

Chapter 1: The Solid State

Examples

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

Answer:

The element Y creates the ccp lattice. The number of octahedral voids formed would be equal to the number of Y atoms present. Because the atoms of X occupy all of the octahedral voids, the number is also equal to that of the element Y. As a result, the compound's formula is XY.

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

Answer:

The number of tetrahedral voids formed is twice the number of element B atoms. However, only $\frac{2}{3}$ of these tetrahedral voids are occupied by atoms of element A.

As a result, the ratio of the number of atoms in A and B is

$$2 \times \frac{2}{3} : 1$$

$$4 : 3$$

Therefore, the formula of the compound is A_4B_3 .

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

Answer:

It is given that the edge length, $a = 288 \text{ pm} = 288 \times 10^{-10} \text{ cm}$

Density, $d = 7.2 \text{ g cm}^{-3}$

As the lattice is bcc type, the number of atoms per unit cell, (z) is 2.

Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Now, using the relation,

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

$$M = \frac{da^3 N_A}{z}$$

$$= \frac{(7.2 \text{ g cm}^{-3})(288 \times 10^{-10} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{2}$$

$$= 51.8 \text{ g mol}^{-1}$$

According to the mole concept, 51.8 g element has 6.022×10^{23} atoms. So, 208 g of element

will have $\frac{208}{51.8} \times 6.022 \times 10^{23}$ atoms or 24.17×10^{23} atoms.

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

Answer:

It is given that the edge length, $a = 3.608 \times 10^{-8}$ cm

Density, $d = 8.92 \text{ g cm}^{-3}$

As the lattice is fcc type, the number of atoms per unit cell, (z) is 4 .

Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Now, using the relation,

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

$$M = \frac{da^3 N_A}{z}$$

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

$$= 63.1 \text{ g mol}^{-1}$$

Therefore, the atomic mass of copper is 63 u.

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

Answer:

Molar mass, $M = 107.9 \times 10^{-3} \text{ kg mol}^{-1}$

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

Since the lattice is ccp, the number of silver atoms per unit cell is 4.

It is known that, Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Applying the relation,

$$d = \frac{z.M}{a^3 .N_A}$$

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

$$\approx 10.5 \text{ g cm}^{-3}$$

Intext Questions

1.1. Why are solids rigid?

Answer: The intermolecular forces of attraction in solids are extremely strong. Solid constituent particles cannot move from their positions, implying that they have fixed positions. They can, however, oscillate around their mean positions. This is why solids are rigid.

1.2. Why do solids have a definite volume?

Answer: The intermolecular forces of attraction in solids are extremely strong. Solid constituent particles have fixed positions, i.e. they are rigid. Hence, solids have a fixed volume.

1.3. Classify the following as amorphous or crystalline solids:

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

Answer: Amorphous solids: Polyurethane, teflon, polyvinyl chloride, cellophane, fibre glass.

Crystalline solids:

Naphthalene, benzoic acid, potassium nitrate, copper.

1.4. 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?

Answer: Physical properties of an isotropic solid are the same when measured in different directions. As a result, the given solid is isotropic in nature because it has the same refractive index value in all directions. As a result, the solid is amorphous. When an amorphous solid is cut with a sharp edged tool, it splits into two irregularly shaped pieces.

1.5. 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.

Answer: Potassium sulphate: Ionic solid

Tin: Metallic solid

Benzene: Molecular (non-polar) solid

Urea: Polar molecular solid

Ammonia: Polar molecular solid

Water: Hydrogen bonded molecular solid

Zinc sulphides: Ionic solid

Graphite: Covalent or network solid

Rubidium: Metallic solid

Argon: Non-polar molecular solid

Silicon carbide: Covalent or network solid

1.6. Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

Answer: The properties listed are those of a covalent or network solid. As a result, the given solid is either a covalent or a network solid. Diamond and quartz are two examples of such solids (SiO_2).

