic lattice. If '*a*' is its edge length then which of the following expression is correct ?

(*a*) $r_{Cs^+}+r_{Cl^-}=\sqrt{3}\,a$ (*b*) $r_{Cs^+}+r_{Cl^-}=3a$

(*c*) $r_{Cs^+}+r_{Cl^-}=\frac{3a}{2}$ (*d*) $r_{Cs^+}+r_{Cl^-}=\frac{\sqrt{3}}{2}a$

(*JEE Main 2014*)

B28. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge 4.29 Å. The radius of sodium atom is approximately

(*a*) 5.72 Å (*b*) 0.93 Å

(*c*) 1.86 Å (*d*) 3.22 Å(*JEE Main 2015*)

B29. Which of the following compound is metallic and ferromagnetic?

(*a*) TiO_2 (*b*) CrO_2

(*c*) VO_2 (*d*) MnO_2(*JEE Main 2016*)

B30. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is '*a*', the closest approach between two atoms in metallic crystal will be

(*a*) $2a$ (*b*) $2\sqrt{2}a$

(*c*) $\sqrt{2}a$ (*d*) $\frac{a}{\sqrt{2}}$ (*JEE Main 2017*)

B31. Which type of 'defect' has the presence of cations in the interstitial sites?

(*a*) Schottky defect (*b*) Vacancy defect

(*c*) Frenkel defect (*d*) Metal deficiency defect

(*JEE Main 2018*)

B32. An ionic compound is expected to have tetrahedral structure if r_+/r_- lies in the range of

(*a*) 0.155 to 0.225 (*b*) 0.732 to 1

(*c*) 0.414 to 0.732 (*d*) 0.225 to 0.414

(*Karnataka C.E.T. 2008*)

B33. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred position and Z atoms at the centres of faces of the unit cell. What is the empirical formula of the compound?

(*a*) XY_2Z_3 (*b*) XYZ_3

(*c*) $X_2Y_2Z_3$ (*d*) X_8YZ_6

(*e*) XYZ (*Kerala P.E.T. 2008*)

B34. KCl crystallizes in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-}=0.55$ and $r_{K^+}/r_{Cl^-}=0.74$, calculate the ratio of the side of the unit cell for KCl to that of NaCl.

(*a*) 1.123 (*b*) 0.891

(*c*) 1.414 (*d*) 0.414

(*e*) 1.732 (*Kerala P.E.T. 2008*)

B35. The white ZnO turns yellow on heating because of

(*a*) Frenkel defect

(*b*) Metal excess defect

(*c*) Metal deficiency defect

(*d*) Schottky defect (*A.M.U. Engg. 2010*)

B36. In face-centred cubic lattice, a unit cell is shared equally by how many unit cells?

(*a*) 6 (*b*) 4

(*c*) 2 (*d*) 8

(*Karnataka C.E.T. 2013*)

B37. Potassium dichromate belongs to which crystal system?

(*a*) Tetragonal (*b*) Orthorthombic

(*c*) Triclinic (*d*) Hexagonal

(*e*) Monoclinic (*Kerala PET 2014*)

B38. Which one of the following is used as a piezoelectric material ?

(*a*) Silicones (*b*) Graphite

(*c*) Silica gel (*d*) Kieselguhr

(*e*) Quartz

(*Kerala PET 2014, Karnataka CET 2016*)

Answers

B23. (*d*) **B24.** (*b*) **B25.** (*c*) **B26.** (*c*) **B27.** (*d*) **B28.** (*c*) **B29.** (*b*) **B30.** (*d*) **B31.** (*c*) **B32.** (*d*)
B33. (*b*) **B34.** (*a*) **B35.** (*b*) **B36.** (*a*) **B37.** (*c*) **B38.** (*e*)

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B39. Suppose the mass of a single Ag atom is '*m*'. Ag metal crystallizes in *fcc* lattice with unit cell of length '*a*'. The density of Ag metal in terms of '*a*' and '*m*' is

(*a*) $\frac{4m}{a^3}$ (*b*) $\frac{2m}{a^3}$

(*c*) $\frac{m}{a^3}$ (*d*) $\frac{m}{4a^3}$

(*WB JEE 2015*)

B40. The unit cell with crystallographic dimensions, $a \neq b \neq c$, $\alpha = \gamma = 90°$ and $\beta \neq 90°$ is

(*a*) monoclinic (*b*) tetragonal

(*c*) triclinic (*d*) orthorhombic

(*Karnataka CET 2015*)

B41. Ionic solids with Schottky defect may contain in their structure

(*a*) cation vacancies only

(*b*) cation vacancies and interstitial cations

(*c*) equal number of cation and anion vacancies

(*d*) anion vacancies and interstitial anions

(*WB JEE 2016, Karnataka CET 2016*)

B42. In a face centred cubic unit cell, what is the volume occupied?

(*a*) $\frac{4}{3}\pi r^3$ (*b*) $\frac{8}{3}\pi r^3$

(*c*) $\frac{16}{3}\pi r^3$ (*d*) $\frac{64r^3}{3\sqrt{3}}$

(*MH–CET 2016*)

B43. An element crystallising in body centred cubic lattice has an edge length of 500 pm. If its density is 4 g cm^{-3}, the atomic mass of the element (in g mol^{-1}) is (consider $N_A = 6 \times 10^{23}$)

(*a*) 100 (*b*) 250

(*c*) 125 (*d*) 150

(*e*) 50

(*Kerala PET 2016*)

B44. The contribution of a particle at the edge centre of a particular unit cell is,

(*a*) $\frac{1}{2}$ (*b*) $\frac{1}{4}$

(*c*) 1 (*d*) $\frac{1}{8}$

(*Karnataka CET 2016*)

B45. The correct statement regarding defect in solids is

(*a*) Schottky defect has no effect on the physical properties of solids

(*b*) Frenkel defect is a dislocation defect

(*c*) Frenkel defect is usually favoured by a very small difference in the sizes of cations and anions

(*d*) Trapping of proton in the lattice leads to the formation of F-centres. (*Karnataka CET 2017*)

B46. Which of the following crystals has unit cell such that $a \neq b \neq c$ and $\alpha \neq \beta \neq \Upsilon \neq 90°$?

(*a*) $K_2Cr_2O_7$ (*b*) $NaNO_3$

(*c*) KNO_3 (*d*) A_8B_7

(*Karnataka CET 2017*)

B47. In a face centred cubic arrangement of A and B atoms in which 'A' atoms are at the corners of the unit cell and 'B' atoms are at the face centres. One of the 'A' atoms is missing from one corner in unit cell. The simplest formula of compound is

(*a*) AB_3 (*b*) A_7B_{24}

(*c*) A_7B_8 (*d*) A_7B_3

(*Karnataka CET 2017*)

B48. A compound formed by elements X and Y crystallises in the cubic structure, where X atoms at the corners of a cube and Y atoms are at the centres of the body. The formula of the compound is

(*a*) XY (*b*) XY_2

(*c*) X_2Y_3 (*d*) XY_3 (*WB JEE 2018*)

B49. Edge length of a cube is 300 pm. Its body diagonal would be

(*a*) 600 pm (*b*) 423 pm

(*c*) 519.6 pm (*d*) 450.5 pm

(*Karnataka CET 2018*)

B50. Which of the following is not a conductor of electricity?

(*a*) Solid NaCl (*b*) Cu

(*c*) Fused NaCl (*d*) Brine solution

(*Karnataka CET 2018*)

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B51. In a solid 'AB' having NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stiochiometry of the solid is

(*a*) AB_2 (*b*) A_2B

(*c*) A_4B_3 (*d*) A_3B_4 (*I.I.T. 2001*)

B52. In which of the following crystals alternate tetrahedral voids are occupied ?

(*a*) NaCl (*b*) ZnS

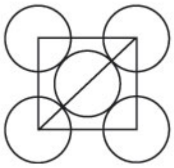
(*c*) CaF_2 (*d*) Na_2O (*I.I.T. 2005*)

Answers

B39. (*a*) **B40.** (*a*) **B41.** (*c*) **B42.** (*c*) **B43.** (*d*) **B44.** (*b*) **B45.** (*b*) **B46.** (*a*) **B47.** (*b*) **B48.** (*a*)
B49. (*c*) **B50.** (*a*) **B51.** (*d*) **B52.** (*b*)

Competition File

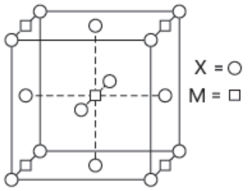
B53. The packing efficiency of the two dimensional square unit cell shown is :



(*a*) 39.27 % (*b*) 68.02%

(*c*) 74.05% (*d*) 78.54% (*I.I.T. 2010*)

B54. A compound M_pX_q has cubic close packing (*ccp*) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is

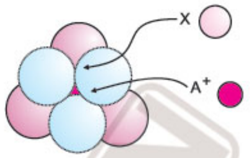


(*a*) MX (*b*) MX_2

(*c*) M_2X (*d*) M_5X_{14}

(*I.I.T. J.E.E. 2012*)

B55. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is



(*a*) 104 pm (*b*) 125 pm

(*c*) 183 pm (*d*) 57 pm

(*JEE Advance 2013*)

B56. If the unit cell of a mineral has cubic close packed (*ccp*) array of oxygen atoms with *m* fraction of octahedral holes occupied by aluminium ions and *n* fraction of tetrahedral holes occupied by magnesium ions, *m* and *n*, respectively, are

(*a*) $\frac{1}{2}, \frac{1}{8}$ (*b*) $1, \frac{1}{4}$

(*c*) $\frac{1}{2}, \frac{1}{2}$ (*d*) $\frac{1}{4}, \frac{1}{8}$

(*JEE Advance 2015*)

Answers

B53. (*d*) **B54.** (*b*) **B55.** (*a*) **B56.** (*a*)

C MULTIPLE CHOICE QUESTIONS

with more than one correct answer

C1. Which of the following is/are not true about hexagonal close packing ?
- (*a*) It has 26% empty space
- (*b*) In this arrangement, third layer is identical to the first layer.
- (*c*) The coordination number in this arrangement is 6.
- (*d*) It is as closely packed as body centred cubic packing.

