

## Chapter 4: Solid State

### Review Questions

1. What kinds of particles are located at the lattice sites in a metallic crystal?

#### Solution

The lattice positions are occupied by metal cations, which are then surrounded by the core electrons of the metal. A sea of valence electrons encompasses the entire metallic solid.

2. What are crystalline solids? State the categories of crystalline solids with examples.

#### Solution

Crystalline solids are solids with highly ordered arrangement of constituent atoms, ions, or molecules that is repeated many times throughout the structure. The pattern is so ordered and regular that if the arrangement at any one site is known, the arrangement of constituent atoms at many sites can be predicted. They are characterized by rigid structures and high and sharp melting points, for example, sodium chloride and ice.

Crystalline solids may be classified on the basis of nature of binding forces as:

- (a) metallic solids (e.g., zinc, chromium, etc.)
- (b) ionic solids (e.g., sodium chloride, potassium bromide)
- (c) covalent solids (e.g., diamond, graphite)
- (d) molecular solids (e.g., iodine, naphthalene)

3. What are the possible types of defects that can occur if a  $\text{Ca}^{2+}$  ion replaces an  $\text{Na}^+$  in a crystal lattice of NaCl?

#### Solution

When a  $\text{Ca}^{2+}$  ion replaces an  $\text{Na}^+$  in a crystal lattice of NaCl, one extra positive charge is produced. The  $\text{Na}^+$  vacancy or  $\text{Cl}^-$  interstitial will be formed to balance the charge. Hence, the possible defects that can occur are impurity defects.

4. Calculate the packing efficiency of a hexagonal close packing (hcp) lattice unit cell.

#### Solution

Let the radius of sphere =  $r$

$$\text{Volume of unit cell} = \frac{\text{Base}}{\text{Area} \times \text{Height}}$$

$$\text{Base area of hexagon} = 6 \times \frac{\sqrt{3}}{4} \times 7(2r)^2 = 6\sqrt{3}r^2$$

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

$$\text{Therefore, the volume of unit cell} = 6 \times \sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}} = 24r^3\sqrt{2}$$

$$\text{The number of atoms (Z)} = 6; \text{ volume of a sphere} = \frac{4}{3}\pi r^3.$$

$$\text{The total volume of all spheres} = 6 \times \frac{4}{3}\pi r^3.$$

$$\begin{aligned} \text{Packing efficiency} &= \frac{\text{Volume of all spheres}}{\text{Volume of unit cell}} \times 100 \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{24 r^3 \sqrt{2}} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 \\ &= \frac{3.14}{3\sqrt{2}} \times 100 = 0.74 \times 100 = 74 \% \end{aligned}$$

5. A compound consisting of the monovalent ions  $A^+$ ,  $B^-$  crystallizes in the body-centered cubic lattice. (a) What is the formula of the compound? (b) If one of  $A^+$  ions from the corner is replaced by a monovalent ion  $C^+$ , what would be the simplest formula of the resulting compound?

**Solution**

(a) In *bcc*  $A^+$  are present at the corners. So their contribution is  $8 \times 1/8 = 1$ . And  $B^-$  is present at the body center, so its contribution will be 1. The formula of the compound is 1:1 = AB.

(b) When  $A^+$  has been replaced by  $C^+$  then the contribution of  $A^+$  is 7/8. Contribution of  $C^+$  present at the corner is 1/8.  $B^-$  is present at the body center, so its contribution will be 1. The ratio of contributions of A:B:C is 7/8:1/8:1, so the formula of the compound is  $A_7BC_8$ .

6. What are the similarities and differences between metallic and ionic crystals?

**Solution**

The basis of similarities between metallic and ionic crystals is that both these crystal types are held by the electrostatic force of attraction. In metallic crystals, the electrostatic force acts between the positive ions and the electrons. In ionic crystals, it acts between the oppositely charged ions. Hence, both have high melting points. The basis of differences between metallic and ionic crystals is that in metallic crystals, the electrons are free to move, so metallic crystals can conduct electricity. However, in ionic crystals, the ions are not free to move. As a result, they cannot conduct electricity. However, in molten state or in aqueous solution, they do conduct electricity.

7. Columbium is another name for one of the elements. This element is shiny, soft, and ductile. It melts at  $2468^\circ\text{C}$ , and the solid conducts electricity. What kind of solid does columbium form?

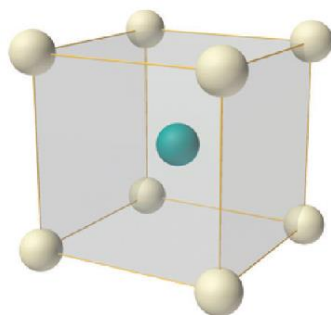
**Answer:**

Metallic solid.

8. Barium metal has body-centered cubic structure. Draw a unit cell of barium atom and calculate the number of barium atoms per unit cell.

**Solution**

Structure of unit cell of barium



The number of atoms in barium unit cell is 2. The atoms at the eight corners of the unit cell are shared by eight other unit cells and thus contribute one-eighth per atom. The atom at the center of the unit cell belongs completely to the unit cell.

9. What type of interactions hold the molecules together in a polar molecular solid?

**Solution**

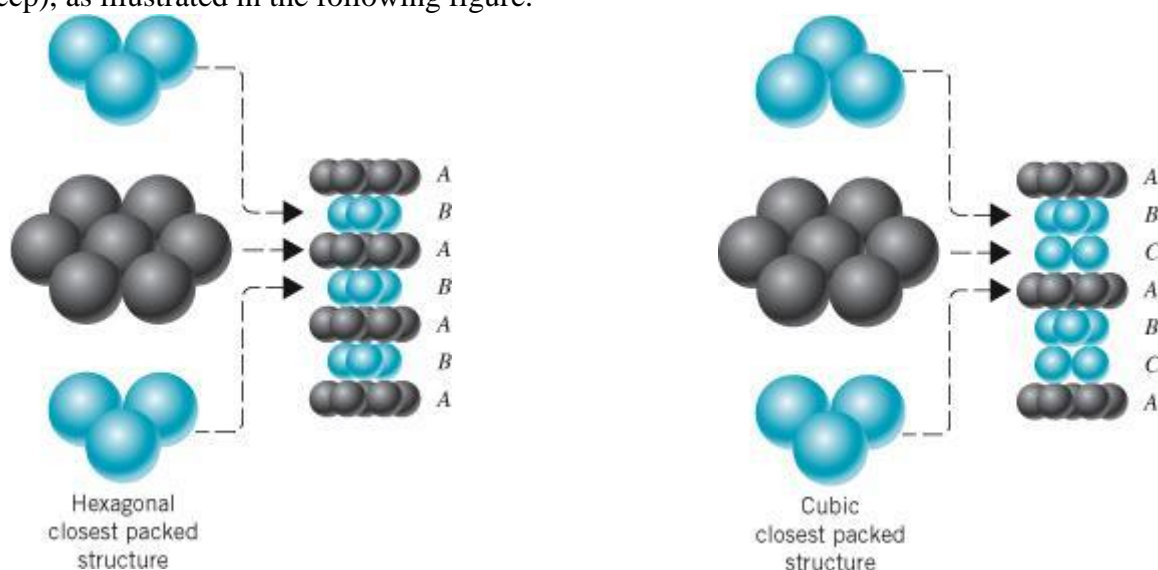
Dipole–dipole interactions hold the molecules together in a polar molecular solid. A polar molecule has separate centers of positive and negative charges. These forces arise due to electrostatic attraction between oppositely charged ends of the polar molecules.

10. Explain the two types of close packing of atoms/ions commonly found in crystalline solids.

**Solution**

The two types are cubic and hexagonal close packing. If we assume that atoms are hard spheres, then it is reasonable to assume that when they are placed in contact, they will pack in such a way as to get as close as possible to each other. By analogy, when we place marbles into a bag, they tend to adopt an arrangement in which the marbles are in contact. These arrangements are called **close packing**.

When three or more layers of spheres are placed on top of each other systematically, then there are two possible structures: hexagonal close packing (hcp) and cubic close packing (ccp), as illustrated in the following figure.



Hexagonal close packing occurs when the third layer of spheres eclipses the first. We call this an ABABAB... arrangement. Cubic close packing occurs when the third layer of spheres does not eclipse the first. We call this an ABCABC... arrangement.

**11.** AgI crystallizes in cubic close-packed ZnS structure. What fraction of tetrahedral sites is occupied by  $\text{Ag}^+$  ions?

**Solution**

In the face-centered unit cell of AgI, there are  $\text{Ag}^+$  ions and  $4\text{I}^-$  ions. As there are  $4\text{I}^-$  ions in the packing, therefore there are eight tetrahedral voids. Of these, half are occupied by silver cations.

**12.** Explain why the presence of Schottky defect in a crystal lowers its density.

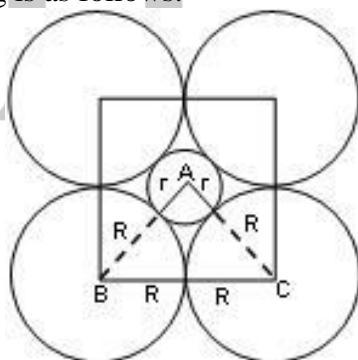
**Solution**

When a pair of one cation and one anion of equal valence is missing from an ionic crystal, the condition of charge neutrality is still maintained. The pair of vacant sites so formed, is called Schottky defect. These ion-pair vacancies decrease the density of the solid and facilitate atomic diffusion.

**13.** If the radius of the octahedral void is  $r$  and radius of the atoms in close packing is  $R$ , derive the relation between  $r$  and  $R$ .

**Solution**

The derivation of the relationship between the radius ( $r$ ) of the octahedral void and the radius ( $R$ ) of the atoms in close packing is as follows.



A sphere is placed in the octahedral void as shown in the figure. A sphere above and a sphere below this small sphere have not been shown in the figure. ABC is a right-angled triangle. The center of void is A. Applying Pythagoras theorem,

$$\begin{aligned} BC^2 &= AB^2 + AC^2 \\ (2R)^2 &= (R+r)^2 + (R+r)^2 = 2(R+r)^2 \\ \frac{4R^2}{2} &= (R+r)^2 \end{aligned}$$

Taking roots, we get

$$\begin{aligned} (\sqrt{2R^2}) &= \sqrt{(R+r)^2} \Rightarrow \sqrt{2}R = R+r \\ r &= \sqrt{2}R - R = (1.414 - 1)R = 0.414 R \end{aligned}$$

14. Discuss Schottky and Frenkel defects. Explain with the help of diagrams.

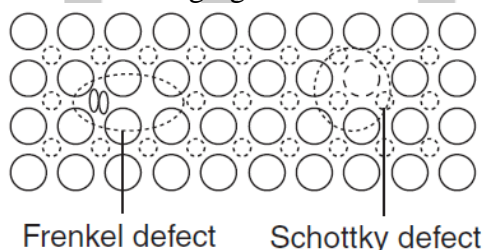
**Solution**

**Schottky defects:**

- (a) The absence of a cation or anion from the position that it is expected to occupy in the periodic arrangement of ions is known as Schottky defect.
- (b) The vacant positions give rise to vacancies or voids in the structure of the substance.
- (c) These defects are more common in ionic compounds with high coordination numbers and where the positive and negative ions are of similar size (e.g., NaCl, CsCl, KCl, and KBr).
- (d) Since the solid with a Schottky defect contains lesser number of ions than a perfect crystal, the density of the crystal exhibiting Schottky defect will be less than that of the perfect crystal (see figure).

**Frenkel defects:**

- (a) In this type of defect, the ion, instead of being in its expected location, is found in one of the interstices.
- (b) Frenkel defects are more common in ionic crystals where size of the cation is such that it can be accommodated in the interstitial sites.
- (c) This type of defect is favored by a large difference in size between the positive and negative ions, and since the size of cation is smaller than that of the anion, the former can be accommodated in the interstitial position (e.g., ZnS, AgCl, AgBr, and AgI).
- (d) The density of crystals exhibiting Frenkel defect remains unchanged as the ions are present in the interstitial sites without changing the volume of the substance.