1.7. Ionic solids conduct electricity in molten state but not in solid state. Explain.

Answer: Ions conduct electricity in ionic compounds. Ions in the solid state are held together by strong electrostatic forces and cannot move freely within the solid. As a result, ionic solids do not conduct electricity in their solid state. However, when the ions are molten or in solution, they are free to move and can conduct electricity.

1.8. What type of solids are electrical conductors, malleable and ductile?

Answer: Metallic solids are electrical conductors, malleable, and ductile.

1.9. Give the significance of a 'lattice point'.

Answer: A lattice point is significant because it represents one constituent particle of a solid, which can be an atom, a molecule (group of atoms), or an ion.

1.10. Name the parameters that characterise a unit cell.

Answer: The following are the six parameters that define a unit cell.

- (i) The lengths of its three edges, a , b , and c . These edges could be equal or unequal.
- (ii) Angles between the edges

The angles α (between edges b and c), β (between edges a and c), and γ (between edges a and b).

1.11. Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells.

Answer: (i) For a hexagonal unit cell,

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$

For a monoclinic cell,

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

$$\beta \neq 90^\circ$$

(ii) Face-centred unit cell:

The constituent particles are present at the corners and one in the center of each face in a face-centered unit cell.

End-centred unit cell:

An end-centered unit cell has particles at each corner and one in the center of any two opposite faces.

1.12. Explain how much portion of an atom located at

(i) corner and

(ii) body-centre of a cubic unit cell is part of its neighboring unit cell.

Answer: (i) Eight adjacent unit cells share an atom located at the corner of a cubic unit cell.

As a result, one unit cell shares $\frac{1}{8}^{th}$ portion of the atom.

(ii) An atom in the body center of a cubic unit cell is not shared by the unit cell next to it. As a result, the atom belongs only to the unit cell in which it is present, implying that its contribution to the unit cell is one.

1.13. What is the two dimensional coordination number of a molecule in square close packed layer?

Answer: A molecule in a square close-packed layer is in contact with four of its neighbors. As a result, a molecule in a square close-packed layer has a two-dimensional coordination number of four.

1.14. 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?

Answer: The number of close-packed particles is calculated as

$$= 0.5 \times 6.022 \times 10^{23}$$

$$= 3.011 \times 10^{23}$$

Therefore, the number of octahedral voids is 3.011×10^{23} .

And, the number of tetrahedral voids is calculated as

$$= 2 \times 3.011 \times 10^{23}$$

$$= 6.022 \times 10^{23}$$

Therefore, the total number of voids is

$$= (3.011 \times 10^{23}) + (6.022 \times 10^{23})$$

$$= 9.033 \times 10^{23}$$

1.15. A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy $1/3^{\text{rd}}$ of tetrahedral voids. What is the formula of the compound?

Answer: The ccp lattice is made up of atoms of the element N.

In this case, the number of tetrahedral voids produced is equal to twice the number of N atoms.

According to the question, the atoms of element $1/3^{\text{rd}}$ M occupy $2 \times \frac{1}{3}$ of the tetrahedral voids.

Therefore, the number of atoms of M is equal to $\frac{2}{3}$ of the number of atoms of N. Hence, the ratio of

the number of atoms of M to that of N is M: N, that is, 2: 3.

Thus, the formula of the compound is M_2N_3 .

1.16. Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centered cubic and (iii) hexagonal close-packed lattice?

Answer: With a packing efficiency of 74%, hexagonal close-packed lattice has the highest packing efficiency. Simple cubic and body-centred cubic lattices have packing efficiencies of 52.4 and 68 percent, respectively.