C2. Which of the following statements are correct ?
- (*a*) The coordination number of each type of ion in CsCl crystal is 8.
- (*b*) A metal that crystallizes in bcc structure has coordination number 12.
- (*c*) A unit cell of an ionic crystal shares some of its ions with other unit cells.
- (*d*) The length of the unit cell in NaCl is 552 pm (r_{Na^+} = 95 pm, r_{Cl^-} = 181 pm)

C3. In which of the following structures, the coordination number of both the ions are same ?
- (*a*) Cesium chloride
- (*b*) Sodium chloride
- (*c*) Zinc sulphide
- (*d*) Sodium oxide

C4. Which of the following is not correct for Frenkel defect in crystals ?
- (*a*) It is due to equal number of cations and anions missing from lattice sites.
- (*b*) It has no effect on density of the crystal.
- (*c*) It occurs in crystals where the difference in the size of cations and anions is small.
- (*d*) Silver halides show Frenkel defect.

C5. The coordination number of eight for cation is found in

(*a*) CsCl (*b*) NaCl

(*c*) CaF_2 (*d*) Na_2O

C6. Which of the following systems do not give correct description of axial lengths and axial angles ?
- (*a*) Hexagonal : $a = b \neq c$, $\alpha = \beta = 90°, \gamma = 120°$
- (*b*) Tetragonal : $a = b \neq c$, $\alpha = \beta = 90°, \gamma \neq 90°$

Answers

C1. (*c*), (*d*) **C2.** (*a*), (*c*), (*d*) **C3.** (*a*), (*b*), (*c*) **C4.** (*a*), (*c*) **C5.** (*a*), (*c*) **C6.** (*b*), (*c*) (*c*) Monoclinic : $a \neq b \neq c$, $\alpha = \beta = \gamma \neq 90°$

(*d*) Cubic : $a = b = c$, $\alpha = \beta = \gamma = 90°$

C7. The correct statement(s) regarding defects in solids is (are)

(*a*) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion

(*b*) Frenkel defect is a dislocation defect

(*c*) Trapping of an electron in the lattice leads to the formation of F-centre

(*d*) Schottky defects have no effect on the physical properties of solids. (*IIT-JEE 2009*)

C8. With respect to graphite and diamond, which of the statement(s) given is(are) correct ?

(*a*) Graphite is harder than diamond.

(*b*) Graphite has higher electrical conductivity than diamond.

(*c*) Graphite has higher thermal conductivity than diamond.

(*d*) Graphite has higher C—C bond order than diamond. (*IIT-JEE 2012*)

C9. Which type of defects are present in AgBr and ZnS crystal systems ?

(*a*) Frenkel and Schottky

(*b*) Schottky and Frenkel

(*c*) Frenkel and Frenkel

(*d*) Schottky and Schottky (*A.M.U. (Engg.) 2015*)

C10. The correct statement(s) for cubic close packed (*ccp*) in three dimensional structure is(are)

(*a*) the number of the nearest neighbours of an atom present in the top most layer is 12.

(*b*) the efficiency of atom packing is 74%.

(*c*) the number of octahedral and tetrahedral voids per atom are 1 and 2, respectively.

(*d*) the unit cell edge length is $2\sqrt{2}$ times the radius of the atom.

(*JEE Advance 2016*)

Answers

C7. (*b*), (*c*) **C8.** (*b*), (*d*) **C9.** (*b*), (*c*) **C10.** (*b*), (*c*), (*d*)

D MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage I.

In the crystalline solids the smallest repeating part in the lattice is known as unit cell. The unit cells are described as simple (points at all the corners), body centred (points at all the corners and in the centre), face centred (points at all the corners and centre of all faces), and end centred (points at all the corners and centres of two opposite end faces) unit cells. In two common types of packing *ccp* and *hcp*, 26% of space is left unoccupied in the form of interstitial sites. For the stable ionic crystalline structures, there is definite radius ratio limit for a cation to fit perfectly in the lattice of anions, called radius ratio rule. This also defines the coordination number of an ion, which is the number of nearest neighbours of opposite charges. This depends upon the ratio of radii of two types of ions, r_+/r_-. This ratio for coordination numbers 3, 4, 6 and 8 is respectively 0.155–0.225, 0.225–0.414, 0.414–0.732 and 0.732–1 respetively.

Answer the following questions :

D1. The number of atoms per unit cell in simple (*s*), body centred (*b*), face centred (*f*) and end centred (*e*) unit cell decreases as

(*a*) $f > b > e > s$ (*b*) $f > b = e > s$

(*c*) $b > f > s = e$ (*d*) $f > b > e = s$

D2. Gold crystallizes in a face centred unit cell. Its edge length is 0.410 nm. The radius of gold atom is

(*a*) 0.205 nm (*b*) 0.290 nm

(*c*) 0.145 nm (*d*) 0.578 nm

D3. In a cubic lattice of XYZ, X atoms are present at all corners except one corner which is occupied by Y atoms. Z atoms are present at face centres. The formula of the compound is

(*a*) X_8YZ_{24} (*b*) XYZ_3

(*c*) $X_7Y_{24}Z$ (*d*) X_7YZ_{24}

D4. The ionic radii of K^+, Rb^+ and Br^- are 137, 148 and 195 pm. The coordination number of cation in RbBr and KBr structures are respectively

(*a*) 8, 6 (*b*) 6, 4

(*c*) 6, 8 (*d*) 4, 6

D5. A face centred cubic lattice of a metal M and a body centred cubic lattice of metal N contain same number of 2.25×10^{22} unit cells. If density of M is twice than that of N, the ratio between the number of atoms per unit cell is

(*a*) 4 : 1 (*b*) 1 : 1

(*c*) 2 : 1 (*d*) 1 : 4

Passage II.

Density of a unit cell is same as the density of the substance. If the density of the substance is known, number of atoms or dimensions of the unit cell can be calculated. The density of the unit cell is related to its mass (M), no. of atoms per unit cell (Z), edge length (*a* in cm) and Avogadro number N_A as :

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

Answers

Passage – I **D1.** (*b*) **D2.** (*c*) **D3.** (*d*) **D4.** (*a*) **D5.** (*c*)

Answer the following questions :

D6. An element crystallizes in a structure having a fcc unit cell of an edge 100 pm. If 24 g of the element contains 24×10^{23} atoms, the density is

(*a*) 2.40 g cm^{-3} (*b*) 40 g cm^{-3}

(*c*) 4 g cm^{-3} (*d*) 24 g cm^{-3}

D7. The number of atoms present in 100 g of a *bcc* crystal (density = 12.5 g cm^{-3}) having cell edge 200 pm is

(*a*) 1×10^{25} (*b*) 1×10^{24}

(*c*) 2×10^{24} (*d*) 2×10^{26}

D8. A metal X (at. mass = 60) has a body centred cubic crystal structure. The density of the metal is 4.2 g cm^{-3}. The volume of unit cell is

(*a*) $8.2 \times 10^{-23} \text{ cm}^3$ (*b*) $4.75 \times 10^{-23} \text{ cm}^3$

(*c*) $3.86 \times 10^{23} \text{ cm}^3$ (*d*) $3.86 \times 10^{-23} \text{ cm}^3$

Passage III.

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (*hcp*), is constituted of a sphere on a flat surface

surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of the three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be '*r*'.

Answer the following questions :

D9. The number of atoms in this *hcp* unit cell is

(*a*) 4 (*b*) 6 (*c*) 12 (*d*) 17

D10. The volume of this *hcp* unit cell is

(*a*) $24\sqrt{2}r^3$ (*b*) $16\sqrt{2}r^3$

(*c*) $12\sqrt{2}r^3$ (*d*) $\dfrac{64}{3\sqrt{3}}r^3$

D11. The empty space in this *hcp* unit cell is

(*a*) 74% (*b*) 47.6%

(*c*) 32% (*d*) 26% (*I.I.T. 2008*)

Answers

Passage–II	**D6.** (*b*)	**D7.** (*c*)	**D8.** (*b*)
Passage–III	**D9.** (*b*)	**D10.** (*a*)	**D11.** (*d*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the correct explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT but reason is INCORRECT.

(*d*) If assertion is INCORRECT but reason is CORRECT.

(*e*) If both assertion and reason are INCORRECT.

1. Assertion : In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.

Reason : Equal number of cation and anion vacancies are present. (*I.I.T. 2001*)

2. Assertion : ZnS has a tetrahedral arrangement.

Reason : In ZnS, S^{2-} ions occupy the tetrahedral sites while Zn^{2+} ions form cubic close packed structure.

3. Assertion : In CsCl structure, the co-ordination number of Cs^+ ion is 8.

Reason : Cl^- ions in CsCl have body centred cubic arrangement.

4. Assertion : In ZnO, the excess Zn^{2+} ions are present in interstitial sites.

Reason : Metal excess crystals have either missing cation or anion in interstitial site.

5. Assertion : FeO is non-stoichiometric with $Fe_{0.95}O$.

Reason : Some Fe^{2+} ions are replaced by Fe^{3+} as $3Fe^{2+} = 2Fe^{3+}$ to maintain electrical neutrality.

6. Assertion : In CaF_2, F^- ions occupy all the tetrahedral sites.

Reason : The number of Ca^{2+} is double the number of F^- ions.

7. Assertion : Size of cation is larger in tetrahedral void than in octahedral void.

Reason : The cations occupy more space than anions in crystal close packing

8. Assertion : Frenkel defect is shown by silver halides.

Reason : Silver ions are small in size and can easily fit in interstitial sites.

9. Assertion : In Frenkel defect, density of the crystalline solid does not change.

Reason : In Frenkel defect, no cation or anion leaves the crystal.

10. Assertion : Frenkel and Schottky defects are stoichiometric defects.

Reason : Both defects change the density of the crystalline solid.

Answers

(1) – (*a*) **(2)** – (*e*) **(3)** – (*c*) **(4)** – (*c*) **(5)** – (*a*) **(6)** – (*c*) **(7)** – (*e*) **(8)** – (*a*) **(9)** – (*a*) **(10)** – (*c*)

Matching Type Questions

Each question has matching list. The codes for the lists have choices *(a)*, *(b)*, *(c)* and *(d)* out of which only one is correct.