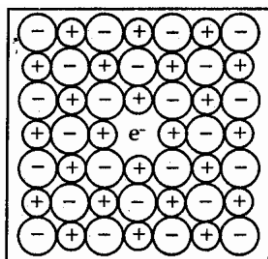


15. Where in the periodic table are the atoms most likely to be involved in the formation of semiconductors located?

**Solution**

Ceramics are formed by the fusion of silicon oxides with non-metal atoms.

16. Figure 4.71 refers to the creation of F-center.



**Figure 4.71**

(a) What type of solids show this type of defect?

(b) How are F-center formed?

**Solution**

(a) Ionic solids and alkali halides show this type of defect.

(b) Exactly how the F-center is formed is not known. One possible mechanism involves the ionizing radiation interacting with the alkaline halide, causing a halide ion to lose an electron, producing a halogen atom. The electron then moves throughout the crystal until it finds a halide vacancy. There the electron is captured by the six surrounding alkaline metal ions. The halogen atom can then interact with a halide ion to form a molecular ion such as  $\text{Cl}_2^-$ .

**17.** Why does germanium act as an *n*-type semiconductor?

**Solution**

Germanium acts as *n*-type semiconductor when a pentavalent impurity atom is added to pure germanium crystal. With addition of each impurity atom, one extra electron is created in crystal lattice of germanium and hence the majority charge carriers are electrons in *n*-type semiconductors.

**18.** The number of vacancies generated in NaCl lattice on addition of divalent ions is twice the number of ions added. Justify.

**Solution**

When a divalent ion is added as impurity to NaCl lattice, it replaces two sodium ions so as to keep the crystal electrically neutral. One of these lattice sites is occupied by the divalent cation and the other remains vacant. These vacancies result in the higher electrical conductivity of the solid.

**19.** Explain the cause of magnetic behavior in the following type of substance:

(a) Ferromagnetic

(b) Paramagnetic

**Solution**

(a) Atomic magnetic moments, in ferromagnetic materials, arise when the electrons of an atom possess a net magnetic moment due to their angular momentum. The metal atoms are grouped together in small regions called domains and each domain acts as a tiny magnet. These domains are randomly oriented in an unmagnetized portion of the substance. However, in presence of an applied field, these domains get aligned with the applied magnetic field and the combined effect of the atomic magnetic moments gives rise to a relatively large magnetization for a given applied field. These ordered domains continue to exist even when the external magnetic field is removed and the ferromagnetic substance becomes a permanent magnet. Examples are, iron, nickel, cobalt  $\text{CrO}_2$ , and others. This is a temperature-dependent property.

(b) Paramagnetic substances are magnetized along the direction of the applied magnetic field. They are weakly attracted by the applied magnetic field. The substances showing paramagnetism contain one or more unpaired electrons and can be of the following types:

(i) All those atoms and molecules, which have an odd number of electrons, are paramagnetic. Such a system, according to quantum mechanics, cannot have zero total spin; therefore, each atom or molecule has a net magnetic moment, which arises from the electron spin angular momentum. Organic free radicals and gaseous nitric oxide are some materials that exhibit paramagnetism.

(ii) All free atoms and ions with unfilled inner electron shells, and many of these ions, when in solid or in solution, are paramagnetic. Some well-known examples are  $\text{KMnO}_4$ , Na, K,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  ions. Paramagnetism is shown by these substances only in the presence of a magnetic field.

**20.** Distinguish between amorphous and crystalline states of solids. What are the characteristic properties of each type?

**Solution**

<b>Amorphous Solids</b>	<b>Crystalline Solids</b>
Solids that do not have definite geometrical shape.	They have characteristic geometrical shape.
Amorphous solids do not have particular melting point. They melt over a wide range of temperature.	They have sharp melting point
Physical properties of amorphous solids are same in different directions, that is, amorphous solids are isotropic	Physical properties of crystalline solids are different in different directions. This phenomenon is known as anisotropy.
Amorphous solids are unsymmetrical.	When crystalline solids are rotated about an axis, their appearance does not change. This shows that they are symmetrical.
Amorphous solids do not break at fixed cleavage planes.	Crystalline solids cleavage along particular direction at fixed cleavage planes.

**21.** Indicate which type of crystal (ionic, molecular, covalent, metallic) each of the following would form when it solidifies: (a)  $\text{Br}_2$ , (b)  $\text{LiF}$ , (c)  $\text{MgO}$ , (d) Mo, (e) Si, (f)  $\text{PH}_3$ , (g)  $\text{NaOH}$ .

**Answer:**

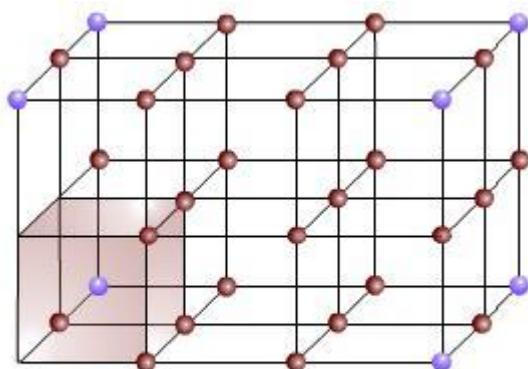
(a) Molecular, (b) ionic, (c) ionic, (d) metallic, (e) covalent, (f) molecular, (g) ionic.

**22.** What relationship is there between a crystal lattice and a unit cell?

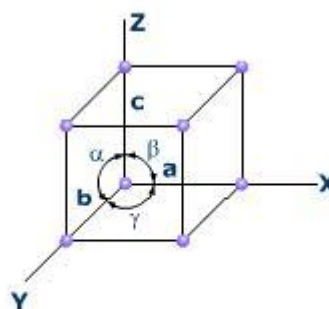
**Solution**

**Crystal lattice:** A regular arrangement of the constituent particles of a crystal in a three-dimensional space is called crystal lattice or space lattice.

**Unit cell:** The smallest three-dimensional portion of a complete space lattice, which when repeated over and over again in different directions produces the complete space lattice. The relation between unit cell and crystal lattice is that the unit cell is part of the lattice as shown in the figure.



Representation of space lattice and unit cell



Representation of dimensions of a unit cell

**23.** How many copper atoms are there within the face-centered cubic unit cell of copper?

**Solution**

The primitive cubic system consists of one lattice point on each corner of the cube. The unit cell, therefore, contains in total one atom  $[(1/8) \times 8]$ . The body-centered cubic system has one atom in the center of the unit cell in addition to the eight corner points. It has a contribution from 2 atoms per cell  $[(1/8) \times 8 + 1]$ . The face-centered cubic has atoms on the faces of the cube of which each unit cube gets exactly one-half contribution, giving a total of 4 atoms per unit cell as follows:

$$\left[ \frac{1}{8} \text{ for each corner} \right] \times 8 \text{ corners} + \left[ \frac{1}{2} \text{ for each face} \right] \times 6 \text{ faces} = 1 + 3 = 4.$$

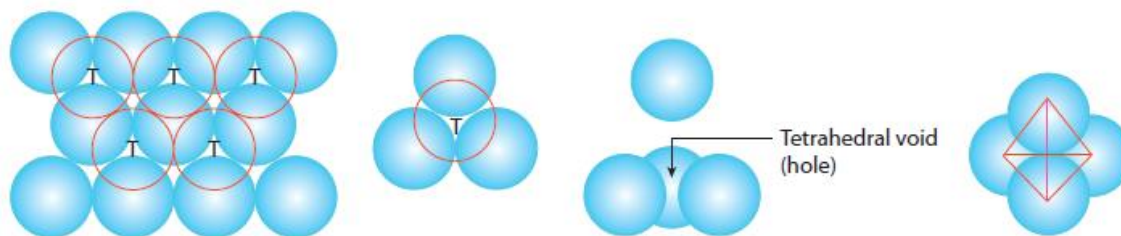
Thus, there are 8 atoms at the corners, 6 atoms in the faces, giving a total of 4 atoms per unit cell.

**24.** What is a tetrahedral void? How many tetrahedral voids can exist per unit cell in a close-packed structure of uniform spheres?

**Solution**

In three-dimensional close packing from two-dimensional hexagonal close packing in which the second layer is placed above the first layer, there is a kind of arrangement in which a sphere of the second layer is above the void of the first layer forming a tetrahedral void. The four spheres touch each other in a manner that tetrahedron is formed when their centers are joined. The space in the center is called a tetrahedral site/hole or void as shown in the figure:





The number of tetrahedral voids per unit cell in case of close-packed structure of uniform spheres is eight.

**25.** What are two ways by which non-stoichiometric defects due to metal deficiency may occur?

**Solution**

Non-stoichiometry implies that either metal or non-metal atoms are present in excess. When non-metal atoms are in excess, two types of defects may arise due to metal deficiency. In the first type of defect, a positive ion is absent from its lattice site and the charge is balanced by adjacent metal (positive) ion having higher oxidation state, for example, FeO, FeS, among others. In the second type of defect, an extra negative ion is present in an interstitial position and the charge balance is maintained by the adjacent metal atom having higher charge.

**26.** In chromium (III) chloride, CrCl<sub>3</sub>, chloride ions have cubic close-packed arrangement and Cr(III) ions are present in the octahedral holes. What fraction of the octahedral holes is occupied? What fraction of the total number of holes is occupied?

**Solution**

In ccp arrangement each chloride ion would have one octahedral void and two tetrahedral voids associated with it.

Number of octahedral voids with 3 chloride ions = 3.

Number of tetrahedral voids with 3 chloride ions =  $3 \times 2 = 6$ .

Total number of voids with 3 chloride ions = 9.

Number of octahedral voids occupied by Cr(III) = 1.

Fraction of octahedral voids occupied =  $1/3$ .

Fraction of total number of voids occupied =  $1/9$ .

**27.** Name the ions that form the close-packed structure (along with the type of packing) and the ions that fill the voids (along with the types of voids) in the compounds: (a) NaCl, (b) ZnS, (c) CaF<sub>2</sub>.

**Solution**

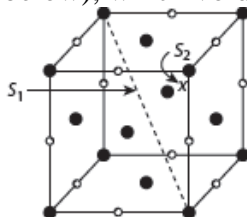
Compound	Ions forming close-packed arrangements	Ions occupying the voids
(a) NaCl	Cl <sup>-</sup> ions (fcc)	Na <sup>+</sup> ions in all octahedral voids
(b) ZnS	S <sup>2-</sup> ions (fcc)	Zn <sup>2+</sup> ions in all alternate tetrahedral voids
(c) CaF <sub>2</sub>	Ca <sup>2+</sup> ions (fcc)	F <sup>-</sup> ions in all tetrahedral voids

28. To which axis is the (1 1 1) plane parallel to?

**Solution**

(1 1 1) requires three axes, that is, X, Y, and Z axes.

29. In the following structure (figure below), which voids do the sites S<sub>1</sub> and S<sub>2</sub> represent?



**Solution**

S<sub>1</sub>: tetrahedral void; S<sub>2</sub>: octahedral void. Tetrahedral void is the empty space left between four spheres and octahedral is the void or the empty space left between six spheres.

30. Which crystal system has no rotation of symmetry?

**Solution**

Triclinic because all the parameters are not equal, that is,  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$ .

**<H2>Numerical Problems**

1. Metallic magnesium has a hexagonal close-packed structure and a density of  $1.74 \text{ g cm}^{-3}$ . Assuming magnesium atoms to be spherical, calculate the radius of magnesium atom. (Atomic mass of Mg = 24.3 u)

**Solution**

Mass of  $1 \text{ cm}^3$  of Mg = volume  $\times$  density =  $1 \times 1.74 = 1.74 \text{ g}$

$$\text{Number of atoms in } 1.74 \text{ g of Mg} = \frac{6.02 \times 10^{23} \times 1.74}{24.3} = 4.31 \times 10^{22} \text{ atoms}$$

Volume occupied by Mg = 74.1 % (for ccp) =  $0.741 \text{ cm}^3$

So,  $4.31 \times 10^{22}$  atoms will have volume =  $0.741 \text{ cm}^3$

$$\text{Volume occupied by 1 atom} = \frac{0.741}{4.31 \times 10^{22}} = 1.72 \times 10^{-23} \text{ cm}^3$$

Let  $r$  be the radius of Mg atom, then

$$\frac{4}{3} \pi r^3 = 1.72 \times 10^{-23} \Rightarrow r^3 = 1.72 \times 10^{-23} \times \frac{3}{4} \times \frac{1}{3.14} \Rightarrow r = (4.108 \times 10^{-24})^{1/3} = 1.6 \times 10^{-8} \text{ cm}$$

2. Iron changes its crystal structure from body-centered to cubic close-packed structure when heated to  $916^\circ\text{C}$ . Calculate the ratio of the density of the bcc crystal to that of ccp crystal, assuming that the metallic radius of the atom does not change.