1.17. An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of the cubic unit cell?

Answer: Given: Density of the element, $d = 2.7 \times 10^3 \text{ kg m}^{-3}$

Molar mass, $M = 2.7 \times 10^{-2} \text{ kg mol}^{-1}$

Edge length, $a = 405 \text{ pm} = 405 \times 10^{-10} \text{ m}$

It is known that, Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Applying the relation,

$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

$$z = \frac{d \cdot a^3 \cdot N_A}{M}$$

$$= \frac{(2.7 \times 10^3 \text{ kg m}^{-3})(4.05 \times 10^{-10} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{(2.7 \times 10^{-2} \text{ kg mol}^{-1})}$$

$$\approx 4$$

This means that each unit cell contains four atoms of the element. As a result, the unit cell is face-centred cubic (fcc) or cubic close-packed (ccp) (ccp).

1.18. What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

Answer: A vacancy defect can occur when a solid is heated. When some of the lattice sites in a solid crystal are empty, this is referred to as a vacancy defect. The density of the solid decreases as a result of the vacancy defect.

1.19. What type of stoichiometric defect is shown by: (i) ZnS (ii) AgBr

Answer: (i) ZnS has a Frenkel defect.
 (ii) AgBr has Frenkel and Schottky defects.

1.20. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

Answer: When a cation of higher valence is added as an impurity to an ionic solid, the cation of higher valence replaces more than one cation of lower valence, allowing the crystal to remain electrically neutral. As a result, some sites become unoccupied. When Sr^{2+} is added to NaCl, for example, each Sr^{2+} ion replaces two Na^+ ions. However, one Sr^{2+} ion takes the place of one Na^+ ion, leaving the other site empty. As a result, vacancies are created.

1.21. Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

Answer: The presence of electrons in the anionic sites causes the color to develop. These electrons absorb energy from visible radiation and become excited. When NaCl crystals are heated in an atmosphere of sodium vapours, sodium atoms are deposited on the crystal's surface, and chloride ions from the crystal diffuse to the surface to form NaCl with

the deposited Na atoms. The Na atoms on the surface lose electrons to form Na^+ ions during this process, and the released electrons diffuse into the crystal to occupy the vacant anionic sites. These electrons are excited by absorbing energy from visible light and give the crystals a yellow color.

1.22. A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Answer: Because of the presence of extra electrons, an n-type semiconductor conducts. As a result, by doping a group 14 element with a group 15 element, a group 14 element can be converted to an n-type semiconductor.

1.23. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Answer: Permanent magnets would be more effective if ferromagnetic materials were used. The metal ions present in ferromagnetic substances are grouped together into small regions in solid state. These regions are referred to as domains, and each domain functions as a tiny magnet. The domains in an unmagnetised piece of a ferromagnetic substance are randomly oriented. As a result, the domains' magnetic moments cancel out. When the substance is placed in a magnetic field, however, all of the domains become oriented in the direction of the magnetic field, resulting in a strong magnetic effect.

The domain ordering persists even after the magnetic field is removed. As a result, the ferromagnetic substance transforms into a permanent magnet.

Exercise questions

1.1. Define the term 'amorphous'. Give a few examples of amorphous solids.

Answer: Amorphous solids are solids with irregularly shaped constituent particles that have short range order. These solids have an isotropic nature and melt at a variety of temperatures. As a result, amorphous solids are also known as pseudo solids or super cooled liquids. They lack a definite heat of fusion. They cut into two pieces with irregular surfaces when cut with a sharp-edged tool. Glass, rubber, and plastic are examples of amorphous solids.

1.2. What makes a glass different from a solid such as quartz? Under what conditions quartz could be converted into glass?

Answer: Glass differs from quartz due to the arrangement of its constituent particles. The constituent particles in glass have a short range order, whereas the constituent particles in quartz have both long and short range orders. By rapidly heating and cooling of quartz, it can be converted into glass.

1.3. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(i) Tetra phosphorus decoxide (P_4O_{10})

(ii) Ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$

(iii) SiC

(iv) I_2

(v) P_4

(vi) Plastic

(vii) Graphite

(viii) Brass

(ix) Rb

(x) LiBr

(xi) Si

Answer: Ionic: (ii) Ammonium phosphate, (x) LiBr

Metallic: (viii) Brass, (ix) Rb

Molecular: (i) Tetra phosphorus decoxide, (iv) I₂, (v) P₄

Covalent (network): (iii) SiC, (vii) Graphite, (xi) Si

Amorphous: (vi) Plastic

1.4. (i) What is meant by the term 'coordination number'?