1. Match the type of crystal system given in List I with its description given in List II.

	List I	**List II**
P.	Monoclinic	1. $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$
Q.	Tetragonal	2. $a \neq b \neq c, \alpha = \beta = \gamma = 90°$
R.	Triclinic	3. $a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$
S.	Rhombic	4. $a = b \neq c, \alpha = \beta = \gamma = 90°$

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	1	2
(c)	3	4	1	2
(d)	2	3	4	1

2. Match the type of crystal given in List I with example in List II.

	List I	**List II**
P.	Ionic	1. AlN
Q.	Network	2. Mg
R.	Metallic	3. MgO
S.	Molecular	4. Solid CO_2

	P	Q	R	S
(a)	3	1	4	2
(b)	3	1	2	4
(c)	1	3	2	4
(d)	4	2	3	1

3. Match the distribution of particles A and B in List I with formula given in List II.

	List I	**List II**
P.	A in *ccp* and B equally distributed in octahedral and tetrahedral	1. A_2B_3
Q.	B in *hcp* and A occupy 2/3rd of octahedral voids	2. A_3B
R.	A at the corners and face centres and B at edge centres and body centre	3. AB
S.	B in ccp and A occupy all the octahedral and tetrahedral sites	4. AB_2

	P	Q	R	S
(a)	4	1	3	2
(b)	4	1	2	3
(c)	3	2	1	4
(d)	4	2	3	1

4. Match the entries of column I with appropriate entries of column II.

	Compound		**Magnetic property**
(A)	NaCl	*(p)*	Ferrimagnetic
(B)	MnO	*(q)*	Paramagnetic
(C)	$CrCl_3$	*(r)*	Ferromagnetic
(D)	CrO_2	*(s)*	Diamagnetic
(E)	$MgFe_2O_4$	*(t)*	Antiferromagnetic

	A	B	C	D	E
(a)	*p*	*r*	*q*	*t*	*s*
(b)	*t*	*q*	*r*	*p*	*s*
(c)	*r*	*t*	*q*	*p*	*s*
(d)	*s*	*t*	*q*	*r*	*p*
(e)	*s*	*r*	*t*	*q*	*p*

(Kerala PMT 2015)

Answers

1. *(c)* **2.** *(b)* **3.** *(a)* **4.** *(d)*

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the given example.

	p	q	r	s
A	○	●	●	○
B	●	○	○	●
C	○	○	●	●
D	○	●	○	○

1. Match the crystal system/unit cells mentioned in column I with their characteristic features mentioned in column II.

Column I	**Column II**
(A) Simple cubic and face centred cubic	*(p)* have these cells parameters $a = b = c$ and $\alpha = \beta = \gamma$
(B) Cubic and rhombohedral	*(q)* are two crystal systems
(C) Cubic and tetragonal	*(r)* have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	*(s)* belong to same crystal system.

(I.I.T. 2007)

Answers

(1) : (A) – *(p)* *(s)* (B) – *(p)* *(q)* (C) – *(q)* (D) – *(q)* *(r)*

2. Match the imperfections in solids mentioned in column I with the characteristic features mentioned in column II.

Column I	Column II
(A) Schottky defects	(*p*) excess cations occupy interstitial sites
(B) Frenkel defects	(*q*) conduct electricity due to free electrons
(C) Metal excess defects	(*r*) act as *p*-type semi-conductors
(D) Metal deficient defects	(*s*) are non-stoichiometric defects

3. Match the type of arrangement in column I with the characteristic feature mentioned in column II.

Column I	Column II
(A) Cubic close packing	(*p*) occupy 74% of the space
(B) Hexagonal close packing	(*q*) occupy 68% of the space
(C) Body centred cubic	(*r*) have 1 atom per unit cell
(D) Simple cubic	(*s*) have more number of atoms per unit cell than simple cubic arrangement

Answers

(2) : (A) – (*q*) (B) – (*p*) (*q*) (C) – (*p*) (*q*) (*s*) (D) – (*r*) (*s*)

(3) : (A) – (*p*) (*s*) (B) – (*p*) (*r*) (*s*) (C) – (*s*) (D) – (*q*).

Integer Type and Numerical Value Type Questions

Interger Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is *(I.I.T. 2010)*

2. In NaCl structure, Cl$^-$ ions have ccp arrangement and Na$^+$ ions occupy all the octahedral sites. The total number of Na$^+$ and Cl$^-$ ions per unit cell is :

3. A metal 'X' crytallizes in a unit cell in which the radius of atom (r) is related to edge of unit cell (a) as $r = 0.3535\,a$. The total number of atoms present per unit cell is

4. The radius ratio of an ionic solid r_+/r_- is 0.524. The coordination number of this type of structure is

5. Atoms of element N form *hcp* arrangement and those of element M occupy 2/3rd of tetrahedral voids. The total number of M and N per formula unit is

6. In hexagonal close packing, the difference in the number of tetrahedral and octahedral voids per unit cell is

7. The ratio of coordination number of each sphere in *ccp* and *hcp* in three dimensions is

8. A compound is formed by two elements X and Y. The element Y form *ccp* and atoms of X occupy 1/3 of tetrahedral voids. If the formula of the compound is $X_a Y_b$, then value of $a + b$ is

9. A cubic unit cell has one atom on each corner and one atom on each body diagonal. The number of atoms in the unit cell is

10. The number of hexagonal faces that are present in a truncated octahedron is *(I.I.T. 2011)*

11. A crystalline solid of a pure substance has a face centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3}, then the number of atoms present in 256 g of the crystal is N × 10^{24}. The value of N is

(JEE Advance 2017)

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

12. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.

(1) Remove all the anions (X) except the central one
(2) Replace all the face centred cations (M) by anions (X)
(3) Remove all the corner cations (M)
(4) Replace the central anion (X) with cation (M)

The value of $\left(\dfrac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is ____________ .

(JEE Advance 2018)

Answers

1. 7 **2.** 8 **3.** 4 **4.** 6 **5.** 7 **6.** 6 **7.** 1 **8.** 5 **9.** 5
10. 8 **11.** 2 **12.** 3.00

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Which of the following conditions favours the existence of a substance in the solid state?

(*a*) High temperature (*b*) Low temperature

(*c*) High thermal energy (*d*) Weak cohesive forces

2. Which of the following is not a characteristic of a crystalline solid ?

(*a*) Definite and characteristic heat of fusion.

(*b*) Isotropic nature.

(*c*) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.

(*d*) A true solid

3. Which of the following is an amorphous solid ?

(*a*) Graphite (C) (*b*) Quartz glass (SiO_2)

(*c*) Chrome alum (*d*) Silicon carbide (SiC)

4. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances ?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

5. Which of the following is true about the value of refractive index of quartz glass?

(*a*) Same in all directions

(*b*) Different in different directions

(*c*) Cannot be measured

(*d*) Always zero

6. Which of the following statement is not true about amorphous solids?

(*a*) On heating they may become crystalline at certain temperature.

(*b*) They may become crystalline on keeping for long time.

(*c*) Amorphous solids can be moulded by heating.

(*d*) They are anisotropic in nature.

7. The sharp melting point of crystalline solids is due to ___________.

(*a*) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.

(*b*) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.

(*c*) same arrangement of constituent particles in different directions.

(*d*) different arrangement of constituent particles in different directions.

8. Iodine molecules are held in the crystals lattice by ___________.

(*a*) London forces

(*b*) dipole-dipole interactions

(*c*) covalent bonds

(*d*) coulombic forces

9. Which of the following is a network solid?

(*a*) SO_2 (Solid) (*b*) I_2

(*c*) Diamond (*d*) H_2O (Ice)

10. Which of the following solids is not an electrical conductor?

(A) Mg(*s*) (B) TiO(*s*) (C) $I_2(s)$ (D) $H_2O(s)$

(*a*) (A) only (*b*) (B) Only

(*c*) (C) and (D) (*d*) (B), (C) and (D)

11. Which of the following is not the characteristic of ionic solids?

(*a*) Very low value of electrical conductivity in the molten state.

(*b*) Brittle nature.

(*c*) Very strong forces of interactions.

(*d*) Anisotropic nature.

12. Graphite is a good conductor of electricity due to the presence of __________.

(*a*) lone pair of electrons (*b*) free valence electrons

(*c*) cations (*d*) anions

13. Which of the following oxides behaves as conductor or insulator depending upon temperature ?

(*a*) TiO (*b*) SiO_2 (*c*) TiO_3 (*d*) MgO

14. Which of the following oxides shows electrical properties like metals ?

(*a*) SiO_2 (*b*) MgO (*c*) $SO_2(s)$ (*d*) CrO_2

15. The lattice site in a pure crystal cannot be occupied by _________.

(*a*) molecule (*b*) ion

(*c*) electron (*d*) atom

16. Graphite cannot be classified as __________.

(*a*) conducting solid (*b*) network solid

(*c*) covalent solid (*d*) ionic solid

17. Cations are present in the interstitial sites in __________.

(*a*) Frenkel defect (*b*) Schottky defect

(*c*) Vacancy defect (*d*) Metal deficiency defect

18. Schottky defect is observed in crystals when __________.

(*a*) some cations move from their lattice site to interstitial sites.

(*b*) equal number of cations and anions are missing from the lattice.

(*c*) some lattice sites are occupied by electrons.

(*d*) some impurity is present in the lattice.

Answers

1. (*b*)	**2.** (*b*)	**3.** (*b*)	**4.** (*d*)	**5.** (*a*)	**6.** (*d*)	**7.** (*b*)	**8.** (*a*)	**9.** (*c*)	**10.** (*c*)
11. (*a*)	**12.** (*b*)	**13.** (*c*)	**14.** (*d*)	**15.** (*c*)	**16.** (*d*)	**17.** (*a*)	**18.** (*b*)		

Competition File

19. Which of the following is true about the charge acquired by *p*-type semiconductors ?
(*a*) positive
(*b*) neutral
(*c*) negative
(*d*) depends on concentration of *p* impurity

20. To get a *n*-type semiconductor from silicon, it should be doped with a substance with valence__________.
(*a*) 2 (*b*) 1 (*c*) 3 (*d*) 5

21. The total number of tetrahedral voids in the face centred unit cell is __________.
(*a*) 6 (*b*) 8 (*c*) 10 (*d*) 12

22. Which of the following point defects are shown by AgBr(*s*) crystals ?
(A) Schottky defect
(B) Frenkel defect
(C) Metal excess defect
(D) Metal deficiency defect
(*a*) (A) and (B) (*b*) (C) and (D)
(*c*) (A) and (C) (*d*) (B) and (D)

23. In which pair most efficient packing is present?
(*a*) *hcp* and *bcc* (*b*) *hcp* and *ccp*
(*c*) *bcc* and *ccp* (*d*) *bcc* and simple cubic cell

24. The percentage of empty space in a body centred cubic arrangement is ________.
(*a*) 74 (*b*) 68
(*c*) 32 (*d*) 26

25. Which of the following statement is not true about the hexagonal close packing ?
(*a*) The coordination number is 12.
(*b*) It has 74% packing efficiency.
(*c*) Tetrahedral voids of the second layer are covered by the spheres of the third layer.
(*d*) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer.