**Solution**

The total space occupied in bcc = 68%, whereas in ccp it is 74%. It means for the same volume, masses of bcc and ccp are in the ratio 68:74 or, in other words, it means that ratio of the density is also 68:74 = 0.919.

3. Barium crystallizes in a body-centered cubic structure in which the cell edge length is 0.5025 nm. Calculate the shortest distance between neighboring barium atoms in the crystal.

**Solution**

From the geometry of the body-centered cubic structure, we find the shortest distance between barium atoms will occur down the body diagonal where

$$\text{Diagonal} = \sqrt{3}a = 4r_{\text{Ba}}$$

$$r_{\text{Ba}} = \frac{\sqrt{3}}{4} \times 0.5025 \times 10^{-7} \text{ cm} = 2.176 \times 10^{-8} \text{ cm}$$

The shortest distance between barium atoms will be  $2r_{\text{Ba}}$ . The Ba–Ba distance =  $4.352 \times 10^{-8}$  cm.

4. Chromium metal ( $\rho = 7.20 \text{ g cm}^{-3}$ ) crystallizes in a body-centered cubic unit cell. Calculate the volume of the unit cell and the radius of a chromium atom.

**Solution**

$$V_{\text{cell}} = 2 \frac{\left( \frac{51.996 \text{ g Cr}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.023 \times 10^{23}} \right)}{7.20 \text{ g cm}^{-3}}$$

Also,  $V_{\text{cell}} = a^3 = 2.40 \times 10^{-23} \text{ cm}^3$ . Therefore,

$$a = \sqrt[3]{2.40 \times 10^{-23} \text{ cm}^3} = 2.88 \times 10^{-8} \text{ cm}$$

The length of the body diagonal ( $d_{\text{body}}$ ) is

$$d_{\text{body}}^2 = (\sqrt{2}a)^2 + a^2 = 3a^2$$

$$d_{\text{body}} = \sqrt{3}a = \sqrt{3} \times (2.88 \times 10^{-8} \text{ cm}) = 5.00 \times 10^{-8} \text{ cm}$$

Now,  $d_{\text{body}} = 4 r_{\text{Cr}}$ . Therefore,

$$r_{\text{Cr}} = \frac{5.00 \times 10^{-8} \text{ cm}}{4} = 1.25 \times 10^{-8} \text{ cm}$$

5. Calcium metal crystallizes in a face-centered cubic lattice with edge length of 0.556 nm. Calculate the density of the metal if it contains (a) 0.5% Frenkel defects and (b) 0.2% Schottky defects.

**Solution**

(a) For fcc,  $Z = 4$ , and given that  $M = 40 \text{ g mol}^{-1}$  (for Ca) and  $a = 0.556 \times 10^{-7} \text{ cm}$ . Therefore, substituting all these values, we get

$$\rho = \frac{Z \times M}{a^3 \times \text{Number of atoms}} = \frac{4 \times 40}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}} = \frac{160}{1.035 \times 10^{-21} \times 10^{23}} = 154.58 \times 10^{-2} = 1.5458 \text{ g cm}^{-3}$$

As the density of the crystal is not effected when Frenkel defect is present, so the density remains the same.

(b) As there are 0.2% Schottky defects present in the crystal, the density of the crystal decreases

$$\text{The new number of atoms per unit cell becomes} = 4 - \frac{0.2}{100} \times 4 = 3.992. \text{ So, the density is}$$

$$\rho = \frac{3.992 \times 40}{(0.556 \times 10^{-7})^3} \times 6.023 \times 10^{23} = 1.5427 \text{ g cm}^{-3}$$

6. Determine whether calcium crystallizes in a primitive cubic, a body-centered cubic, or a face-centered cubic unit cell, assuming that the cell edge length is 0.5582 nm and the density of the metal is 1.55 g cm<sup>-3</sup>.

**Solution**

It is given that density of calcium metal,  $\rho = 1.55 \text{ g cm}^{-3}$ ; molar mass,  $M = 40.078 \text{ g mol}^{-1}$ ; edge length,  $a = 0.5582 \text{ nm} = 5.582 \times 10^{-8} \text{ cm}$ . Also, Avogadro's number,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ . Applying the density relation, we get

$$\rho = \frac{Z M}{a^3 N_A} \Rightarrow 1.55 = \frac{Z \times 40.078}{(5.528 \times 10^{-8})^3 \times (6.023 \times 10^{23})}$$

Therefore,

$$Z = \frac{1.55 \times (5.528 \times 10^{-8})^3 \times (6.023 \times 10^{23})}{40.078} = 3.9 \approx 4$$

Hence, the calcium crystallizes in face-centered cubic unit cell type.

7. A compound with fcc crystal structure has a density of  $2.163 \times 10^3 \text{ kg m}^{-3}$ . Calculate the edge length of its unit cell.

**Solution**

For an element, the density of a crystal is given by

$$\rho = \frac{Z \times M}{a^3 \times N_A} \quad (1)$$

where  $Z$  is the number of particles present per unit cell;  $M$  is the atomic mass of the element;  $a$  is the edge length of the unit cell;  $N_A$  is the Avogadro number;  $\rho$  is density of the crystal given as  $2.163 \times 10^3 \text{ kg m}^{-3}$ . Since density is usually expressed in  $\text{g cm}^{-3}$ , so

$$\rho = \frac{2.163 \times 10^3 \times 10^3}{(1 \times 10^2)^3} = \frac{2.163 \times 10^6}{10^6} = 2.163 \text{ g cm}^{-3}$$

For fcc crystal structure,  $Z = 4$  and we know that  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$  and  $M = 58.2 \text{ g mol}^{-1}$ . Rearranging Eq. (1) in terms of  $a$ , we get

$$\begin{aligned} a^3 &= \frac{z \times M}{\rho \times N_A} = \frac{4 \times 58.2 \text{ g mol}^{-1}}{2.163 \times 6.02 \times 10^{23} \text{ mol}^{-1} \text{ g cm}^{-3}} \\ &= \frac{232.8 \text{ g mol}^{-1}}{13.02 \times 10^{23} \text{ g cm}^{-3} \text{ mol}^{-1}} = 17.880 \times 10^{-23} \text{ cm}^3 \\ &= 178.8 \times 10^{-24} \text{ cm}^3 \end{aligned}$$

So, the edge length of the unit cell is  $a = (178.8)^{1/3} \times 10^{-8} = 5.634 \times 10^{-8} \text{ cm}$  or 563.4 pm.

8. By X-ray diffraction methods, the unit length of NaCl is observed to be 0.5627 nm. The density of NaCl is found to be  $2.164 \text{ g cm}^{-3}$ . What type of defect exists in the crystal? Calculate the percentage of Na<sup>+</sup> and Cl<sup>-</sup> ions missing.

**Solution**

For NaCl (fcc structure),  $Z = 4$ ,  $M$  (molecular mass of NaCl) =  $58.5 \text{ g mol}^{-1}$  and  $a$  (edge length) =  $0.5627 \times 10^{-7} \text{ cm}$ . Therefore, density is calculated as

$$\rho = \frac{Z \times M}{a^3 \times \text{Number of atoms}} = \frac{4 \times 58.5}{(0.5627 \times 10^{-7})^3 \times 6.022 \times 10^{23}} = 2.1809 \text{ g cm}^{-3}$$

As the observed density ( $2.164 \text{ g cm}^{-3}$ ) is less than the calculated density, this means that some  $\text{Na}^+$  and  $\text{Cl}^-$  ions are missing from their lattice sites (Schottky defect).

$$Z = \frac{a^3 \times \rho \times \text{Number of atoms}}{M} = \frac{(0.5627 \times 10^{-7})^3 \times 2.164 \times 6.023 \times 10^{23}}{58.5} = 3.968$$

So, the number of formula units missing per unit cell =  $4 - 3.968 = 0.032$

$$\text{Percentage of missing } \text{Na}^+ \text{ and } \text{Cl}^- = \frac{0.032}{4} \times 100 = 0.8\%$$

**9.** The atomic radius of nickel is 124 pm. Nickel crystallizes in face-centered cubic lattice. What is the edge length of the unit cell expressed in pm and Å?

**Solution**

The volume of the unit cell is related to density and molecular mass by relation

$$V_{\text{Cell}} = \frac{Z \times M}{\rho N_A}$$

where  $Z$  is the formula units per unit cell,  $M$  the molar mass per formula unit,  $\rho$  the density in  $\text{g cm}^{-3}$ , and  $N_A$  the Avogadro constant. If nickel is crystallized in a face-centered cubic structure, the six atoms on the faces of the unit cell would contribute three net nickel atoms, for a total of four atoms per unit cell.

In a face-centered cubic structure:

$$\left( 8 \text{ corners} \times \frac{1}{8} \right) + \left( 6 \text{ faces} \times \frac{1}{2} \right) = 1 + 3 = 4 \text{ atoms}$$

Thus,  $Z = 4$ . For nickel,  $M = 58.69 \text{ g mol}^{-1}$ . As the cell is a cube, the lattice parameter

$$a = \sqrt[3]{V_{\text{cell}}} = \sqrt[3]{\frac{Z \times M}{\rho N_A}} = \sqrt[3]{\frac{4 \times 58.69}{8.92 \times 6.023 \times 10^{23}}} = 3.52 \times 10^{-8} \text{ cm} = 352 \text{ pm} = 3.54 \text{ Å}$$

Therefore, the unit cell edge length is 352 pm or 3.52 Å.

**10.** For a cubic crystal, the face diagonal is 3.50 Å. Calculate the face length.

**Solution**

Face diagonal =  $(a^2 + a^2)^{1/2} = (2)^{1/2} a$ . Therefore,

$$\text{Face length } (a) = \frac{\text{Face diagonal}}{(2)^{1/2}} = \frac{3.50}{1.414} = 2.475 \text{ Å}$$

**11.** Lithium borohydride,  $\text{LiBH}_4$ , crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are:  $a = 6.81 \text{ Å}$ ,  $b = 4.43 \text{ Å}$ , and  $c = 7.17 \text{ Å}$ . Calculate the density of the crystal. Take atomic mass of Li = 7 u, B = 11 u, and H = 1 u.

**Solution**

From the atomic masses, the molar mass ( $M$ ) for  $\text{LiBH}_4 = 22 \text{ g mol}^{-1}$ .

$$\text{Now, mass of the unit cell} = \frac{4 \times 22}{6.02 \times 10^{23}} = 14.62 \times 10^{-23} \text{ g}$$

$$\text{Volume of unit cell} = a \times b \times c = 6.81 \times 10^{-8} \times 4.43 \times 10^{-8} \times 7.17 \times 10^{-8} = 21.63 \times 10^{-23} \text{ cm}^3$$

$$\text{Therefore, Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{14.62 \times 10^{-23}}{21.63 \times 10^{-23}} = 0.676 \text{ g cm}^{-3}$$

12. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? [IIT-JEE 1997]

**Solution**

NaCl has 4 formula units, that is, number of atoms per unit cell = 4. This indicates fcc arrangement for which

$$r = \frac{a}{2\sqrt{2}} = \frac{0.564}{2 \times 1.414} = 1.99 \times 10^{-8} \text{ cm}$$

and density is

$$\rho = \frac{M_A \times Z}{N_A a^3} = \frac{58.5 \times 4}{6.023 \times 10^{23} \times 0.564 \times 10^{-7}} = 2.16 \text{ g cm}^{-3}$$

13. Sodium chloride has face-centered cubic (fcc) structure. The density of NaCl is 2.163 g cm<sup>-3</sup>. Calculate

(a) edge length of cubic cell;

(b) distance between two adjacent atoms.