(ii) What is the coordination number of atoms:

(a) in a cubic close-packed structure?

(b) in a body-centred cubic structure?

Answer: (i) The coordination number of any constituent particle present in the crystal lattice is the number of nearest neighbors of that constituent particle.

(ii) The coordination number of atoms is 12 in a cubic close-packed structure and 8 in a body-centered cubic structure.

1.5. How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

Answer: The atomic mass of an unknown metal can be calculated by knowing its density and the dimension of its unit cell.

Let 'a' be the edge length of a crystal unit cell, 'd' be the metal's density, 'm' be the metal's atomic mass, and 'z' be the number of atoms in the unit cell.

Now, the density of the unit cell is expressed as

$$d = \frac{zm}{a^3} \dots \dots (1)$$

Since the mass of the unit cell is equal to the product of the number of atoms in the unit cell and Atomic mass.

Volume of the unit cell = (Edge length of the cubic unit cell)³

From equation (1):

$$m = \frac{da^3}{z} \dots \dots (2)$$

Now, the mass of the metal (m) is equal to $\frac{\text{Atomic number } (z)}{\text{Avogadro's number } (N_A)}$

$$\text{Hence, } M = \frac{da^3 N_A}{z} \dots \dots (3)$$

Therefore, if the edge lengths are different (say a, b and c), then equation

(ii) becomes:

$$m = \frac{d(abc)N_A}{z} \dots \dots (4)$$

From equations (3) and (4), the atomic mass of the unknown metal is to be determined.

1.6. 'Stability of a crystal is reflected in the magnitude of its melting point'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Answer: The greater the melting point, the greater the intermolecular force of attraction, and thus the greater the stability. A substance that has a higher melting point is more stable than one that has a lower melting point.

The melting points of the following substances are as follows:

Solid water: 273 K

Ethyl alcohol: 158.8 K

Diethyl ether: 156.85 K

Methane: 89.34 K

Based on the melting point values, it can be concluded that the intermolecular force in solid water is the strongest, while that in methane is the weakest.

1.7. How will you distinguish between the following pairs of terms:

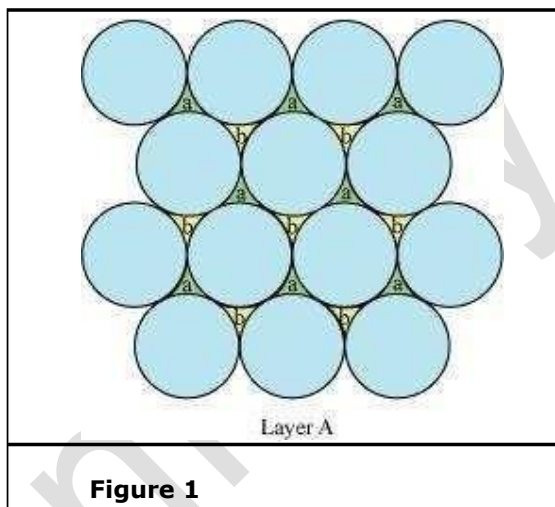
(i) Hexagonal close-packing and cubic close-packing?

(ii) Crystal lattice and unit cell?