26. In which of the following structures coordination number for cations and anions in the packed structure will be same?
(*a*) Cl^- ions form *fcc* lattice and Na^+ ions occupy all octahedral voids of the unit cell.
(*b*) Ca^{2+} ions form *fcc* lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell.
(*c*) O^{2-} ions form *fcc* lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell.
(*d*) S^{2-} ions form *fcc* lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell.

27. What is the coordination number in a square close packed structure in two dimensions ?
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 6

28. Which kind of defects are introduced by doping?
(*a*) Dislocation defect
(*b*) Schottky defect
(*c*) Frenkel defects
(*d*) Electronic defects

29. Silicon doped with electron-rich impurity forms ________.
(*a*) *p*-type semiconductor
(*b*) *n*-type semiconductor
(*c*) intrinsic semiconductor
(*d*) insulator

30. Which of the following statements is not true ?
(*a*) Paramagnetic substances are weakly attracted by magnetic field.
(*b*) Ferromagnetic substances cannot be magnetised permanently.
(*c*) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.
(*d*) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.

31. Which of the following is not true about the ionic solids?
(*a*) Bigger ions form the close packed structure.
(*b*) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size.
(*c*) Occupation of all the voids is not necessary.
(*d*) The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids.

32. A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field becuase ________.
(*a*) all the domains get oriented in the direction of magnetic field.
(*b*) all the domains get oriented in the direction opposite to the direction of magnetic field.
(*c*) domains get oriented randomly.
(*d*) domains are not affected by magnetic field.

33. The correct order of the packing efficiency in different types of unit cells is ________.
(*a*) *fcc* < *bcc* < simple cubic
(*b*) *fcc* > *bcc* > simple cubic
(*c*) *fcc* < *bcc* > simple cubic
(*d*) *bcc* < *fcc* > simple cubic

34. Which of the following defects is also known as dislocation defect?
(*a*) Frenkel defect
(*b*) Schottky defect
(*c*) Non-stoichiometric defect
(*d*) Simple interstitial defect

35. In the cubic close packing, the unit cell has ________.
(*a*) 4 tetrahedral voids each of which is shared by four adjacent unit cells.
(*b*) 4 tetrahedral voids within the unit cell.
(*c*) 8 tetrahedral voids each of the which is shared by four adjacent unit cells.
(*d*) 8 tetrahedral voids within the unit cells.

Answers

19. (*b*)	**20.** (*d*)	**21.** (*b*)	**22.** (*a*)	**23.** (*b*)	**24.** (*c*)	**25.** (*d*)	**26.** (*a, d*)	**27.** (*c*)	**28.** (*d*)
29. (*b*)	**30.** (*b*)	**31.** (*d*)	**32.** (*a*)	**33.** (*b*)	**34.** (*a*)	**35.** (*d*)			

Competition File

36. The edge lengths of the unit cells in terms of the radius of spheres constituting *fcc*, *bcc* and simple cubic unit cell are respectively________.

(*a*) $2\sqrt{2r}$, $\frac{4r}{\sqrt{3}}$, $2r$ (*b*) $\frac{4r}{\sqrt{3}}$, $2\sqrt{2r}$, $2r$

(*c*) $2r$, $2\sqrt{2r}$, $\frac{4r}{\sqrt{3}}$ (*d*) $2r$, $\frac{4r}{\sqrt{3}}$, $2\sqrt{2r}$

37. Which of the following represents correct order of conductivity in solids?

(*a*) $\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$

(*b*) $\kappa_{\text{metals}} << \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$

(*c*) $\kappa_{\text{metals}} \simeq \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} = \text{zero}$

(*d*) $\kappa_{\text{metals}} < \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

Answers

36. (*a*) **37.** (*a*)

Multiple Choice Questions (Type-II)

Note : *In the following questions two or more options may be correct.*

38. Which of the following is not true about the voids formed in three dimensional hexagonal close packed structure ?

(*a*) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.

(*b*) All the triangular voids are not covered by the spheres of the second layer.

(*c*) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap.

(*d*) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.

39. The value of magnetic moment is zero in the case of antiferromagnetic substances because the domains ________.

(*a*) get oriented in the direction of the applied magnetic field.

(*b*) get oriented opposite to the direction of the applied magnetic field.

(*c*) are oppositely oriented with respect to each other without the application of magnetic field.

(*d*) cancel out each other's magnetic moment.

40. Which of the following statements are not true?

(*a*) Vacancy defect results in a decrease in the density of the substance.

(*b*) Interstitial defects results in an increase in the density of the substance.

(*c*) Impurity defect has no effect on the density of the substance.

(*d*) Frenkel defect results in an increase in the density of the substance.

41. Which of the following statements are true about metals ?

(*a*) Valence band overlaps with conduction band.

(*b*) The gap between valence band and conduction band is negligible.

(*c*) The gap between valence band and conduction band cannot be determined.

(*d*) Valence band may remain partially filled.

42. Under the influence of electric field, which of the following statements is true about the movement of electrons and holes in a *p*-type semiconductor?

(*a*) Electron will move towards the positvely charged plate through electron holes.

(*b*) Holes will appear to be moving towards the negatively charged plate.

(*c*) Both electrons and holes appear to move towards the positively charged plate.

(*d*) Movement of electrons is not related to the movement of holes.

43. Which of the following statements are true about semiconductors?

(*a*) Silicon doped with electron rich impurity is a *p*-type semiconductor.

(*b*) Silicon doped with an electron rich impurity is an *n*-type semiconductor.

(*c*) Delocalised electrons increase the conductivity of doped silicon.

(*d*) An electron vacancy increases the conductivity of *n*-type semiconductor.

44. An excess of potassium ions makes KCl crystals appear violet or lilac in colour since ________.

(*a*) some of the anionic sites are occupied by an unpaired electron.

(*b*) some of the anionic sites are occupied by a pair of electrons.

(*c*) there are vacancies at some anionic sites.

(*d*) F-centres are created which impart colour to the crystals.

45. The number of tetrahedral voids per unit cell in NaCl crystal is ________.

(*a*) 4

(*b*) 8

(*c*) twice the number of octahedral voids.

(*d*) four times the number of octahedral voids.

Answers

38. (*c*), (*d*) **39.** (*c*), (*d*) **40.** (*c*), (*d*) **41.** (*a*), (*b*), (*d*) **42.** (*a*), (*b*) **43.** (*b*), (*c*) **44.** (*a*), (*d*) **45.** (*b*), (*c*)

Competition File

46. Amorphous solid can also be called ________.

(*a*) pseudo solids (*b*) true solids

(*c*) super cooled liquids (*d*) super cooled solids

47. A perfect crystal of silicon (Fig.1) is doped with some elements as given in the options. Which of these options show *n*-type semiconductors?

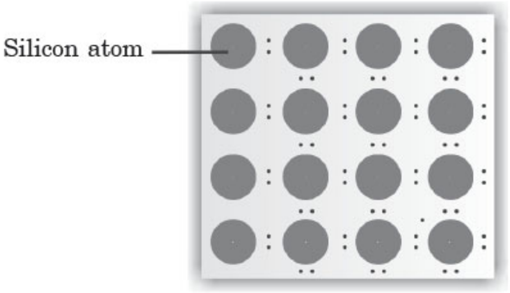
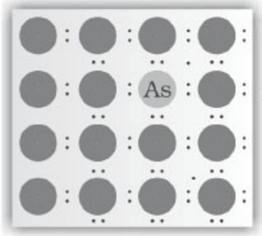
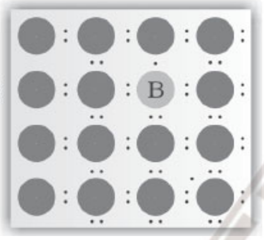
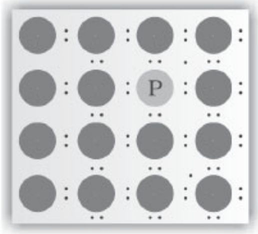
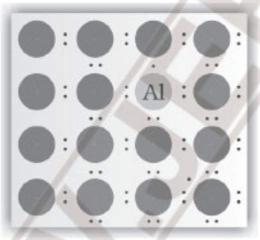


Fig. 1. Pure crystal

(*a*)


(*b*)


(*c*)


(*d*)


48. Which of the following statements are correct?

(*a*) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic.

(*b*) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.

(*c*) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.

(*d*) In ferromagnetic substances all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

49. Which of the following features are not shown by quartz glass?

(*a*) This is a crystalline solid.

(*b*) Refractive index is same in all the directions.

(*c*) This has definite heat of fusion.

(*d*) This is also called super cooled liquid.

50. Which of the following cannot be regarded as molecular solid?

(*a*) SiC (Silicon carbide) (*b*) AlN

(*c*) Diamond (*d*) I_2

51. In which of the following arrangements octahedral voids are formed?

(*a*) *hcp* (*b*) *bcc*

(*c*) simple cubic (*d*) *fcc*

52. Frenkel defect is also known as ________.

(*a*) stoichiometric defect

(*b*) dislocation defect

(*c*) impurity defect

(*d*) non-stoichometric defect

53. Which of the following defects decrease the density?

(*a*) Interstitial defect (*b*) Vacancy defect

(*c*) Frenkel defect (*d*) Schottky defect

Answers

46. (*a*), (*c*) **47.** (*a*), (*c*) **48.** (*a*), (*d*) **49.** (*a*), (*c*) **50.** (*a*), (*b*), (*c*) **51.** (*a*), (*d*) **52.** (*a*), (*b*) **53.** (*b*), (*d*)

Matching Type Questions

Note : *In the following questions match the items given in Column I with the items given in Column II. In some questions more than one item of Column I and Column II may match.*

54. Match the defects given in Column I with the statements in given Column II.

Column I	*Column II*
(*a*) Simple vacancy defect	(*i*) shown by non-ionic solids and increases density of the solid.
(*b*) Simple interstitial defect	(*ii*) shown by ionic solids and decreases density of the solid.
(*c*) Frenkel defect	(*iii*) shown by non ionic solids and density of the solid decreases.
(*d*) Schottky defect	(*iv*) shown by ionic solids and density of the solid remains the same.