Given that mass weight of sodium = 23 and mass weight of chlorine = 35.5.

**Solution**

(a) Density ( $\rho$ ) of the unit cell of a cubic crystal is given by:

$$\rho = \frac{zM}{a^3 N_A}$$

where  $n$  = number of atoms per unit cell,  $M$  = molar mass,  $N_A$  = Avogadro's constant, and  $a$  = edge length of unit cell. Given that  $n = 4$  (for fcc),  $M = 58.5 \text{ g mol}^{-1}$ ,  $N_A = 6.023 \times 10^{23}$ ,  $\rho = 2.163 \text{ g cm}^{-3}$ . Now, edge length is

$$a^3 = \frac{zM}{\rho N_A}$$

Substituting values, we get

$$a = \left( \frac{zM}{\rho N_A} \right)^{1/3} = \left( \frac{4 \times 58.5 \text{ g mol}^{-1}}{2.163 \text{ g cm}^{-3} \times 6.023 \times 10^{23} \text{ mol}^{-1}} \right)^{1/3} = (17.972 \times 10^{-23})^{1/3}$$

$$= (179.72 \times 10^{-24})^{1/3} = 5.667 \times 10^{-8} \text{ cm}$$

(b) For fcc structure, distance between two adjacent atoms is given by

$$r^+ + r^- = 2r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 5.667}{4} \times 10^{-8} \text{ cm} = 2.003 \times 10^{-8} \text{ cm}$$

or

$$r = \frac{2.003}{2} \times 10^{-8} \text{ cm} = 1.001 \times 10^{-8} \text{ cm}$$

14. The distance between layers of NaCl crystal is 282 pm. X-rays are diffracted from these layers at an angle of 23.0° with first-order diffraction. Calculate the wavelength of X-rays in nm.

**Solution**

According to Bragg's equation,  $n\lambda = 2d \sin \theta$ . Given that  $n = 1$ ,  $d = 282 \text{ pm}$ , and  $\theta = 23^\circ$ . Therefore,

$$1 \times \lambda = 2 \times 282 \times 0.846$$

or

$$\lambda = 477.14 \text{ pm} = 0.477 \text{ nm}$$

**15.** CuCl has face-centered cubic structure. Its density is  $3.4 \text{ g cm}^{-3}$ . What is the length of unit cell?

**Solution**

Molecular mass of CuCl = 99,  $n = 4$  for face-centered cubic cell

$$\text{Density} = \frac{n \times \text{Molecular weight}}{V \times \text{Avogadro's number}} = \frac{4 \times 99}{a^3 \times 6.023 \times 10^{23}}$$

or 
$$3.4 = \frac{4 \times 99}{a^3 \times 6.023 \times 10^{23}} \text{ or } a = 5.783 \times 10^{-8} \text{ cm} = 5.783 \text{ \AA}$$

**16.** 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?

**Solution**

The number of close-packed particles in 0.5 mol =  $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

Therefore, number of octahedral voids =  $3.011 \times 10^{23}$

And, the number of tetrahedral voids =  $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Therefore, total number of voids =  $3.011 \times 10^{23} + 6.022 \times 10^{23} = 9.033 \times 10^{23}$ .

**17.** Caesium chloride forms simple cubic lattice in which  $\text{Cs}^+$  ions are the corners and  $\text{Cl}^-$  ion is in the center. The cation-anion contact occurs along the body diagonal of the unit cell. (The body diagonal starts at one corner and then runs through the center of the cell to the opposite corner.) The length of the edge of the unit cell is 412.3 pm. The  $\text{Cl}^-$  ion has a radius of 181 pm. Calculate the radius of  $\text{Cs}^+$  ion.

**Solution**

According to the Pythagorean theorem,

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

for a right triangle. First, we need to find the length of a diagonal on a face of the unit cell. Since  $a = b$  here, we may rewrite this as

$$2l^2 = c^2$$

where  $l$  = length of the edge of the unit cell and  $c$  = the diagonal length. Using the given 412.3 pm as the length of the edge,  $c = 583.1$  pm. The diagonal length inside the cell from corner to opposite corner may now be found by the same theorem:

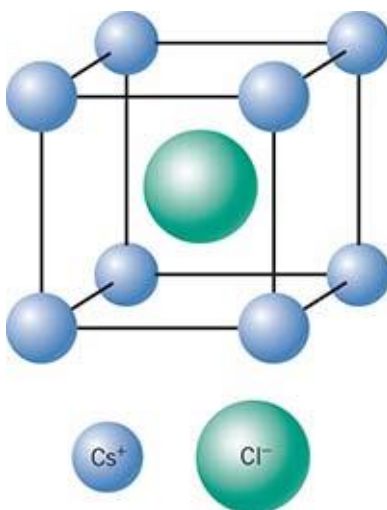
$$\begin{aligned} a^2 + b^2 &= c^2 \\ (412.3)^2 + (412.3)^2 &= c^2 \\ c &= 714.1 \text{ pm} \end{aligned}$$

This diagonal length inside the cell from corner to opposite corner is due to one  $\text{Cs}^+$  ion and one  $\text{Cl}^-$  ion (see figure). Therefore,

$$2r_{\text{Cs}^+} + 2r_{\text{Cl}^-} = 714.1 \text{ pm}$$

$$2r_{\text{Cs}^+} + 2(181 \text{ pm}) = 714.1 \text{ pm}$$

$$2r_{\text{Cs}^+} = 352 \text{ pm and } r_{\text{Cs}^+} = 176 \text{ pm}$$



### Additional Objective Questions

#### Single Correct Choice Type

1. Fraction of total volume occupied by atoms in a simple cube is

- (A)  $\frac{\pi}{2}$                       (B)  $\frac{\sqrt{3}\pi}{8}$                       (C)  $\frac{\sqrt{2}\pi}{6}$                       (D)  $\frac{\pi}{6}$

#### Solution

(D) In a simple cubic system, number of atoms  $a = 2r$ . Therefore,

$$\text{Packing fraction} = \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

2. Which of the following is an amorphous solid?

- (A) Rubber                      (B) Plastic                      (C) Glass                      (D) All of these

#### Solution

(D) Amorphous solids neither have ordered arrangement (i.e., no definite shape) nor have sharp melting point, but when heated, they become soft until they assume the properties usually related to liquid. Therefore, they are regarded as super cooled liquids.

3. The unit cell of a metallic element of atomic mass 108 and density  $10.5 \text{ g cm}^{-3}$  is a cube with edge length of 409 pm. The structure of the crystal lattice is

- (A) fcc.                      (B) bcc.                      (C) hcp.                      (D) none of these.

#### Solution

(A)  $\rho = \frac{Z \times M}{N \times a^3}$ . Here,  $M = 108$ ,  $N_A = 6.023 \times 10^{23}$ ,  $a = 409 \text{ pm} = 4.09 \times 10^{-8} \text{ cm}$ ,  $\rho = 10.5 \text{ g cm}^{-3}$

Substituting the values, we get  $z = 4 =$  Number of atoms per unit cell. So, the structure of the crystal lattice is fcc.

4. Which of the following statements is correct?

- (I) The coordination number of cation occupying a tetrahedral hole is 4.  
 (II) The coordination number of cation occupying an octahedral hole is 6.  
 (III) In Schottky defects, density of the lattice decreases.



- (A) I, II                                      (B) II, III                                      (C) I, II, III                                      (D) I, III

**Solution**

(C) Since tetrahedral holes are surrounded by 4 nearest neighbors. So, the coordination number (CN) of cation occupying tetrahedral hole is 4. Since octahedral hole is surrounded by six nearest neighbors. Therefore, CN of cation occupying octahedral is 6. In Schottky a pair of anion and cation leaves the lattice. Thus, the density of lattice decreases.

5. A compound formed by elements A and B crystallizes in a cubic structure where A atoms are at the corners of a cube and B atoms are at the face center. The formula of the compound is

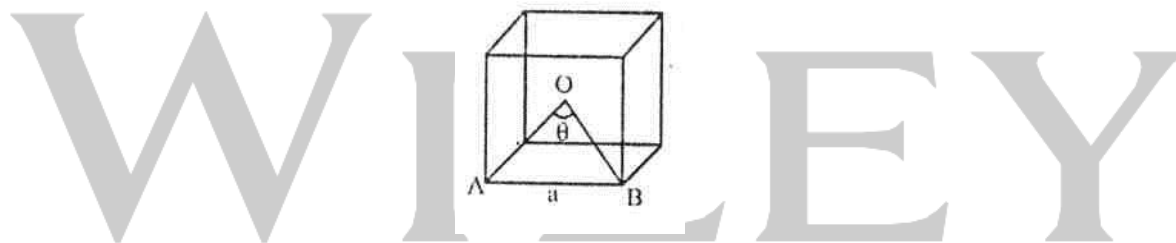
- (a) AB<sub>3</sub>                                      (b) AB<sub>2</sub>                                      (c) AB<sub>4</sub>                                      (d) None of these

**Solution**

(A) Number of atoms of 'A' in a unit cell =  $\frac{1}{8} \times 8 = 1$ ; number atoms of 'B' in a unit cell =

$$\frac{1}{2} \times 6 = 3 \text{ (face center)}$$

Formula of the compound = AB<sub>3</sub>



6. Which arrangement of electrons leads to anti-ferromagnetism?

- (A) ↑↑↑                                      (B) ↑↓↑↓                                      (C) Both A and B                                      (D) None of these

**Solution**

(B) Anti-ferromagnetic substances possess complementary dipoles alignment, giving net dipole moment equal to zero.

7. CsBr has bcc structure with edge length 4.3 Å. The shortest interionic distance in between Cs<sup>+</sup> and Br is

- (A) 3.72 Å                                      (B) 1.86 Å                                      (C) 7.44 Å                                      (D) 4.3 Å                                      (IIT-JEE 1995)

**Solution**

$$(A) d = \left(\frac{3^{1/2}}{2}\right)a = \left(\frac{3^{1/2}}{2}\right) \times 4.3 = 3.7238$$

8. When NaCl is doped with MgCl<sub>2</sub>, the nature of defect produced is

- (A) interstitial.                                      (B) Frenkel.                                      (C) Schottky.                                      (D) none of these.

**Solution**

(C) It is Schottky defect.

9. In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions. One-fifth of tetrahedral voids are occupied by divalent ( $X^{2+}$ ) ions, while one-half of the octahedral voids are occupied by trivalent ions ( $Y^{3+}$ ), then the formula of the oxide is  
 (A)  $XY_2O_4$  (B)  $X_2YO_4$  (C)  $X_4Y_5O_{10}$  (D)  $X_5Y_4O_{10}$

**Solution**

(C) Contribution of X =  $1/5(2N)$   
 Contribution of Y =  $(1/2)(N)$   
 Contribution of O = N  
 X:Y:O

$$\frac{2}{5} : \frac{1}{2} : 1$$

Therefore, the formula of the oxide is  $X_4Y_5O_{10}$

10. The limiting radius ratio of the complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is  
 (A) 0.225 – 0.414 (B) 0.414 – 0.732 (C) 0.155 – 0.225 (D) None of these

**Solution**

(B) The complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar. So, it has limiting radius ratio as octahedral structure, that is, 0.414 – 0.732.

11. How many tetrahedral holes are occupied in diamond?  
 (A) 25% (B) 50% (C) 75% (D) 100%

**Solution**

(B) It is a fact.

12. A substance  $A_xB_y$  crystallizes in a face-centered cubic lattice in which atoms A occupy each corner of the cube and atoms B occupy the centers of each face of the cube. Identify the corner composition of the substance  $A_xB_y$ .  
 (A)  $AB_3$  (B)  $A_4B_3$  (C)  $A_3B$  (D) Cannot be determined.