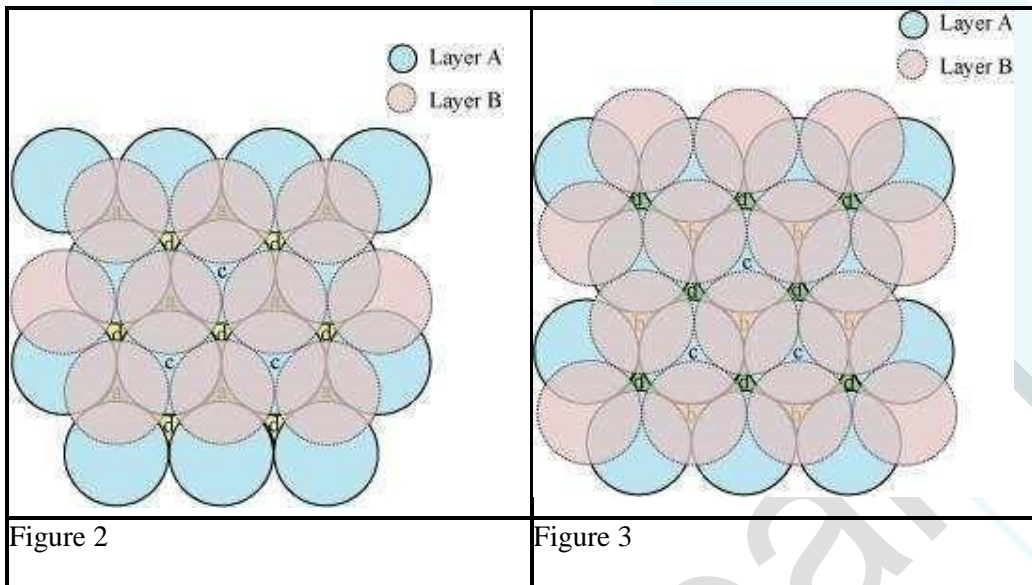
(iii) Tetrahedral void and octahedral void?

Answer:

Figure 1 depicts a 2-D hexagonal close-packing with two types of triangular voids (a and b). This 2-



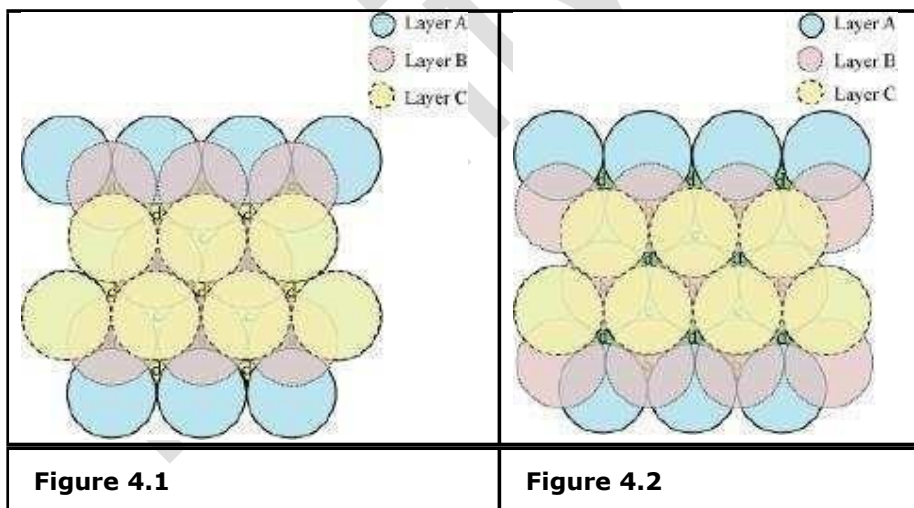
D structure will be referred to as layer A. Particles are now kept in the voids in layer A. (it can be easily observed from figures 2 and 3 that only one of the voids will be occupied in the process, i.e., either a or b). Layer B will be the particles or spheres that are present in the voids of layer A. Layer B now contains two types of voids (c and d). Unlike the voids in layer A, the two types of voids in layer B are not the same. Void c is known as the tetrahedral void because it is surrounded by four spheres. The octahedral void d is surrounded by six spheres.



The next layer can now be placed over layer B in two ways.