Competition File

55. Match the type of unit cell given in Column I with the features given in Column II.

Column I	*Column II*
(*a*) Primitive cubic unit cell.	(*i*) Each of the three perpendicular edges compulsorily have the different edge length *i.e.*, $a \neq b \neq c$.
(*b*) Body centred cubic unit cell.	(*ii*) Number of atoms per unit cell is one.
(*c*) Face centred cubic unit cell.	(*iii*) Each of the three perpendicular edges compulsorily have the same edge length *i.e.*, $a = b = c$.
(*d*) End centred orthorhombic.	(*iv*) In addition to the contribution from unit cell the corner atoms the number of atoms present in a unit cell is one.
	(*v*) In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three.

56. Match the types of defect given in Column I with the statement given in Column II.

Column I	*Column II*
(*a*) Impurity defect.	(*i*) NaCl with anionic sites called F-centres.
(*b*) Metal excess defect.	(*ii*) FeO with Fe^{3+}.
(*c*) Metal deficiency defect.	(*iii*) NaCl with Sr^{2+} and some cationic sites vacant.

57. Match the items given in Column I with the items given in Column II.

Column I	*Column II*
(*a*) Mg in solid state.	(*i*) *p*-Type semiconductor.
(*b*) $MgCl_2$ in molten state.	(*ii*) *n*-Type semiconductor.
(*c*) Silicon with phosphorus.	(*iii*) Electrolytic conductors.
(*d*) Germanium with boron.	(*iv*) Electronic conductors.

58. Match the type of packing given in Column I with the items given in Column II.

Column I	*Column II*
(*a*) Square close packing in two dimensions.	(*i*) Triangular voids.
(*b*) Hexagonalclose packing in two dimensions.	(*ii*) Pattern of spheres is repeated in every fourth layer.
(*c*) Hexagonal close packing in three dimensions.	(*iii*) Coordination number 4.
(*d*) Cubic close packing in three dimensions.	(*iv*) Pattern of sphere is repeated in alternate layers.

Answers

54. (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*iv*); (*d*)–(*ii*) **55.** (*a*)–(*ii, iii*); (*b*)–(*iii, iv*); (*c*)–(*iii, v*); (*d*)–(*i, iv*) **56.** (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*ii*)
57. (*a*)–(*iv*); (*b*)–(*iii*); (*c*)–(*ii*); (*d*)–(*i*) **58.** (*a*)–(*iii*); (*b*)–(*i*); (*c*)–(*iv*); (*d*)–(*ii*)

Assertion and Reason Type Questions

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*

(*a*) *Assertion and reason both are correct statements and reason is correct explanation for assertion.*
(*b*) *Assertion and reason both are correct statements but reason is not correct explanation for assertion.*
(*c*) *Assertion is correct statement but reason is wrong statement.*
(*d*) *Assertion is wrong statement but reason is correct statement.*

59. Assertion : The total number of atoms present in a simple cubic unit cell is one.

Reason : Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.

60. Assertion : Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

Reason : Graphite is soft in nature on the other hand diamond is very hard and brittle.

61. Assertion : Total number of octahedral voids present in unit cell of cubic close packing including the one that is present at the body centre, is four.

Reason : Besides the body centre there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

62. Assertion : The packing efficiency is maximum for the *fcc* structure.

Reason : The cordination number is 12 in *fcc* structures.

63. Assertion : Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^{4}$ $ohm^{-1}m^{-1}$.

Reason : Intermediate conductivity in semiconductor is due to partially filled valence band.

Answers

59. (*a*) **60.** (*b*) **61.** (*c*) **62.** (*b*) **63.** (*c*)

Competition File

Hints & Explanations for Difficult Objective Type Questions

A. mcq with only one correct answer

A8. (*c*) : $a = 2\sqrt{2}\ r$

$= 2 \times 1.414 \times 141.5 = 400$ pm

Volume of unit cell

$= (400 \times 10^{-10}\ \text{cm})^3 = 6.4 \times 10^{-23}\ \text{cm}^3$

No. of unit cells in 64 cm^3

$$= \frac{64}{6.4\times10^{-23}} = 1 \times 10^{24} \text{ unit cells}$$

A9. (*c*) : For simple cubic, distance between nearest neighbours $= a$

Empty space = 0

For *fcc* distance between nearest neighbours,

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

$$\text{Empty space} = a - \frac{a}{\sqrt{2}} = a\left(1-\frac{1}{\sqrt{2}}\right)$$

For *bcc*, $d = \dfrac{\sqrt{3}a}{2}$

$$\text{Empty space} = a - \frac{\sqrt{3}a}{2} = a\left(1-\frac{\sqrt{3}}{2}\right)$$

A10. (*c*) : No of atoms present in *fcc* unit cell = 4

Total volume of atoms present in *fcc* unit cell

$$= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

A14. (*b*) : In *bcc*, radius of atom,

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

where a is the edge length

The edge length not covered by atoms $= a - 2r$

$$= a - 2\times\frac{\sqrt{3}}{4}a = a\left(\frac{2-\sqrt{3}}{2}\right)$$

$$= \frac{a(2-1.732)}{2} = 0.134a$$

Percentage of edge length not covered

$$= \frac{0.134a}{a}\times 100 = 13.4\%$$

A15. (*c*) : $r = \dfrac{a}{2\sqrt{2}} = \dfrac{620}{2\times1.414} = 219.20$ pm

A16. (*a*) : No. of NaCl molecules in a unit cell = 4

$$\text{Mass of unit cell} = \frac{4\times58.5}{6.022\times10^{23}}$$

$$\text{No. of unit cells in 1g} = \frac{1\times6.022\times10^{23}}{4\times58.5}$$

$= 2.57 \times 10^{21}$

A18. (*a*) : No. of A atoms per unit cell = 8 (at corners) × $\dfrac{1}{8}$ = 1

No. of B atoms per unit cell

= 6 (at the face centre) × $\dfrac{1}{2}$ = 3

Formula AB_3

A20. (*d*) :
$$d = \frac{Z\times M}{a^3\times N_A}$$

$$2.7 = \frac{Z\times27}{(405\times10^{-10})^3\times(6.02\times10^{23})}$$

$$\text{or}\quad Z = \frac{2.7\times(405\times10^{-10})^3\times6.02\times10^{23}}{27} = 4$$

∴ Lattice is *fcc*.

A21. (*a*) : No. of O^{2-} ions in *ccp* = 4

There will be 8 tetrahedral sites and 4 octahedral sites

No. of Fe^{2+} ions $= \dfrac{1}{8}\times8 = 1$

No. of Fe^{3+} ions $= \dfrac{1}{8}\times8 + \dfrac{1}{4}\times4 = 2$

Formula of magnetite : $Fe^{2+}Fe_2{}^{3+}O_4{}^{2-} \cong Fe_3O_4$

A22. (*c*) : No. of Cu atoms = 4 (*ccp* arrangement)

No. of Ag atoms = 12 (edges) × $\dfrac{1}{4}$ = 3

No. of Au atoms = 1 (body centre)

Formula $Cu_4\,Ag_3\,Au$

A23. (*b*) : No. of O^{2-} ions in *ccp* arrangement = 4

No. of octahedral holes = 4

No. of B^{3+} ions = 4 × $\dfrac{1}{2}$ = 2

No. of tetrahedral holes = 4 × 2 = 8

No. of A^{2+} ions = 8 × $\dfrac{1}{8}$ = 1

Formula $A\,B_2O_4$

A24. (*c*) : No. of W atoms per unit cell = 1

No. of O atoms per unit cell $= 12\times\dfrac{1}{4}$ (edge centre)

= 3

No. of Na atoms per unit cell = 1 (cube centre)

Formula $NaWO_3$

A25. (*c*) : No of Ca atoms per unit cell = 8 (corners) × $\dfrac{1}{8} = 1$

O atoms per unit cell = 6 (face centres) × $\dfrac{1}{2} = 3$

Ti atoms per unit cell = 1

∴ Formula of mineral = $Ca\,TiO_3$

Suppose oxidation state of Ti be x

$+2 + x + 3(-2) = 0$ or $x = +4$

A26. (*d*) : No. of atoms per unit cell of hexagonal primitive unit cell = 6

No of tetrahedral holes = 6 × 2 = 12

No. of octahedral holes = 6 × 1 = 6

A28. (*d*) : No. of atoms at the corners = 6

Contribution of each atom = 1/8

∴ No. of P atoms = 6 × $\dfrac{1}{8}$ = 3/4

No. of atoms at the faces = 6

Contribution of each atom = 1/2

$\therefore$ No. of Q atoms $= 6 \times \frac{1}{2} = 3$

Formula $P_{\frac{3}{4}}Q_3$ or PQ_4

A29. (*d*) Molar volume from pyknometer density

$$= \frac{M}{2.165 \times 10^3}\ m^3$$

Molar volume from X-ray density

$$= \frac{M}{2.178 \times 10^3}\ m^3$$

$$\therefore \text{Volume unoccupied} = \frac{M}{10^3}\left[\frac{1}{2.165} - \frac{1}{2.178}\right] m^3$$

$$= \frac{0.013\ M \times 10^{-3}}{2.165 \times 2.178}$$

$$\therefore \text{Fraction unoccupied} = \frac{0.013\ M \times 10^{-3}}{2.165 \times 2.178} \Big/ \frac{M \times 10^3}{2.165}$$

$$= \mathbf{5.96 \times 10^{-3}}.$$

A30. (*c*) : No. of 'A' atoms $= \frac{1}{8} \times 8 = 1$

No. of 'B' atoms $= 1 \times 1 = 1$

No. of 'C' atoms $= \frac{1}{4} \times 12 = 3$

Formula = ABC_3

A31. (*c*) :

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

$$11.2 = \frac{4 \times M}{(400 \times 10^{-10})^3 \times (6.02 \times 10^{23})}$$

or $$M = \frac{11.2 \times (400 \times 10^{-10})^3 \times (6.02 \times 10^{23})}{4} = 107.8$$

A32. (*c*) :

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

$$6.23 = \frac{4 \times 60}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{4 \times 60}{6.23 \times 6.02 \times 10^{23}} = 64 \times 10^{-24}$$

$$a = 4 \times 10^{-8}\ \text{cm} = 400\ \text{pm}$$

A33. (*d*) : Volume of unit cell $= (100 \times 10^{-10}\ \text{cm})^3$

$= 10^{-24}\ \text{cm}^3$

Mass of unit cell $= V \times d = 10^{-24} \times 10.0 = 10^{-23}$ g

No. of unit cells in 100 g $= \frac{100}{10^{-23}} = 10^{25}$

Since lattice is fcc and each unit cell has 4 atoms per unit cell.