**Solution**

(A) Number of A atoms =  $8/8 = 1$   
 Number of B atoms =  $6/2 = 3$   
 Therefore, the formula is  $AB_3$

13. A metal crystallizes in two cubic phases – face-centered cubic (fcc) and body-centered cubic (bcc) – whose unit cell length are 3.5 Å and 3.0 Å, respectively. Calculate the ratio of density of fcc and bcc.  
 (A) 2.123 (B) 1.259 (C) 5.124 (D) 3.134

**Solution**

(B)  $\rho = \frac{n \times M_m}{N_A \times a^3}$

For fcc-centered cubic cell  $n = 4$ ,  $a = 3.5 \text{ \AA}$

$$\rho_{\text{fcc}} = \frac{4 \times M_m}{N_A \times (3.5)^3} \quad (1)$$

For bcc lattice  
 $N = 2$ ,  $a = 3.0 \text{ \AA}$

$$\rho_{\text{bcc}} = \frac{2 \times M_m}{N_A \times (3.0)^3}$$

From Eqs. (1) and (2), we get

$$\frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{4}{2} \times \frac{3^3}{(3.5)^3} = \frac{4 \times 3 \times 3 \times 3}{2 \times 3.5 \times 3.5 \times 3.5} = 1.259$$

**14.** Xenon crystallizes in face-centered cubic lattice and edge of the unit cell is 620 pm, then the radius of xenon atom is

- (A) 219.20 pm      (B) 438.5 pm      (C) 265.5 pm      (D) 536.94 pm

**Solution**

(A) For the lattice

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

where  $a = 620 \text{ pm}$ , as face diagonal atoms touches each other.

$$r = \frac{1}{2\sqrt{2}} \times a = \frac{1}{2\sqrt{2}} \times 620 \text{ pm} = 219.20 \text{ pm}$$

**15.** In a face-centered cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?

- (A) 0.543      (B) 0.732      (C) 0.414      (D) 0.637

**Solution**

(A) Consider one tetrahedral void. If the side length of the tetrahedron is  $f$  and if  $d$  is the distance from the center to the corner, then

$$l^2 = 2d^2 - 2d^2 \cos \theta = 2d^2 \left(1 + \frac{1}{3}\right) = \frac{4}{3} \times 2d^2$$

Therefore,

$$l = \sqrt{\frac{8}{3}}$$

But if  $a$  is the side length of the unit cell

$$l = \frac{a}{\sqrt{2}} \text{ and } d = r_1 + r_2 \text{ where } r_1 \text{ is the radius of the corner}$$

atom and  $r_2$  the radius of the tetrahedral void. Therefore,

$$\sqrt{\frac{8}{3}}(r_1 + r_2) = \frac{a}{\sqrt{2}} \Rightarrow r_1 + r_2 = \frac{a}{\sqrt{2}} \times \frac{\sqrt{3}}{\sqrt{8}} = \frac{\sqrt{3}a}{4}$$

But  $l = 2r_1 \Rightarrow r_1 = \frac{l}{2} = \frac{a}{2\sqrt{2}}$ , or

$$r_2 = \frac{\sqrt{3}a}{4} - \frac{\sqrt{2}a}{4} = \frac{a}{4}(\sqrt{3} - \sqrt{2})$$

For the octahedral void, if the radius of the void is  $r_3$ , then  $2(r_1 + r_3) = a$

$$r_1 + r_3 = \frac{a}{2} \Rightarrow r_3 = \frac{a}{2} - r_1$$

$$r_3 = \frac{a}{2} - \frac{a}{2\sqrt{2}} = \frac{2a}{4} - \frac{\sqrt{2}a}{4} = \frac{(2-\sqrt{2})a}{4}$$

Therefore, ratio of the sizes of tetrahedral to octahedral voids is

$$\frac{r_2}{r_3} = \frac{\frac{a}{4}(\sqrt{3}-\sqrt{2})}{\frac{a}{4}(2-\sqrt{2})} = \frac{1.732-1.414}{2-1.414} = \frac{0.318}{0.586} = 0.543$$

16. Frenkel defect is noticed in

- (A) AgBr      (B) ZnS      (C) AgI      (D) all of these.

**Solution**

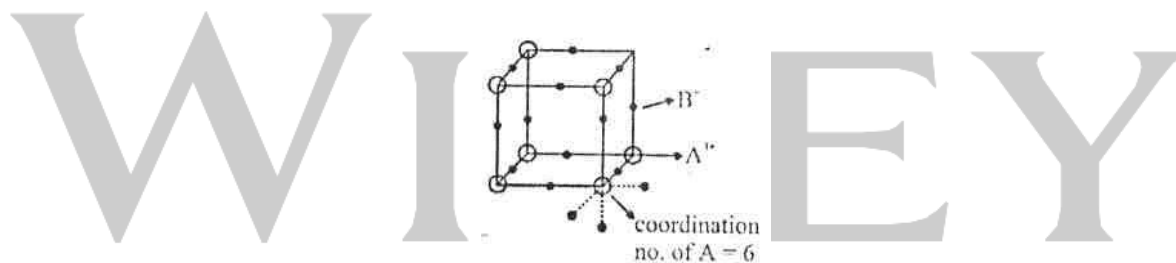
(D) Because the difference in the size of cation and anion is large.

17. A crystal formula  $AB_3$  has A ions at the cube corners and B ions at the edge centers. The coordination numbers of A and B are, respectively,

- (A) 6 and 6      (B) 2 and 6      (C) 6 and 2      (D) 8 and 8

**Solution**

(C)  $\frac{\text{Coordination number of cation}}{\text{Coordination number of anion}} = \frac{\text{Charge of cation}}{\text{Charge of anion}} = \frac{3}{1} = 3$



Now coordination number of A is 6 as shown, so of B is 2.

18. A compound of CuCl has face-centered cubic structure. Its density is  $3.4 \text{ cm}^{-3}$ . The length of unit cell is

- (A)  $5.783 \text{ \AA}$       (B)  $6.789 \text{ \AA}$       (C)  $7.783 \text{ \AA}$       (D)  $8.783 \text{ \AA}$

**Solution**

(A) Molecular mass of CuCl =  $99 \text{ g mol}^{-1}$  and  $z = 4$  for face-centered cubic cell, so

$$\text{Density} = \frac{n \times \text{Molecular weight}}{V \times \text{Avogadro's number}} = \frac{4 \times 99}{a^3 \times 6.023 \times 10^{23}}$$

or 
$$3.4 = \frac{4 \times 99}{a^3 \times 6.023 \times 10^{23}}$$

Solving, we get  $a = 5.783 \times 10^{-8} \text{ cm} = 5.783 \text{ \AA}$ .

19. If the ratio of coordination numbers P to that of Q be  $y:z$ , then the formula of the solid is

- (a)  $P_yQ_z$       (b)  $P_zO_y$       (c)  $P_{1/y}Q_{1/z}$       (d) none of these.

**Solution**

(B) Since the ratio of the coordination number P to that of Q is  $y : z$   
That is, P is surrounded by  $y$  atoms of Q while Q is surrounded by  $z$  atoms of P, that is, number of atoms of P is  $z$  and number of atoms of Q is  $y$ . So, the formula is  $P_zQ_y$ .

20. The coordination number of a metal crystallizing in a hexagonal close-packed structure is  
(A) 12 (B) 4 (C) 8 (D) 6 (IIT-JEE 1999)

**Solution**

(A) Three spheres above, three below, and total six in that, makes it 12.

21. The number of tetrahedral and octahedral voids in hexagonal primitive unit cell are  
(A) 8, 4 (B) 2, 1 (C) 12, 6 (D) 6, 12

**Solution**

(C) Number of atoms = 6

Number of octahedral voids = Number of atoms = 6

Number of tetrahedral voids = 2. Number of atoms = 12

22. In the fluorite structure ( $\text{CaF}_2$ ),

(A)  $\text{Ca}^{2+}$  ions are ccp and  $\text{F}^-$  ions are present in all the tetrahedral voids.

(B)  $\text{Ca}^{2+}$  ions are ccp and  $\text{F}^-$  ions are present in all the octahedral voids.

(C)  $\text{Ca}^{2+}$  ions are ccp and  $\text{F}^-$  ions are present in all the octahedral voids and half of ions are present in tetrahedral voids.

(D) None of these.

**Solution**

(A)  $\text{Ca}^{2+}$  ions are ccp and F ions are present in the tetrahedral voids. So, the number of  $\text{Ca}^{2+}$  ions is 4 and number of  $\text{F}^{2-}$  ions is 8.

23. The lattice parameters are  $a = 5.62 \text{ \AA}$ ,  $b = 7.41 \text{ \AA}$ ,  $c = 9.48 \text{ \AA}$ . The three coordinates are mutually perpendicular to each other. The crystal is

(A) tetragonal. (B) orthorhombic. (C) monoclinic. (D) trigonal.

**Solution**

(B) For orthorhombic crystal,  $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ .

24. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

(A)  $\text{AB}_2$  (B)  $\text{A}_2\text{B}$  (C)  $\text{A}_4\text{B}_3$  (D)  $\text{A}_3\text{B}_4$  [IIT-JEE 2001]

**Solution**

(D) Number of A atoms =  $8/8 + 4/2 = 3$

Number of B atoms =  $12/4 + 1 = 4$

Therefore, the formula is  $\text{A}_3\text{B}_4$ .

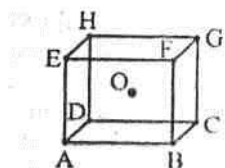
25. Ice belongs to which of the following structures?

(A) Cubic (B) Hexagonal (C) Orthorhombic (D) Tetragonal

**Solution**

(D)

26. A body-centered cubic arrangement is shown. O is the body center; A, B, C, D, ..., H are the corners. What is the magnitude of the angle AOB?



- (A)  $120^\circ$                       (B)  $109^\circ 28'$                       (C)  $104^\circ 31'$                       (D)  $70^\circ 32'$

**Solution**

(D) Let  $AO = OB = \frac{\sqrt{3}}{2}a = l$ , therefore,

$$a^2 = 2l^2 - 2l^2 \cos \theta = 2l^2(1 - \cos \theta)$$

Therefore,

$$a^2 = \frac{3}{2}a^2(1 - \cos \theta)$$

Hence,

$$1 - \cos \theta = \frac{2}{3} \Rightarrow \cos \theta = \frac{1}{3} \Rightarrow \theta = 70^\circ 32'$$

27. A binary solid ( $A^+B^-$ ) has a zinc blende structure with  $B^-$  ions, constituting the lattice and  $A^+$  ions occupying 25% tetrahedral holes. The formula of solid is

- (A) AB                      (B)  $A_2B$                       (C)  $AB_2$                       (D)  $AB_4$

**Solution**

(C) Suppose number of  $B^-$  ions constituting the lattice = 100

Number of tetrahedral sites = 200

As 25% are occupied by  $A^+$  ions, their number = 50

Therefore, Ratio of  $A^+ : B^- = 50 : 100 = 1 : 2$ .

That is, the formula is  $AB_2$ .

28. Iron crystallizes in a body-centered cubic structure. The radius of Fe atom (if edge length of unit cell is 286 pm) is

- (A) 120.9 pm                      (B) 123.8 pm                      (C) 23.8 pm                      (D) 223.8 pm

**Solution**

(B) Edge length,  $a = 286$  pm

For bcc, radius of atom,  $r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 286 = \frac{1.732 \times 286}{4} = 123.8$  pm (body diagonal)

29. Gold crystallizes in the face-centered lattice. The number of unit cells in 1 g of gold (atomic mass = 197 u) will be

- (A)  $6.02 \times 10^{23}$                       (B)  $7.64 \times 10^{20}$                       (C)  $3.82 \times 10^{20}$                       (D)  $15.28 \times 10^{20}$

**Solution**

(B) 1 mol of gold =  $197 \text{ g} \times 6.02 \times 10^{23}$

Therefore,  $1 \text{ g gold} = \frac{6.02 \times 10^{23}}{197} \text{ atoms}$

As fcc contains 4 atoms per unit cell, the number of unit cells in 1 g gold will be

$$\frac{6.02 \times 10^{23}}{197 \times 4} = 7.64 \times 10^{20}$$

**30.** Potassium is crystallized in a body-centered cubic lattice. What is the approximate number of unit cells in 4.0 g of potassium? (Atomic mass of potassium = 39 u.)