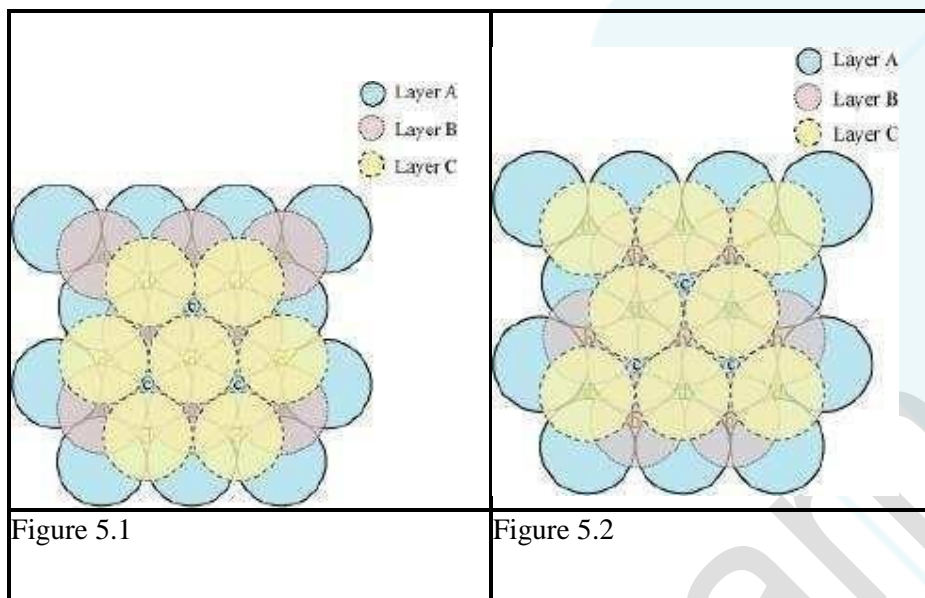
Case 1: When the third layer (layer C) is placed on top of the second layer (layer B), the spheres of layer C occupy the tetrahedral void c.

We get hexagonal close-packing in this case. Figure 4 depicts this. Layer B is present over the voids an in figure 4.1, and layer C is present over the voids c. Layer B is present over the voids b in figure 4.2, and layer C is present over the voids c. The spheres in layer C are directly above the spheres in layer A in this arrangement, as shown in the figure. As a result, the layers in hexagonal close-packing are arranged in an ABAB....pattern.

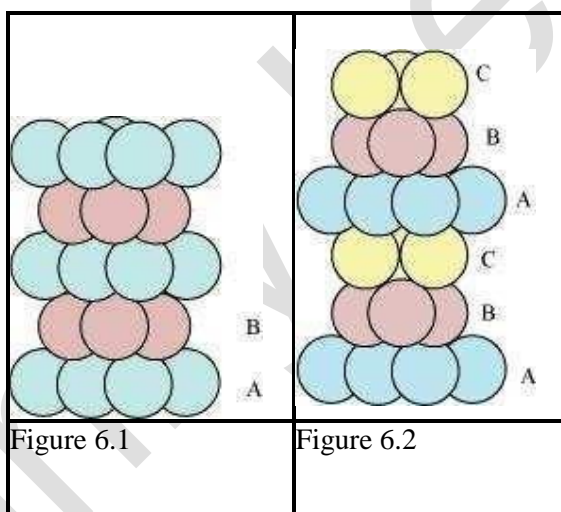


Case 2: When the third layer (layer C) is positioned over layer B so that the spheres of layer C fill the octahedral voids d.

We get cubic close-packing in this case. Layer B is present over the voids an in figure 5.1, and layer C is present over the voids d. Layer B is above void b in Figure 5.2 and layer C is above void d. The figure shows that the particle arrangement in layer C is completely different from that in layers A or B. When the fourth layer is placed over the third layer, the particle arrangement in this layer is similar to that in layer A. As a result, the layers in cubic close-packing are arranged in an ABCABC.. pattern.