No. of atoms $= 4 \times 10^{25}$.

A34. (*c*) : For *fcc*, $r = \frac{a}{2\sqrt{2}}$

or $a = 2\sqrt{2}\,r = 2 \times 1.414 \times 128$

$= 362$ pm

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

$$= \frac{4 \times 63.5}{(362 \times 10^{-10})^3 \times (6.02 \times 10^{23})}$$

$$= 8.9\ \text{g cm}^{-3}$$

A38. (*c*) :

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

$$4 = \frac{Z \times 72}{(5 \times 10^{-8})^3 \times (6.02 \times 10^{23})}$$

or $$Z = \frac{4 \times (5 \times 10^{-8})^3 \times (6.02 \times 10^{23})}{72} = 4$$

No. of Fe^{2+} and O^{2-} ions present in each unit cell = 4

B. *mcq from Competitive Examinations*

B1. (*b*) : One cation of Sr^{2+} would create one cation vacancy in NaCl. Therefore, the number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added.

No. of moles of cationic vacancies

$$= \frac{10^{-4}}{10^2} = 10^{-6}\ \text{mol}$$

No. of cation vacancies

$= 10^{-6} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{17}$

B2. (*d*) : Packing fraction of a simple cube

$$= \frac{\text{Volume of one sphere}}{\text{Volume of cubic unit cell}}$$

Edge length $a = 2r$ or $r = a/2$

$$\therefore \text{Packing fraction} = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6}.$$

B3. (*a*) : For simple cubic, $a = 2r$ $\therefore$ $r = \frac{a}{2}$

For *bcc*, $4r = \sqrt{3}a$ $\therefore$ $r = \frac{\sqrt{3}a}{4}$

For *fcc*, $4r = \sqrt{2}a$ $\therefore$ $r = \frac{\sqrt{2}a}{4}$

Ratio is : $\frac{a}{2} : \frac{\sqrt{3}a}{4} : \frac{\sqrt{2}a}{4}$

or $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$

B4. (*a*) : For *bcc* structure,

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351 = 151.98\ \text{pm}$$

B5. (*a*) : For *fcc* lattice, radius (r) is related to edge length (a)

$$r = \frac{a}{2\sqrt{2}};\quad a = 408\ \text{pm}$$

$$r = \frac{408}{2 \times 1.414} = 144\ \text{pm}$$

$\therefore$ Diameter $= 2 \times 144 = 288$ pm

Competition File

B6. (*a*) :

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

$$d = 2.72 \text{ g cm}^{-3}, Z = 4,$$
$$a = 404 \text{ pm} = 4.04 \times 10^{-8} \text{ cm}$$

$$2.72 = \frac{4 \times M}{(4.04 \times 10^{-8})^3 \times 6.02 \times 10^{23}}$$

or $M = 27 \text{ g mol}^{-1}$

B7. (*d*) : Carbon has structure similar to ZnS (zinc blende). Carbon forming *fcc* or *ccp* and also occupying half tetrahedral sites.

Total no. of carbon atoms = $8 \times \frac{1}{8}$ (corners) + $6 \times \frac{1}{2}$ (faces) + 4 (tetrahedral sites) = 8.

B8. (*d*) : The distance between body centred atom and one corner atom is $\frac{\sqrt{3}\,a}{2}$ (*i.e.* half of body diagonal)

B9. (*b*) : In *bcc* arrangement, volume of space occupied = 68%

$\therefore$ Vacant space = 100 – 68 = 32%

B11. (*d*) : For Z = 4, structure is *fcc*

$$r = \frac{\sqrt{2}a}{4} = \frac{1.414 \times 361}{4} = 127 \text{ pm}$$

B12. (*d*) : $\rho = \frac{Z \times M}{a^3 \times N_A}$

For *bcc*, Z = 2, M = 6.94 g mol^{-1}

$$\rho = 530 \text{ kg m}^{-3} = \frac{530 \text{ g} \times 10^3}{\text{cm}^3 \times 10^6} = 0.530 \text{ g cm}^{-3}$$

$$0.53 = \frac{2 \times 6.94}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{2 \times 6.94}{0.53 \times 6.02 \times 10^{23}} = 43.5 \times 10^{-24} \text{ cm}^3$$

$$\therefore \quad a = 3.52 \times 10^{-8} \text{ cm} = 352 \text{ pm}$$

B13. (*c*) : $\frac{r_+}{r_-} = \frac{0.98 \times 10^{-10} \text{m}}{1.81 \times 10^{-10} \text{m}} = 0.54$

Since the radius ratio lies between 0.414 – 0.732, its coordination number is 6.

B15. (*c*) **:** In Frenkel defect the size of cation should be smaller than that of anion.

(*d*) **:** is also incorrect because $Fe_{0.93}O$ is metal deficient non-stoichiometric compound.

B16. (*c*) **:** For bcc structure : $4r = \sqrt{3}\,a$

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

$Z = 2$

For fcc structure : $4r = \sqrt{2}a$

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

$Z = 4$

$$\frac{d(\text{bcc})}{d(\text{fcc})} = \frac{\frac{Z(\text{bcc}) \times M}{a^3 \times N_A}}{\frac{Z(\text{fcc}) \times M}{a^3 \times N_A}} = \frac{\frac{2 \times M}{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A}}{\frac{4 \times M}{\left(\frac{4r}{\sqrt{2}}\right)^3 \times N_A}}$$

$$= \frac{2 \times M}{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A} \times \frac{\left(\frac{4r}{\sqrt{2}}\right)^3 \times N_A}{4 \times M}$$

$$= \frac{1}{2}\left(\frac{3}{2} \times \frac{\sqrt{3}}{\sqrt{2}}\right) = \frac{3\sqrt{3}}{4\sqrt{2}}$$

B17. (*c*) : For 1 mol of a compound, number of tetrahedral and octahedral voids = 2 + 1 = 3

$\therefore$ No. of voids = $3 \times 0.5 \times 6.022 \times 10^{23} = 9.033 \times 10^{23}$

B18. (*c*) : AgBr shows both Schottky and Frenkel defects

B19. (*c*) : Let *x* atoms of Fe^{3+} ions are present. This means *x* Fe^{3+} ions have been replaced by Fe^{2+} ions.

No. of Fe^{2+} ions = $0.93 - x$

For electrical neutrality,

$2(0.93 - x) + 3x = 2$

$1.86 + x = 2$ or $x = 0.14$

Fraction of Fe^{3+} = 0.14, Fe^{2+} = 0.93 – 0.14 = 0.79

Formula : $Fe^{2+}_{0.79}\,Fe^{3+}_{0.14}\,O^{2-}_{1.0}$

Total molar mass = 0.93 × 56 + 1 × 16 = 68.08

$$\% \text{ of Fe (III)} = \frac{0.14 \times 56}{68.08} \times 100 = 11.5\%$$

B20. (*b*) **:** No. of Y atoms in a unit cell = 4

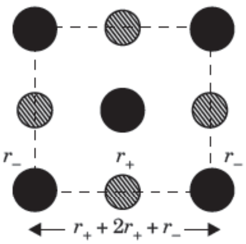
No. of tetrahedral sites = 4 × 2 = 8

No. of X atoms in unit cell = $8 \times \frac{2}{3} = \frac{16}{3}$

Formula : $X_{\frac{16}{3}}Y_4$ or $X_{\frac{1}{3}}Y_{\frac{1}{4}}$ or X_4Y_3

B21. (*b*) : For *fcc*

$$a = 2r_+ + 2r_-$$
$$a = 2(r_+ + r_-)$$



or $$r_+ + r_- = \frac{a}{2}$$

$$r_- = \frac{a}{2} - r_+ = \frac{508}{2} - 110 = 144 \text{ pm}$$

B22. (*d*) : Percentage of free space in *ccp* = 26% and in *bcc* = 32%.

B23. (*d*) : No. of 'A' atoms at corners $= 8\times\frac{1}{8} = 1$

No. of 'B' atoms at face centres $= 5\times\frac{1}{2} = \frac{5}{2}$

Formula = $AB_{5/2}$ or A_2B_5

B24. (*b*) : In a *fcc* lattice

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

$$r = \frac{\sqrt{2}a}{4} = \frac{1.414\times 361}{4} = 127.61 \simeq \mathbf{128\ pm}$$

B25. (*c*) : For *bcc* structure,

$$r = \frac{a\sqrt{3}}{4} = \frac{351\times 1.732}{4} = 152 \text{ pm}$$

B26. (*c*) : Let fraction of metal which exits as M^{3+} be x

Fraction of metal as $M^{2+} = 0.98 - x$

$\therefore 3x + 2(0.98 - x) = 2$

$x + 1.96 = 2$ or $x = 0.04$

$$\% \text{ of } M^{3+} = \frac{0.04}{0.98}\times 100 = 4.08$$

B27. (*d*) : Body diagonal $= \sqrt{3}\,a$

or $2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3}\,a$

$$\therefore \quad r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}\,a}{2}$$

B28. (*c*) : For *bcc* lattice,

$$r = \frac{\sqrt{3}a}{4} = \frac{1.732\times 4.29}{4} = 1.86\ \text{Å}$$

B29. (*b*) : CrO_2 is metallic and ferromagnetic.

B30. (*d*) : In *fcc*, the closest approach distance between two atoms,

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

B31. (*c*) : In Frenkel defect, the cations are dislocated from their normal sites to interstitial sites.

B33. (*b*) : Atoms of X per unit cell $= 8 \times \frac{1}{8} = 1$

Atoms of Y per unit cell = 1

Atoms of Z per unit cell $= 6 \times \frac{1}{2} = 3$

$\therefore$ Formula of the compound is XYZ_3.

B34. (*a*) : $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55, \qquad \frac{r_{K^+}}{r_{Cl^-}} = 0.74$

or $\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.55 + 1, \qquad \frac{r_{K^+}}{r_{Cl^-}} = 0.74 + 1$

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.55, \qquad \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.74$$

Edge length ratio is

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.74}{1.55} \Rightarrow \frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.122$$

B36. (*a*) : Each unit cell is surrounded by 6 other unit cells because a *fcc* unit cell has six faces.