- (A)  $3.09 \times 10^{22}$       (B)  $2.09 \times 10^{21}$       (C)  $4.10 \times 10^{21}$       (D)  $3.09 \times 10^{20}$

**Solution**

(A) There will be eight atoms at corners of the cube and one atom at the body center.

Hence,  $\text{Number of atoms per unit cell} = \left( 8 \times \frac{1}{8} \right) + 1 = 2$

$$\text{Number of atoms in 4.0 g of potassium} = \frac{4}{39} \times 6.023 \times 10^{23}$$

$$\text{Number of unit cells in 4.0 g of potassium} = \frac{4}{39} \times \frac{6.023 \times 10^{23}}{2} = 3.09 \times 10^{22}$$

**31.** In a crystal, both ions are missing from normal sites in equal number. This is an example of

- (A) F-centers.      (B) interstitial defect.      (C) Frenkel defect.      (D) Schottky defect.

**Solution**

(D) It results in decrease in density.

**32.** When transition metals form interstitial compounds, the non-metals (H, B, C, N) are accommodated in

- (A) voids or holes in cubic in cubic-packed structure.      (B) tetrahedral voids.  
(C) octahedral voids.      (D) all of these.

**Solution**

(D)

**33.** Among the following types of voids, which one is the largest void?

- (A) Triangular system      (B) Tetragonal system      (C) Monoclinic system      (D) Octahedral system

**Solution**

(D) The vacant spaces between the spheres in closed-packed structure is called void. The voids are of two types: tetrahedral voids and octahedral voids. Also radius of tetrahedral voids and octahedral voids are  $r_{\text{Void}} = 0.225 \times r_{\text{sphere}}$  and  $r_{\text{Void}} = 0.411 \times r_{\text{sphere}}$ , respectively. Thus, octahedral void is larger than tetrahedral void.

34. The anions A form hexagonal closest packing and atoms C occupy only 2/3 of octahedral voids in it; then the general formula of the compound is

- (A) CA (B) A<sub>2</sub> (C) C<sub>2</sub>A<sub>3</sub> (D) C<sub>3</sub>A<sub>2</sub>

**Solution**

(C) Hexagonal close packing contains 6 atoms per unit cell and hence the number of octahedral voids per unit cell is 6. Hence, number of A atoms per unit cell = 6

and number of C atoms per unit cell =  $6 \times \frac{2}{3} = 4$ .

The formula of ionic compound is given as simplest formula and hence formula is C<sub>2</sub>A<sub>3</sub>.

35. A metallic element exists as cubic lattice. Each edge of the unit cell is 241 Å. The density of the metal is 7.20 g cm<sup>-3</sup>. How many unit cell will be present in 100 g of the metal?

- (A)  $6.85 \times 10^2$  (B)  $5.82 \times 10^{23}$  (C)  $4.37 \times 10^5$  (D)  $2.12 \times 10^6$

**Solution**

(B) The volume of the unit cell =  $(2.88 \text{Å})^3 = 23.9 \times 10^{-24} \text{ cm}^3$

The volume of 100 g of the metal =  $\frac{m}{\rho} = \frac{100}{7.20} = 13.9 \text{ cm}^3$

Number of unit cells in this volume =  $\frac{13.9 \text{ cm}^3}{32.9 \times 10^{-24}} = 5.82 \times 10^{23}$

36. The most efficient packing of similar spheres is obtained in

- (A) the simple cubic system and the body-centered cubic system.  
(B) the simple cubic system and the hexagonal close-packed system.  
(C) the face-centered cubic system and the hexagonal close-packed system.  
(D) the body-centered cubic system and the face-centered cubic system.

**Solution**

(C) The hexagonal close packing and the face-centered cubic system have the closest packing as their packing efficiency is 74 %.

37. Bragg's equation is

- (A)  $n\lambda = 2d \sin \theta$  (B)  $n\lambda = 2d \sin \theta$  (C)  $2n\lambda = d \sin \theta$  (D)  $\lambda = (2d/n) \sin \theta$

**Solution**

(B) Bragg's equation is  $\lambda = 2d \sin \theta$

38. A solid PQ has rock salt type structure in which Q atoms are at the corners of the unit cell. If the body-centered atoms in all the unit cells are missing, the resulting stoichiometry will be

- (A) PQ (B) PQ<sub>2</sub> (C) P<sub>3</sub>Q<sub>4</sub> (D) P<sub>4</sub>Q<sub>3</sub>

**Solution**

(C) In rock salt structure, atoms at the corner are also present at the face centers; hence

$$z_Q = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

and the atoms at the body center are also present at edge centers. But from question, body centers are missing and hence



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

Thus, formula of resulting solid is  $P_3Q_4$ .

39. Choose the correct matching sequence from the possibilities given

(a) Crystal defect	(p) AB AB AB type crystal
(b) hcp	(q) Covalent crystal
(c) CsCl	(r) Frenkel
(d) Diamond	(s) Face-centered in cube
(e) NaCl	(t) Body-centered in cube

- |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
|     | (a) | (b) | (c) | (d) | (e) |
| (A) | (r) | (p) | (q) | (t) | (s) |
| (B) | (r) | (p) | (t) | (q) | (s) |
| (C) | (r) | (t) | (p) | (q) | (s) |
| (D) | (t) | (p) | (s) | (q) | (p) |

**Solution**

(B) Crystal defects are referred as Frenkel and Schottky defects.

**Multiple Correct Choice Type**

1. Which of the following statement(s) is(are) correct? (IIT JEE 1998)

- (A) The coordination number of each type of ion in CsCl crystal is 8.  
 (B) A metal that crystallizes in bcc structure has a coordination number of 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).

**Solution**

(A, C, D) CsCl is bcc because the coordination number = 8.

2. Which of the following compounds represent a normal 2:3 spinel structure?

- (A)  $Mg^{II}Al_2^{III}O_4$       (B)  $Co^{II}(Co^{III})_2O_4$       (C)  $Zn(TiZn)O_4$       (D)  $Ni(CO)_4$

**Solution**

(A, B) As spinel has  $AB_2O_4$ , where A has oxidation state = +2 and B has oxidation state = +3.

3. Pick up the correct statements

- (A) The ionic crystal of AgBr has Schottky defect.  
 (B) The unit cell having crystal parameters,  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  is hexagonal.  
 (C) In ionic compounds having Frenkel defect, the ratio  $r^+/r^-$  is high.  
 (D) The coordination number of  $Na^+$  ion in NaCl is 4.

**Solution**

(B, C) AgBr has both Frenkel and Schottky defects. The coordination number of  $Na^+$  is 6.

4. Select the correct statements:

- (A) The conductance through electrons is called *p*-type conduction.  
 (B) The conductance through positive holes is called *p*-type conduction.

- (C) The conductance through electrons holes is called *n*-type conduction.  
(D) The band gap in germanium is small.

**Solution**

(B, C, D) Conductance through electrons is called *n*-type conduction.

5. Which of the following are not the characteristics of crystalline solids?

- (A) They are isotropic. (B) They are polymorphism.  
(C) After melting, they become non-crystalline. (D) They do not have thermodynamic defects.

**Solution**

(A, D) (A) is wrong as crystalline solids are anisotropic; (D) is wrong because they have thermodynamic defects.

6. The hcp and ccp structure for a given element would be expected to have

- (A) the same coordination number. (B) the same density.  
(C) the same packing fraction. (D) all of these.

**Solution**

(A, C) Coordination number = 12 in both the cases.

7.  $\text{TiO}_2$  (rutile) shows 6:3 coordination. Which of the following solids have a rutile-like structure?

- (A)  $\text{MnO}_2$  (B)  $\text{ZnS}$  (C)  $\text{KCl}$  (D)  $\text{SnO}_2$

**Solution**

(A, D)

8. Select the correct statements about three-dimensional hcp system:

- (A) The volume atoms in hcp unit cell is six. (B) The volume of hcp unit cell is  $24\sqrt{2}r^3$ .  
(C) The empty space in hcp unit cell is 26%. (D) The base are of hcp unit is  $6\sqrt{3}r^3$ .

**Solution**

(A,B,C,D)

9. In the fluorite structure if the radius ratio is  $(\sqrt{3}/2 - 1)$ . How many ions does each cation touch?

- (A) 4 anions (B) 12 cations (C) 8 anions (D) No cations

**Solution**

(B,C) In flourite structure, cations form the lattice and anions occupy each of the tetrahedral voids.

10. The density of a certain solid AB (formula mass = 119) is  $2.75 \text{ g cm}^{-3}$ . The edge of the unit cell is 654 pm long. What is/are true about the solid AB?

- (A) It has bcc unit cell. (B) There are four constituents per unit cell.  
(C) Unit cell constituted by anions of fcc. (D) Structure is similar to  $\text{ZnS}$ .

**Solution**

$$(B, C) \frac{a^3 \times d \times N}{M} = \frac{(654 \times 10^{-10})^3 \times 2.75 \times 6.023 \times 10^{23}}{119} \approx 4$$

- 11.** If the radius of  $\text{Na}^+$  ion is 95 pm and that of  $\text{Cl}^-$  ion is 181 pm, then  
 (A) coordination number of  $\text{Na}^+$  is 6. (B) Structure of NaCl is octahedral.  
 (C) Radius of the unit cell is 552 pm. (D) Edge of the unit cell is 276 pm.

**Solution**

$$(A, B, C) \frac{r_+}{r_-} = \frac{95}{181} = 0.525$$

which lies in the range 0.414–0.732. Hence, its coordination number is 6 and structure is octahedral.

$$\text{Length of the unit cell} = 2r_N = r(r_{\text{Na}^+} + r_{\text{Cl}^-}) = 2(95 + 181) = 552 \text{ pm}$$

- 12.** The correct statement(s) regarding defects in solids is (are)  
 (A) Frenkel defects are usually favored by a very small difference in the sizes of a cation and anion.  
 (B) Frenkel defect is a dislocation defect.  
 (C) Trapping of an electron in the lattice leads to the formation of F-center.  
 (D) Schottky defects have no effect on the physical properties of solids.

**Solution**

(B, C) Frenkel defect is also called dislocation defect because smaller ions are dislocated from their lattice sites into the interstitial sites. Hence, option (B) is correct. Trapping of an electron leads to the formation of F-center. Hence, option (C) is correct.

- 13.** In which of the following lattice systems does a primitive unit cell have  $a \neq b \neq c$ ?  
 (A) Orthorhombic (B) Monoclinic (C) Triclinic (D) Hexagonal

**Solution**

(A, B, C)

- 14.** Which of the following statement is correct?  
 (A) A rutile ( $\text{TiO}_2$ ) structure consists of an hcp anion lattice with cations occupying half the octahedral holes.  
 (B) The wurtzite structure is derived from an expanded hcp anion array with cation occupying one type of octahedral holes.  
 (C) In the fluorite structure ( $\text{CaF}_2$ ), anions occupy both types of tetrahedral holes in an expanded fcc lattice of cations.  
 (D) None of these.

**Solution**

(A, B, C) It is a fact.

- 15.** Which of the following is/are true?  
 (A) In hexagonal close packing, each atom has a coordination number of 6.

- (B) In body-centered cubic, the space occupied by spheres is 68%.  
(C) Solids have either tetrahedral voids or octahedral voids.  
(D) There is no difference between fcc and ccp arrangements.

**Solution**

(B, D) Options (B) and (D) are true. (A) is false because in hcp, each atom has a coordination number of 12. (C) is wrong because solids have both types of voids.

**16.** The elements of symmetry in a crystal are

- (A) plane of symmetry. (B) axis of symmetry. (C) center of symmetry. (D) none of these.

**Solution**

(A, B, C)

**17.** Ferromagnetic substances among the following are

- (A) gold. (B) nickel. (C) silver. (D) gadolinium.

**Solution**

(B,D) Ni and Gd are ferromagnetic whereas silver and gold are not.