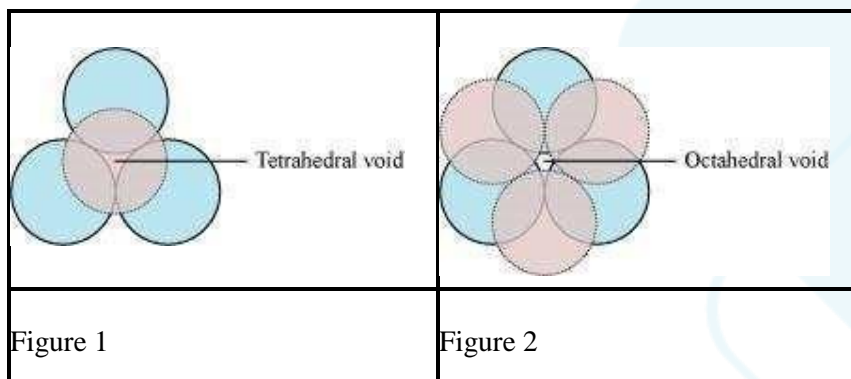
Figures 6.1 and 6.2 show the side views of hcp and ccp, respectively.



(ii) A crystal lattice is a diagrammatic representation of the constituent particles (atoms, ions, or molecules) present in a crystal in a regular three-dimensional arrangement.

The smallest three-dimensional portion of a crystal lattice is called a unit cell. It generates the entire crystal lattice when repeated in different directions.

(iii) A void surrounded by four spheres is referred to as a tetrahedral void, and a void surrounded by six spheres is referred to as an octahedral void. Figure 1 depicts a tetrahedral void, while Figure 2 depicts an octahedral void.



1.8. How many lattice points are there in one unit cell of each of the following lattice?

- (i) Face-centred cubic
- (ii) Face-centred tetragonal
- (iii) Body-centred

Answer: (i) In face-centered cubic, there are 14 lattice points (8 from the corners + 6 from the faces).

(ii) In face-centered tetragonal, there are 14 lattice points (8 from the corners + 6 from the faces).

(iii) In body-centred cubic, there are 9 lattice points (1 from the center + 8 from the corners).

1.9: Explain

(i) **The basis of similarities and differences between metallic and ionic crystals.**

(ii) **Ionic solids are hard and brittle.**

Answer: (i) The fact that both metallic and ionic crystals are held together by electrostatic attraction is the source of their similarities. The electrostatic force acts between positive ions and electrons in metallic crystals. It acts between oppositely charged ions in ionic crystals. As a result, both have high melting points.

The difference between metallic and ionic crystals is that electrons in metallic crystals are free to move, allowing metallic crystals to conduct electricity. Ionic crystals, on the other hand, do not allow the ions to move freely. As a result, they are unable to conduct electricity. They do, however, conduct electricity when molten or in aqueous solution.

(ii) Ions are the constituent particles of ionic crystals. The electrostatic force of attraction holds these ions together in three-dimensional arrangements. Because the electrostatic force of attraction is so strong, the charged ions are held in place. This is why ionic crystals are so hard and brittle.

1.10. Calculate the efficiency of packing in case of a metal crystal for

- (i) simple cubic

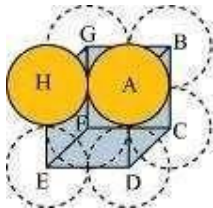
(ii) body-centred cubic

(iii) face-centred cubic (with the assumptions that atoms are touching each other).

Answer:

(i) Simple cubic

The particles in a simple cubic lattice are only found at the cube's corners and are in contact with each other along the edge.



Let the edge length of the cube be 'a' and the radius of each particle be r.

So, $a = 2r$

Now, the volume of the cubic unit cell is equal to a^3 .

Therefore, $(2r)^3$

It is known that, the number of particles per unit cell is 1.

Therefore, volume of the occupied unit cell is $\frac{4}{3}\pi r^3$.