B39. (*a*) : Density $= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$$= \frac{\text{No. of atoms} \times \text{Mass of each atom}}{\text{Volume of unit cell}}$$

For *fcc*, no. of atoms per unit cell = 4

$$\text{Density} = \frac{4\times m}{a^3}$$

B41. (*c*) : In Schottky defect equal number of cations and anions are missing from their lattice sites.

B42. (*c*) : No. of atoms in *fcc* unit cell = 4

Volume occupied by 1 atom $= \frac{4}{3}\pi r^3$

$$\text{Volume occupied by 4 atoms} = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

B43. (*d*) : $\rho = \frac{Z \times M}{a^3 \times N_A}$

For *bcc*, Z = 2, $a = 500 \times 10^{-10}$ cm

$d = 4$ g cm^{-3}

$$4 = \frac{2\times M}{(500\times 10^{-10})^3 \times (6\times 10^{23})}$$

$$M = \frac{4\times(500\times 10^{-10})^3 \times 6\times 10^{23}}{2}$$

$= 150$ g mol^{-1}

B44. (*b*) : Each particle at the edge centre is surrounded by four unit cells. Therefore, its contribution per unit cell is $\frac{1}{4}$.

B45. (*b*) : Frenkel defect is a dislocation defect.

B46. (*a*) : The dimensions; $\alpha \neq \beta \neq \gamma \neq 90°$ and $a \neq b \neq c$ represent triclinic crystal system. Among the given options only $K_2Cr_2O_7$ exhibits triclinic crystal system.

B47. (*b*) : No. of A atoms at the corners $= 7 \times \frac{1}{8} = \frac{7}{8}$

No. of B atoms at face centres $= 6 \times \frac{1}{2} = 3$

Ratio of A : B $= \frac{7}{8} : 3$

Formula of compound is A_7B_{24}

B48. (*a*) : No. of X atoms $= 8\times\frac{1}{8} = 1$

No. of Y atoms = 1

Formula : XY

B49. (*c*) : Length of body diagonal $= \sqrt{3}.a$

$= 1.732 \times 300$

$= 519.6$ pm

B51. (*d*) : No. of atoms (A) on the corners = 8

No. of atoms (A) on the face centres = 6

Removing face centred atoms along one of the axes means removal of 2A atoms so that

$$\text{No. of A atoms per unit cell} = 8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 3$$

No. of B atoms per unit cell in NaCl type structure = 4

Formula = A_3B_4

B52. (*b*) **:** In ZnS, S^{2-} ions are present in all the corners and centres of each face (*fcc* or *ccp* arrangement). Zn^{2+} ions occupy alternate tetrahedral sites.

B53. (*d*) : Packing efficiency $= \dfrac{\text{Area covered by particles}}{\text{Total area}}$

If a is the length of unit cell

Face diagonal, AC $= \sqrt{2}\,a$

$$\begin{aligned} \text{But} \quad AC &= 4r \\ \therefore \quad \sqrt{2}\,a &= 4r \\ a &= \frac{4r}{\sqrt{2}} = 2\sqrt{2}r \end{aligned}$$

$$\text{No. of particles} = 4\times\frac{1}{4}+1 = 2$$

Area occupied by particles $= 2 \times \pi r^2$

$$\therefore \text{Packing efficiency} = \frac{2\times\pi r^2}{(2\sqrt{2}r)^2} = \frac{\pi}{4}$$

$$= 0.7857 \text{ or } 78.57\ \%.$$

B54. (*b*) : X are present at all the corners and face centres

No. of X atoms $= 8\times\frac{1}{8}+6\times\frac{1}{2} = 4$

M are present at 4 edges and at body centre

No. of M atoms $= 4\times\frac{1}{4}+1\times1 = 2$

The empirical formula of compound : M_2X_4 or MX_2

B55. (*a*) : Cation A^+ occupies octahedral void of arrangement of X^- anions

$$\frac{r_{A^+}}{r_{X^-}} = 0.414 \Rightarrow \frac{r_{A^+}}{250} = 0.414$$

or $r_{A^+} = 0.414 \times 250 = 104$ pm.

B56. (*a*) : For *ccp* arrangement, Z = 4

$\therefore$ No. of O atoms = 4

No. of octahedral voids = 4

No. of tetrahedral voids = 4 × 2 = 8

No. of Al^{3+} ions $= m \times 4$

No. of Mg^{2+} ions $= n \times 8$

Thus the formula of mineral is

$Al_{4m}\,Mg_{8n}\,O_4$

$$\begin{aligned} 4m(+3) + 8n(+2) + 4(-2) &= 0 \\ 12\,m + 16\,n - 8 &= 0 \\ 4(3m + 4n - 2) &= 0 \\ \therefore \quad 3m + 4n &= 2 \end{aligned}$$

Possible values of m and n are

$$3\times\frac{1}{2}+4\times\frac{1}{8} = 2 \quad \text{true}$$

$$3\times1+4\times\frac{1}{4} = 2 \quad \text{not true}$$

$$3\times\frac{1}{2}+4\times\frac{1}{2} = 2 \quad \text{not true}$$

$$3\times\frac{1}{4}+4\times\frac{1}{8} = 2 \quad \text{not true}$$

C. mcq with more than one correct answer

C1. (*c,d*) : A hexagonal close packing has coordination number 12 and is not as closely packed as *bcc*.

C2. (*a,c,d*) : (*b*) is not correct because it has coordination number 8.

C3. (*a,b,c*) : $Cs^+(8), Cl^-(8); Na^+(6); Cl^-(6); Zn^{2+}(4), S^{2-}(4); Na^+(4), O^{2-}(8)$.

C9. (*b,c*) : ZnS shows Frenkel defect while AgBr shows both Frenkel and Schottky defects. Therefore, options (*b*) and (*c*) are correct.

D. mcq based on passage/comprehension

Passage I.

D1. (*b*) : The number of atoms per unit cell in different types of unit cells are :

$f = 4, b = 2, e = 2$ and $s = 1$

D2. (*c*) : From geometry we can prove that, $r = \dfrac{a}{2\sqrt{2}}$

$$\therefore \quad r = \frac{0.410}{2\times1.414} = 0.145 \text{ nm}$$

D3. (*d*) :

$$\text{No. of X atoms} = 7 \times \frac{1}{8} = 7/8$$

$$\text{No. of Y atoms} = 1 \times \frac{1}{8} = 1/8$$

$$\text{No. of Z atoms} = 6 \times \frac{1}{2} = 3$$

$$\text{Formula} = X_{7/8}\,Y_{1/8}\,Z_3 = X_7YZ_{24}$$

D4. (*a*) :

$$\frac{r(Rb^+)}{r(Br^-)} = \frac{148}{195} = 0.76 \text{ (C.N. 8 above 0.732)}$$

$$\frac{r(K^+)}{r(Br^-)} = \frac{137}{195} = 0.702$$

(C.N. 6 between 0.414 – 0.732)

D5. (*c*) : *fcc* arrangement has 4 atoms per unit cell while *bcc* arrangement has 2 atoms per unit cell. Therefore, ratio between atoms is 4 : 2 or 2 : 1. Here density does not make any difference.

Passage II.

D6. (*b*) :

$$\begin{aligned} \text{Vol. of unit cell} &= (100 \times 10^{-10}\text{ cm})^3 \\ &= 1 \times 10^{-24}\text{ cm}^3 \end{aligned}$$

$$\text{Mass of an atom} = \frac{24.0}{24\times10^{23}} = 1 \times 10^{-23}\text{ g}$$

(No. of atoms in *fcc* = 4)

Mass of unit cell $= 4 \times 1 \times 10^{-23} = 4 \times 10^{-23}$ g

$$\text{Density} = \frac{4\times10^{-23}}{1\times10^{-24}} = \mathbf{40\ g\ cm^{-3}}$$

D7. (*c*) : Vol. of unit cell $= (200 \times 10^{-10})^3 = 8 \times 10^{-24}$ cm^3

$$\text{Volume of 100 g of element} = \frac{100}{12.5} = 8\text{ cm}^3$$

$$\text{No. of unit cell} = \frac{8}{8\times10^{-24}} = 1 \times 10^{24}$$

No. of atoms in 100 g $= 2 \times 1 \times 10^{24} = \mathbf{2 \times 10^{24}}$

(No. of atoms in *bcc* unit cell = 2)

D8. (*b*) : Mass of unit cell $= \dfrac{2\times 60}{6.02\times 10^{23}}$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$4.2 = \frac{2\times 60}{6.02\times 10^{23}\times \text{V}}$$

$$\text{or V} = \frac{2\times 60}{6.02\times 10^{23}\times 4.2} = \mathbf{4.75\times 10^{-23}\ cm^3.}$$

Passage III.

D9. (*b*) : Effective no. of atoms present in unit cell of *hcp*

$$= 2\times\frac{1}{2} + 3\times 1 + 12\times\frac{1}{6} = 6$$

D10. (*a*) : Volume = Base area × Height

$$= 6\times\frac{\sqrt{3}}{4}a^2\times 2\times\sqrt{\frac{2}{3}}a$$

Putting $a = 2r$

$$6\times\frac{\sqrt{3}}{4}(2r)^2\times 2\times\sqrt{\frac{2}{3}}.2r$$

$$= 6\times\frac{\sqrt{3}}{4}\times 4r^2\times 2\sqrt{\frac{2}{3}}.2r = 24\sqrt{2}r^3$$

D11. (*d*) : Packing fraction in *hcp* = 0.74

∴ Void fraction = 1 – 0.74 = 0.26

∴ Empty space in *hcp* unit cell = 26%.

Assertion Reason Type Questions

2. (*e*) : **Correct assertion :** ZnS has *fcc* structure.
   Correct reason : S^{2-} ions adopt *ccp* or *fcc* arrangement and Zn^{2+} ions occupy alternate tetrahedral sites.
3. (*c*) : **Correct reason :** Cl^- ions in CsCl have simple cubic arrangement.
5. (*a*) : Both assertion and reason are correct.
6. (*c*) : **Correct reason :** Since there are two tetrahedral sites for each Ca^{2+} ion, the number of F^- ions are double the number of Ca^{2+} ions.
7. (*e*) : **Correct assertion :** Octahedral void is larger in size than tetrahedral void.
   Correct reason : Cations are generally smaller than anions and therefore occupy less space.
8. (*a*) : Both assertion and reason are correct.
9. (*a*) : Both assertion and reason are correct.
10. (*c*) : **Correct reason :** In Frenkel and Schottky defect, the number of cations and anions remains the same.