**18.** Which of the following crystals have 8:8 coordination?

- (A)  $\text{NH}_4\text{Cl}$  (B)  $\text{AlFe}$  (C)  $\text{MnO}$  (D)  $\text{NH}_4\text{Br}$

**Solution**

(A, B, D) Such coordinates are exhibited by compounds that have been lattice structures.

**19.** Which of the following is/are false?

- (A)  $\text{MgFe}_2\text{O}_4$  is a ferrite but  $\text{ZnFe}_2\text{O}_4$ .  
(B) Ferrites have spine structure.  
(C) The number of tetrahedral voids is four times that of octahedral voids.  
(D) If the radius of anion is double than that of cations, the crystalline solid has octahedral structure.

**Solution**

(A,C) Out of the statements, (A) is false because both are ferrites. (C) is false because number of tetrahedral voids is double the number of octahedral voids.

**20.** If radius of anion is 0.20 nm, the maximum radius of cations that can be filled in respective voids are correctly matched in:

- (A)  $r^+ = 0.0828$  nm for tetrahedral void (B)  $r^+ = 0.045$  triangular void  
(C)  $r^+ = 0.1464$  nm for octahedral void (D) none of these.

**Solution**

(A, B, C)

**21.** Choose the correct statements:

- (a) Vacancy defects lower the density of a substance.

- (B) Interstitial defects increase the density of a substance.  
(C) Schottky defects preserve the electrical neutrality of a crystal.  
(D) Frenkel defects do not affect the density of a crystal.

**Solution**

(A, B, C, D)

22. Molecular crystals may exist in

- (A) crystalline state. (B) amorphous state. (C) non-crystalline state. (D) none of these.

**Solution**

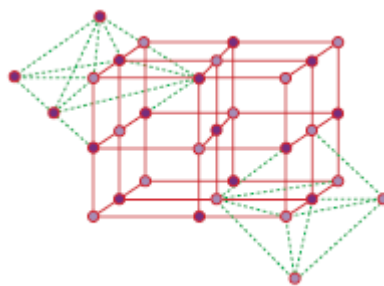
(A, B, C)

23. Which of the following statement are correct for the rock salt structure?

- (A) The tetrahedral sites are smaller than octahedral sites.  
(B) The octahedral sites are occupied by cations and the tetrahedral sites are empty.  
(C) The radius ratio is 0.732.  
(D) The radius ratio is 0.999.

**Solution**

W I L



(A, C) The rock salt structure can be depicted as follows:  
The radius ratio is 0.732.

24. *p*-Type semiconductors are produced when

- (A) silicon is doped with boron. (B) germanium is doped with phosphorus.  
(C) germanium is doped with aluminium. (D) silicon is doped with arsenic.

**Solution**

(A, C) *p*-Type semiconductors are produced when an electron-deficit impurity is added, that is, in (A) and (C) and not in (B) and (D).

25. Select the correct statements about solid crystals.

- (A) High pressure decreases coordination number.  
(B) High pressure increases coordination number  
(C) High temperature increases coordination number.  
(D) High temperature decreases coordination number.

**Solution**

(B, D)

26. Which of the following possesses rock salt-type structure?

- (A) KBr                      (B) CsBr                      (C) CaO                      (D) BeS

**Solution**

(A,C) KBr and CaO possess rock salt-type structure. CsBr has CsCl-type structure while BeS has zinc blende-type structure.

**27.** The space in which atoms are not present in unit cell is(are)

- (A) In sc 48%    (B) In fcc 26%                      (C) In bcc 32%                      (D) In hexagonal 26%

**Solution**

(A, B, C, D) Percentage of empty space = 1 – packing fraction

**Assertion–Reasoning Type**

Choose the correct option from the following:

- (A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.  
(B) Statement 1 is True Statement 2 is True; Statement 2 is NOT, a correct explanation for Statement 1.  
(C) Statement 1 is True, Statement 2 is False.  
(D) Statement 1 is False, Statement 2 is True.

**1. Statement 1:** The number of the nearest neighbors of any constituent particle is called its coordination number.

**Statement 2:** Coordination number of atoms in a cubic close-packed structure is 8.

**Solution**

(C) The coordination number in ccp is 12.

**2. Statement 1:** A tetrahedral void is formed when one sphere (or particle) is placed in the depression formed by three particles placed in a plane.

**Statement 2:** The empty space at the center of six spheres placed octahedrally is the octahedral void.

**Solution**

(B)

**3. Statement 1:** Due to Frenkel defect, there is no effect on the density of crystalline solid.

**Statement 2:** In Frenkel defect, no cation or anion leaves the crystal.

**Solution**

(A) This defect is caused when some of the ions leave their lattice sites to occupy an interstitial site.

**4. Statement 1:** In close packing of spheres, a tetrahedral void is surrounded by four spheres, whereas an octahedral void is surrounded by six spheres.

**Statement 2:** A tetrahedral void has a tetrahedral shape, whereas an octahedral void has an octahedral shape.

**Solution**

(B) A tetrahedral void is formed when one sphere (or particle) is placed in the depression formed by three particles placed in a plane. The octahedral void is formed at the center of six spheres placed octahedrally.

**5. Statement 1:** In hcp, voids are between three touching spheres whose centers lie at the corners of an equilateral triangle.

**Statement 2:** In hcp, voids are called as square voids.

**Solution**

(C) In hcp voids are triangular voids.

**6. Statement 1:** The effective number of octahedral voids in ccp structure is 4 per unit cell.

**Statement 2:** In the ccp structure, there is one octahedral void in the center of the body and 12 octahedral voids on the 12 edges of the cube and each of these edge-based voids is shared by four unit cells.

**Solution**

(A) The number of octahedral voids are equal to the rank of the unit cell, that is, is equal to 4 in ccp.

**7. Statement 1:** Due to the presence of strong coulombic forces between the ions, and a close-packed structure, ionic solids are hard.

**Statement 2:** In ionic solids, the shearing stress is different in different directions.

**Solution**

(B) The first statement is self-explanatory. The explanation for second statement is as follows: The ionic solids have different shearing stress in different directions because in one direction rows having alternate types of atoms are displaced, while in the other direction, the rows displaced consist of one type of atoms.

**8. Statement 1:** In AgCl crystal, Frenkel defect can be observed.

**Statement 2:**  $\text{Ag}^+$  is a small-sized atom.

**Solution**

(A)

**9. Statement 1:** In hcp, the third layer duplicates the first layer.

**Statement 2:** In hcp, the pattern is ABABAB....

**Solution**

(A)

**10. Statement 1:** The melting point decreases in the order: Water > ethyl alcohol > diethyl ether > methane.

**Statement 2:** The strength of the intermolecular forces between these molecules follow the order Water > ethyl alcohol > diethyl ether > methane.

**Solution**

(A) Assuming that the melting points are mainly affected by the intermolecular forces, the strength of the intermolecular forces between these molecules follow the order Water > ethyl alcohol > diethyl ether > methane.

Hence, the melting point decreases in the order: Water > ethyl alcohol > diethyl ether > methane.

**11. Statement 1:** In primitive unit cell, the number of octahedral voids is 1.

**Statement 2:** The number of octahedral voids in a unit cell containing in it is equal to the number of atoms the unit cell contains.

**Solution**

(D) In primitive unit cell the atoms are present only at the corners, that is, a total of 8 atoms present in a unit cell.

**12. Statement 1:** Glass is an amorphous material, whereas quartz is a crystalline substance.

**Statement 2:** Glass has only short-range order, whereas quartz has a long-range order.

**Solution**

(B)

**13. Statement 1:** The 8:8 coordination of CsCl at low temperature changes to 6:6 coordination at 760 K.

**Statement 2:** Temperature also influences the structure of solid.

**Solution**

(A)

**14. Statement 1:** Octahedral holes are present at edge center and at body center in fcc unit cell.

**Statement 2:** Contribution of holes (octahedral) at edge center is (1/4) and that at body center is 1.

**Solution**

(A)

**15. Statement 1:** The stability of a crystal gets reflected in its melting point.

**Statement 2:** The stability of a crystal depends upon the strength of the interparticle attractive force. The melting point of a solid depends on the strength of the attractive force acting between the constituent particles.

**Solution**

(A) The stability of a crystal depends on the strength of the interparticle attractive force. The melting point of a solid depends on the strength of the attractive force acting between the constituted particles. Therefore, the stability of a crystal gets reflected in its melting point.

### Comprehension Type

Read the paragraphs and answer the questions that follow.

#### Paragraph I



In a primitive cubic unit cell, all the eight corners of the cube are occupied by the same atoms/ions and not found anywhere else in the cube. The number of atoms within a unit cell is called the rank of a unit cell. For primitive cubic unit cell, the rank ( $z$ ) is 1. In a bcc, the same atoms/ions are present at all the eight corners of a cube and one atom/ion is also present at the center of the cube. These atoms/ions are not present anywhere else in the cube. The rank of a bcc is 2. In an fcc, the same atoms/ions are present at all the corners of the cube and are also present at the center of each square face. These atoms/ions are not present anywhere else in the unit cell. The rank of an fcc is 4.

1. How many unit cells are present in 39 g of potassium that crystallizes in bcc structure (atomic mass of K = 39 u)?

- (A)  $0.5 N_A$                       (B)  $0.25 N_A$                       (C)  $N_A$                               (D)  $0.75 N_A$

where  $N_A$  means Avogadro's constant.

**Solution**

(A) 39 g of K = 1 mol, so in a bcc unit cell, number of K atoms = 2  
Therefore, 1 mol of K are in  $N_A/2$  mol unit cells.

2. Li crystallizes in bcc. The edge length of unit cell is 351 pm. What would be radius of Li atom?

- (A) 151.98 pm                      (B) 273 pm                              (C) 290 pm                              (D) 76 pm

**Solution**

(C) Edge length,  $a = 351$  pm in bcc unit cell  $\sqrt{3}a = 4r$  ;  $r = \frac{\sqrt{3}}{4}a = 151.98 = 152$

3. Sodium crystallizes in bcc lattice. If the length of the edge of the unit cell is 424 pm, density of sodium is (atomic mass of sodium = 23 u)

- (A)  $10.4 \text{ g cm}^{-3}$                       (B)  $1.002 \text{ g cm}^{-3}$                       (C)  $50.4 \text{ g cm}^{-3}$                       (D) none of these

**Solution**

(A) Given that  $a = 424$  pm and  $z = 2$ , so density is

$$\rho = \frac{Z \times M}{N_A \times a^3 \times 10^{-30}} = \frac{2 \times 39}{6.02 \times 10^{23} \times (424)^3 \times 10^{-30}} = 10.4 \text{ g cm}^{-3}$$

**Paragraph II**

Solids have an ordered arrangement of atoms, but they do not possess a perfect structure. There imperfections or defects in their structure are of different types – point defects and line defects. Point defects are of three types – stoichiometric defects, impurity defects and non-stoichiometric defects.

The two types of stoichiometric defects are vacancy defects and interstitial defects. In ionic solids, these defects are present as Frenkel and Schottky defects.

Non-stoichiometric defects are of metal excess type and metal deficient type. Some solids are difficult to prepare in the stoichiometric composition, for example, pure FeO is difficult to obtain and normally we get a composition of Fe<sub>0.95</sub>O but it may range from Fe<sub>0.93</sub>O to Fe<sub>0.96</sub>O. ZnO is normally a white, finely divided material with the wurtzite

structure. On heating, the color changes to yellow due to the evaporation of oxygen from the lattice to give a non-stoichiometric phase. This produces lattice defects that trap electrons that can subsequently be excited by absorption of visible light. Defects are introduced in ionic solids by adding ions having different charge from that of constituting ions.

Impurity defects occur when a molten metal containing impurities is crystallized, the impurity occupies the sites of the metal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Sometimes calculated amounts of impurities are introduced by doping in semiconductors that change their electrical properties. These are widely used in electronics industry. Solids show magnetic properties such as paramagnetism, diamagnetism, ferromagnetism, anti-ferromagnetism, and ferrimagnetism.

**4.** In the presence of Frenkel defects in a crystal, the density of the crystal

- (A) decreases. (B) increases.  
(C) does not change. (D) increases or decreases depending on the material.

**Solution**

(C) As none of the ions leave the crystal.