Integer Type or Numerical Value Type Questions

1. (7) : $\text{Density} = \dfrac{\text{Mass}}{\text{Volume}}$

10.5 g/cm³ means in 1 cm³ Ag = 10.5 g

$$\text{No. of atoms in 1 cm}^3 = \frac{10.5}{108}\text{N}_\text{A}$$

$$\text{No. of atoms in 1 cm} = \left(\frac{10.5}{108}\text{N}_\text{A}\right)^{1/3}$$

$$\text{No. of atoms in 1 cm}^2 = \left(\frac{10.5}{108}\text{N}_\text{A}\right)^{2/3}$$

No. of atoms in 10^{-12} m² or 10^{-8} cm²

$$= \left(\frac{10.5}{108}\text{N}_\text{A}\right)^{2/3}\times 10^{-8}$$

$$= \left(\frac{10.5\times 6.022\times 10^{23}}{108}\right)^{2/3}\times 10^{-8}$$

$$= 1.50\times 10^7$$

$$\therefore\quad x = 7$$

2. (8) : There are $4Na^+$ ion and $4Cl^-$ ions per unit cell. Total Na^+ and Cl^- ions are 8.

3. (4) : It corresponds to fcc unit cell. Therefore, the number of atoms present per unit cell is 4.

4. (6) : Since radius ratio lies between 0.414 – 0.732, its coordination number is 6.

5. (7) : Suppose number of atoms N in *hcp* lattice = *n*

No. of tetrahedral voids = 2*n*

$$\text{No. of M atoms} = \frac{2}{3}\times 2n = \frac{4n}{3}$$

$$\text{Formula} = \text{M}_{\frac{4n}{3}}\text{N}_n \text{ or } \text{M}_{\frac{4}{3}}\text{N}_1 \text{ or } \text{M}_4\text{N}_3.$$

Total number of M and N atoms = 7.

6. (6) : In one *hcp* unit cell, there are 6 atoms.

No. of octahedral voids = 6

No. of tetrahedral voids = 12

Difference = 12 – 6 = 6.

7. (1) : Coordination no. in *ccp* = 12

Coordination no. in *hcp* = 12

Ratio = 12/12 = 1.

8. (5) : Suppose the atoms Y in *ccp* = *n*

No. of tetrahedral voids = 2*n*

No. of X atoms = 2*n*/3

Formul $X_{2/3n}Y_n$ or X_2Y_3

∴ $a + b = 5$

9. (5) : Contribution of atoms on the corners $= 8\times\dfrac{1}{8} = 1$.

Since atoms on the body diagonal are not shared by any other unit cell and there are four body diagonals, their contribution per unit cell = 4

∴ Total number of atoms in the unit cell = 4 + 1 = 5.

10. (8) : A truncated octahedron has 14 faces (8 regular hexagons and 6 squares), 36 edges and 24 vertices.

11. (2) : Volume of unit cell = $(400\times 10^{-10})^3$ cm³

Mass of element = 256 g

Density of element = 8 g cm⁻³

$$\text{Volume of 256 g of element} = \frac{256}{8} = 32\text{ cm}^3$$

$$\text{No. of unit cells} = \frac{32}{\left(400\times 10^{-10}\right)^3} = 5\times 10^{23}\text{ unit cells}$$

Since the structure is *fcc*, number of atoms present in a unit cell = 4

No. of atoms in 256 g = $5\times 10^{23}\times 4$

$$= \mathbf{2\times 10^{24}\ atoms}$$

Competition File

12. (3.00) : MX having NaCl structure

No. of M^+ ions = 4 No. of X^- ions = 4

For structure Z constructed from MX

(*i*) After removing all X^- ions except the centred one,

No. of M^+ ions = 4 No. of X^- ions = 1

(*ii*) No. of face centred M^+ ions removed $= 6\times\frac{1}{2} = 3$

No. of M^+ ions replaced by X^- ions = 3

$\therefore$ No. of M^+ ions left = 1 No. of X^- ions = 1 + 3 = 4

(*iii*) No. of corners M^+ ions $= 8\times\frac{1}{8} = 1$.

No. of M^+ ions left =1–1=0 No. of X^- ions = 4

(*iv*) Replacing central X^- by M^+

No. of M^+ ions = 0+1=1 No. of X^- ions =4–1=3

$$\frac{\text{No. of } X^- \text{ ions}}{\text{No. of } M^+ \text{ ions}} = \frac{3}{1} = 3.00$$

NCERT Exemplar Problems : MCQs Type-I

2. (*b*) : Crystalline solids are not isotropic in nature. These are anisotropic in nature.

4. (*d*) : In antiferromagnetism, the magnetic moments are in a compensatory way so as to give zero net magnetic moment because of cancellation of individual magnetic moments.

5. (*a*) : Quartz glass is amorphous and therefore, refractive index is same in all directions.

12. (*b*) : Graphite is a good conductor of electricity due to the presence of free (π) electrons.

14. (*d*) : CrO_2 show electrical behaviour as metals.

19. (*b*) : The overall charge is neutral.

20. (*d*) : *n*-type of semiconductor is formed when silicon is doped with atoms having more than four electrons (*e.g.* P, As).

21. (*b*) : A *fcc* unit cell has 4 atoms per unit cell and each atom has two tetrahedral sites. Therefore, the number of tetrahedral sites in *fcc* unit cell is eight.

22. (*a*) : AgBr shows both Schottky defect and Frenkel defect.

23. (*b*) : *hcp* and *ccp* occupy 74% of the available space and have most efficient packing.

25. (*d*) : It has AB AB AB type of arrangement and therefore, fourth layer is not aligned with particles of first layer.

26. (*a*), (*d*) : In NaCl, both Na^+ and Cl^- ions have six C.N. (*d*) is also correct. The C.N. of both Zn^{2+} and S^{2-} ions are four.

28. (*d*) : Electronic defects are introduced by doping.

30. (*b*): In ferromagnetic substances ordering of magnetic moments may persist even when magnetic field is removed. Therefore, these can be magnetised permanently.

31. (*d*) : Opposite to the direction of magnetic field.

33. (*b*) : *fcc* (74%) > *bcc* (68%) > Simple cubic (52.4%)

34. (*a*): because cations are dislocated to interstitial sites.

35. (*d*) : In *ccp*, there are four atoms per unit cell and therefore eight tetrahedral voids.

36. (*a*) : In *fcc*; $a = \frac{4r}{\sqrt{2}}$ or $2\sqrt{2}r$; in *bcc* $a = \frac{4r}{\sqrt{3}}$ and in cubic, $a = 2r$.

37. (*a*): The conductivity of metals is much more than that of insulators but the conductivity of semiconductors is less than metals and more than insulators.

NCERT Exemplar Problems : MCQs Type-II

40. (*c, d*) : (*c*) is not true because impurity defect changes the mass but not the volume and therefore, density changes.

(*d*) Frenkel defect neither changes mass nor volume.

42. (*a, b*) : (*c*) is wrong because electrons move towards anode and holes move towards cathode.

(*d*) is also not true.

43. (*b, c*) : (*a*) is false because silicon doped with electron rich impurity is *n*-type semiconductor.

(*d*) is false because conductivity of *n*-type semiconductor increases due to extra electrons and not due to vacancy.

45. (*b, c*) : In NaCl, Cl^- ions have fcc arrangement and number of Cl^- ions per unit cell = 4. Number of tetrahedral voids will be 4 × 2 = 8.

Tetrahedral voids are double the number of octahedral voids.

47. (*a, c*) : Impurities of As and P when doped to silicon give *n*-type semiconductor.

50. (*a, b, c*) : SiC, AlN and diamond are covalent network solids.

53. (*b, d*) : Vacancy defect and Schottky defect decrease the density.

NCERT Exemplar Problems : Assertion Reason Type Questions

59. (*a*) : Simple cubic unit cell has one atom because there are 8 atoms at the corners, each contributing 1/8.

60. (*b*) : Graphite is a good conductor of electricity because of the presence of π electrons.

61. (*c*) : Reason is not correct though assertion is correct.

62. (*b*) : Both assertion and reason statements are correct but reason is not correct explanation for the assertion.

63. (*c*) : Assertion is correct but the reason is not the correct explanation of assertion. This is because intermediate conductivity of semiconductors is due to small energy gap between filled valence band and empty conduction band.

❑❑❑

Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. Maximum Marks : 25

1. What is the maximum coordination number of an atom in a *hcp* crystal structure of an element? (1)
2. Both diamond and rhombic sulphur are covalent solids but the latter has very low melting point than the former. Why? (1)
3. Why is Frenkel defect not found in pure alkali metal halides? (1)
4. A group 14 element is to be converted into *n*-type semiconductor by doping with a suitable impurity. To which group should this impurity belong? (1)
5. How do the structures of quartz and quartz glass differ from each other. (1)
6. Analysis of a metal oxide shows its empirical formula $M_{0.96}O_{1.0}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal. (2)
7. What are Schottky and Frenkel defects? How does density of a solid get affected by these defects? (2)
8. Ferric oxide crystallizes in a hexagonal close packed array of oxide ions with two out of every three octahedral voids occupied by ferric ions. Derive the formula of the ferric oxide. (2)
9. An element crystallizes in a body centred cubic structure with a cell edge of 288 pm. The density of the element is 7.2 *g* cm^{-3}. How many atoms are present in 208 *g* of the element ? (3)
10. Explain
    - (*i*) Some of the very old glass objects appear slightly milky instead of being transparent.
    - (*ii*) Zinc oxide exhibits enhanced electrical conductivity on heating.
    - (*iii*) $CdCl_2$ will induce Schottky defect if added to silver chloride crystal. (3)
11. Explain the following terms with suitable examples :
    - (*i*) Ferrimagnetism
    - (*ii*) Intrinsic conduction of solids
    - (*iii*) Ferromagnetism. (3)
12. (*a*) If the radius of octahedral void is *r* and the radius of the atoms in the close packing is R, derive a relationship between *r* and R.
    - (*b*) What is a semiconductor ? Describe the two main types of semiconductors and contrast conduction mechanism in them. (5)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.