**5.** Yellow form of ZnO shows enhanced electrical conductivity due to

- (A) the electrons trapped in neighborhood of excess metal accommodated interstitially.  
(B) an excess of  $O^{2-}$  ions.  
(C) an excess of metal ions accommodated interstitially.  
(D) high temperature.

**Solution**

(A) Electrons are responsible for conductivity in this case.

**6.** When a group 13 element is added in small amounts to germanium, we get

- (A) *n*-type semiconductors. (B) *p*-type semiconductors. (C) insulators. (D) rectifiers.

**Solution**

(B) As germanium belongs to group 14.

**7.**  $Fe_{0.95}O$  can be due to presence of iron in +2 and +3 oxidation numbers. Then iron present in +3 oxidation state will be

- (A) 15% (B) 13.5% (C) 10.5% (D) 8.85%

**Solution**

(C) Let iron present in +3 oxidation state be  $x$ ; then +2 state would be  $0.95x$ .

$$3x + 2x(0.95 - x) = 2 \Rightarrow x = 0.1$$

% of Fe in +3 oxidation state =  $0.1/0.95 \times 100 = 10.5\%$

**8.** An atom containing an odd number of electrons is

- (A) paramagnetic. (B) diamagnetic. (C) ferromagnetic. (D) anti-ferromagnetic.

**Solution**

(A) If all the electrons are paired, it is diamagnetic.

9. If AgCl is doped with  $10^{-4}$  mol% of CdCl<sub>2</sub>, then the concentration of cation vacancies per mol will be

- (A)  $6.02 \times 10^{16}$                       (B)  $6.02 \times 10^{17}$                       (C)  $6.02 \times 10^{18}$                       (D)  $6.02 \times 10^{14}$

**Solution**

(B) For every Cd<sup>2+</sup> ion introduced in NaCl crystal, two Na<sup>+</sup> ions are removed to maintain electrical neutrality. One lattice site occupied by Cd<sup>2+</sup> ion and the other remains vacant. Hence, a cationic vacancy is created in NaCl by doping with CdCl<sub>2</sub>. Since by the addition of one Cd<sup>2+</sup> ion, one cationic vacancy is created; therefore, by the addition of  $10^{-3}$  mol of Cd<sup>2+</sup> ion,  $10^{-3}$  mol% of cationic vacancy will be created. Hence, 1 mol% of a substance contains  $6.023 \times 10^{23}$  atoms/molecules/ions/vacancies.

Therefore,  $10^{-4}$  mol% of cationic vacancy =  $6.023 \times 10^{23} \times 10^{-4} / 100 = 6.023 \times 10^{17}$

**Paragraph III**

Density of a unit cell is the same as the density of the substance. So, if the density of the substance is known, we can calculate the number of atoms or dimensions of the unit cell. The density of the unit cell is related to its mass ( $M$ ), number of atoms per unit cell ( $z$ ), edge length ( $a$  in cm), and Avogadro's constant  $N_A$  as:

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

10. An element X crystallizes in a structure having an fcc unit cell of an edge 100 pm. If 24 g of the element contains  $24 \times 10^{23}$  atoms, the density is

- (A)  $2.40 \text{ g cm}^{-3}$                       (B)  $40 \text{ g cm}^{-3}$                       (C)  $4 \text{ g cm}^{-3}$                       (D)  $24 \text{ g cm}^{-3}$

**Solution**

(B)  $24 \times 10^{23}$  atoms has mass 24 g.

So,  $6.023 \times 10^{23}$  atoms will have mass  $\frac{24 \times 6.023 \times 10^{23}}{24 \times 10^{23}} = M = 6.02 \text{ g}$

The density is given by

$$\rho = \frac{Z \times M}{a^3 \times N_A} = \frac{4 \times 6.02}{100 \times 100 \times 100 \times 10^{-30} \times 6.02 \times 10^{23}} = 40 \text{ g cm}^{-3}$$

11. The number of atoms present in 100 g of a bcc crystal (density =  $12.5 \text{ g cm}^{-3}$ ) having cell edge 200 pm is

- (A)  $1 \times 10^{25}$                       (B)  $1 \times 10^{24}$                       (C)  $2 \times 10^{24}$                       (D)  $2 \times 10^{26}$

**Solution**

(C) The density is given by  $\rho = \frac{Z \times M}{a^3 \times N_A}$ . Therefore,

$$12.5 = \frac{2 \times M}{200 \times 200 \times 200 \times 10^{-30} \times 6.02 \times 10^{23}} \Rightarrow M = 30.1 \text{ g}$$

Now, 30.1 g contains  $6.023 \times 10^{23}$  atoms

So, 100 g will contain  $\frac{6.023 \times 10^{23} \times 100}{30.1} = 2 \times 10^{24}$  atoms

12. A metal A (atomic mass = 60) has a body-centered cubic crystal structure. The density of the metal is  $4.2 \text{ g cm}^{-3}$ . The volume of unit cell is  
 (A)  $8.2 \times 10^{-23} \text{ cm}^3$  (B)  $4.74 \times 10^{-23} \text{ cm}^3$  (C)  $3.86 \times 10^{-23} \text{ cm}^3$  (D) None of these.

**Solution**

(B) The density is given by  $\rho = \frac{z \times M}{a^3 \times N_A}$ . Therefore,

$$a^3 = \frac{2 \times 60}{4.2 \times 6.023 \times 10^{23}} = 4.74 \times 10^{-23} \text{ cm}^3$$

### Integer Answer Type

The answer is a **non-negative integer**.

1. In hexagonal primitive unit cell, the corner is shared by \_\_\_ atoms.

**Solution**

(6)  $1/6$  (corners)  $\times 12 = 2$   
 $1/2$  (face centers)  $\times 2 = 1$   
 $2 + 1 + 3$  (in the body) = 6

2. How many octahedral voids are present per unit cell in an fcc arrangement of particles?

**Solution**

(4) Number of octahedral voids is 4 as it is equal to the number of atoms in closed packed structure, that is, the rank of the unit cell.

3. What will be the coordination number of  $\text{Ca}^{2+}$  ion in a fluorite crystal?

**Solution**

(8)  $\text{CaF}_2$  has fcc structure with 8:4 coordination and has four units of  $\text{CaF}_2$  per unit cell.

4. How many molecules of NaCl are there in an unit cell of its crystal?

**Solution**

(4) In NaCl number of  $\text{Na}^+$  ion =  $12$  (at edge center)  $\times 1/4 + 1 = 4$   
 Number of Cl =  $8$  (corner)  $\times 1/8 + 6$  (at face)  $\times 1/2 = 4$   
 As, NaCl has rock salt arrangement.

5. Iron(II) oxide has a cubic structure and each unit cell has side 500 pm. If the density of the oxide is  $4 \text{ g cm}^{-3}$ , the number of oxide ions present in each unit cell is \_\_\_\_\_. (Molar mass of  $\text{FeO} = 72 \text{ g mol}^{-1}$ ,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ .)

**Solution**

(4) The density is given by  $d = \frac{Z \times M}{a^3 \times N_A}$ . Therefore,

$$4 = \frac{Z \times 72}{500 \times 500 \times 500 \times 10^{-30} \times 6.023 \times 10^{23}} \Rightarrow Z = 4$$

6. A atoms construct fcc type structure in which B atoms occupy all the octahedral voids. If all the atoms are removed from one of the face of unit cell, then the new empirical formula is  $A_xB_y$ . The value of  $(x + y)$  is \_\_\_\_.

**Solution**

(6) Number of octahedral voids = Rank

Rank of fcc = 4

Number of octahedral voids = 4

Therefore, formula  $x + y = 6$

7. The rank of atoms in the hexagonal unit cell is \_\_\_\_.

**Solution**

(6)  $1/6$  (corners)  $\times 12 = 2$

$1/2$  (face centers)  $\times 2 = 1$

$2 + 1 + 3$  ( in the body) = 6

8. The radius of  $Ag^+$  ion is 126 pm whereas that of  $I^-$  ion is 216 pm. The coordination number of Ag in AgI is \_\_\_\_.

**Solution**

(6) Radius ratio  $\frac{r^+}{r^-} = \frac{126}{216} = 0.58$ ; Thus, radius ratio suggests coordination number is six.

**Matrix–Match Type**

1. Match the crystals with their structural characteristic.

Column I	Column II
(A) ZnS crystal	(p) fcc
(B) $CaF_2$ crystal	(q) hcp
(C) NaCl crystal	(r) Distance between closest particles is $(\sqrt{3}/4)a$
(D) Diamond crystal	(s) Only one type of voids are occupied

**Solution**

A  $\rightarrow$  (p,q,r,s); B  $\rightarrow$  (p,r,s); C  $\rightarrow$  (p,s); D  $\rightarrow$  (p,r,s)

A  $\rightarrow$  (p,q,r,s) Zinc blende (spalерite) has ccp arrangement.

B  $\rightarrow$  (p,r,s) Wurtzite has hcp arrangement.

C  $\rightarrow$  (p,s) NaCl has fcc arrangement.

D  $\rightarrow$  (p,r,s) Diamond has fcc arrangement.

2. Match the structure/compound with the percentage of tetrahedral and octahedral voids.

Column I	Column II
(A) Normal spinel structure	(p) 50% tetrahedral and 100% octahedral voids are unoccupied
(B) Inverse spinel structure	(q) 87.5% tetrahedral and 50% octahedral voids are occupied

(C) Diamond	(r) 100% tetrahedral void are occupied
(D) Na <sub>2</sub> O	(s) 50% tetrahedral and 87.5% octahedral voids are unoccupied

**Solution**

A → (q); B → (s); C → (p); D → (r)

**Normal spinel structure:** (AB<sub>2</sub>O<sub>4</sub>)

Number of A<sup>+2</sup> in tetrahedral void = 1

Number of A<sup>+3</sup> in octahedral void = 2

Thus,  $\frac{1}{8}$  th of the tetrahedral and  $\frac{1}{2}$  of the octahedral void are occupied.

**Inverse spinel structure:**

Number of A<sup>+2</sup> in octahedral void = 1

Number of A<sup>+3</sup> in tetrahedral void = 1

Number of A<sup>+3</sup> in octahedral void = 1

Thus  $\frac{1}{2}$  of the octahedral and  $\frac{1}{8}$  of the tetrahedral void are occupied.

**Diamond:** Alternate tetrahedral voids are occupied.

**Na<sub>2</sub>O:** All tetrahedral voids are occupied.

**3. Match the imperfection in solids with the characteristic features.**

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) Form <i>p</i> -type semiconductors
(D) Metal deficient defects	(s) Are non-stoichiometric defects

**Solution**

A → (q); B → (p, q); C → (p, q, s); D → (r, s)

In Schottky defect, equal number of cations and anions are missing from their lattice points.

Frenkel defect arises when an ion goes missing from its lattice site and occupies an interstitial site. Here excess cations occupy interstitial sites.

Metal excess defect is a type of non-stoichiometric defect as the ratio of cation to anion differs from that in normal chemical formula. Metal excess defect is caused due to anion vacancies and is similar to Schottky defect, here also conduction is due to free electrons.

Metal deficient defect, is also a type of non-stoichiometric defect that occurs when a cation goes missing from a lattice site and a similar cation with greater charge occupies adjacent site. Here the conduction is due to positive holes, so it acts as a *p*-type semiconductor.

**4. Match the unit cells with their characteristics.**

Column I	Column II
(A) sc	(p) $z = 4; r = \frac{a}{2\sqrt{2}}$
(B) bcc	(q) $z = 2; r = \frac{\sqrt{3}a}{4}$

(C) fcc	(r) $z = 1; r = \frac{a}{2}$
(D) hcp	(s) $z = 6; r = \frac{a}{2}$

**Solution**

A  $\rightarrow$  (r); B  $\rightarrow$  (q); C  $\rightarrow$  (p); D  $\rightarrow$  (s)

For simple cubic: rank = 1 and  $r = a/2$ .

For bcc: rank = 2 and  $r = (3a)^{1/2}/4$

For fcc: rank = 4 and  $r = a/2(2)^{1/2}$

For hcp: rank = 6 and  $r = a/2$

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