Hence, the packing efficiency = $\frac{\text{volume of one particle}}{\text{volume of cubic unit cell}} \times 100\%$

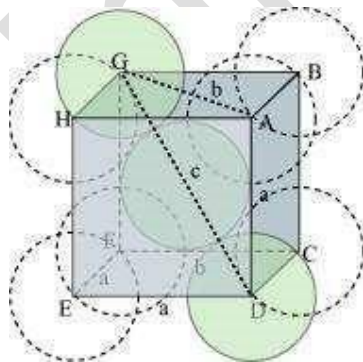
Now, substitute all the values,

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

$$= \frac{1}{6}\pi \times 100\%$$

$$= 52.4\%$$

(ii) Body-centred cubic



The atom in the center is in contact with the other two atoms arranged diagonally, as shown in the above figure.

From $\triangle FED$,

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

$$= 2a^2$$

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

Again, from $\triangle AFD$,

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

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

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

Let the radius of the atom be r . Length of the body diagonal, $c = 4r$

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

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

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

The volume of the cube is shown below.

$$a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3$$

A body-centred cubic lattice contains 2 atoms. So, the volume of the occupied cubic lattice is

$$2\pi \frac{4}{3}r^3.$$

Packing efficiency is the ratio of volume occupied by two spheres in the unit cell and total volume of the unit cell multiplied by 100%.

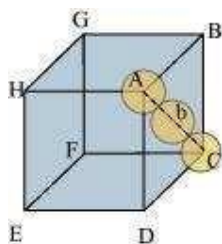
$$\text{Packing efficiency} = \frac{\frac{8}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100\%$$

$$= \frac{\frac{8}{3}\pi r^3}{\left(\frac{64}{3\sqrt{3}}r\right)^3} \times 100\%$$

$$= 68\%$$

(iii) Face-centred cubic

Let the edge length of the unit cell be 'a' and the length of the face diagonal AC be b.



From $\triangle ABC$,

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

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

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

Let r be the radius of the atom.

Now, from the figure, it can be observed that:

$$b = 4r$$

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

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

Now, the volume of the cube, $a^3 = (2\sqrt{2}r)^3$

It is known that the number of atoms per unit cell is 4. So, volume of the occupied unit cell is

$$4 \times \frac{4}{3} \pi r^3.$$

$$\begin{aligned}
 \text{Packing efficiency} &= \frac{\frac{16}{3} \pi r^3}{(2\sqrt{2}r)^3} \times 100\% \\
 &= \frac{\frac{16}{3} \pi r^3}{(16\sqrt{2}r)^3} \times 100\% \\
 &= 74\%
 \end{aligned}$$

1.11. Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.

Answer: It is given that the edge length, $a = 4.07 \times 10^{-8}$ cm

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

As the lattice is fcc type, the number of atoms per unit cell, (z) is 4.

Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Now, using the relation,

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

$$M = \frac{da^3 N_A}{z}$$

$$= \frac{(10.5 \text{ g cm}^{-3})(4.077 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{4}$$

$$= 107.13 \text{ g mol}^{-1}$$

Therefore, the atomic mass of silver is 107.13 u.

1.12. A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Answer: It is given that the atoms of Q are present at the corners of the cube.

Therefore, the number of atoms of Q in one unit cell is $8 \times \frac{1}{8}$ or 1.

It is also given that the atoms of P are present at the body-centre.

Therefore, number of atoms of P in one unit cell = 1

This means that the number of P atoms to the number of Q atoms ratio, P:Q = 1:1.

Hence, the formula of the compound is PQ.

The coordination number of both P and Q is 8.

1.13. Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium using its atomic mass 93 u.

Answer: It is given that the density of niobium, $d = 8.55 \text{ g cm}^{-3}$

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

Since the lattice is bcc type, the number of atoms per unit cell, (z) is 2.

Avogadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Now, using the relation,

$$\begin{aligned}
 a^3 &= \frac{zM}{dN_A} \\
 &= \frac{2 \times 93 \text{ g mol}^{-1}}{(8.55 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})} \\
 &= 3.612 \times 10^{-23} \text{ cm}^3
 \end{aligned}$$

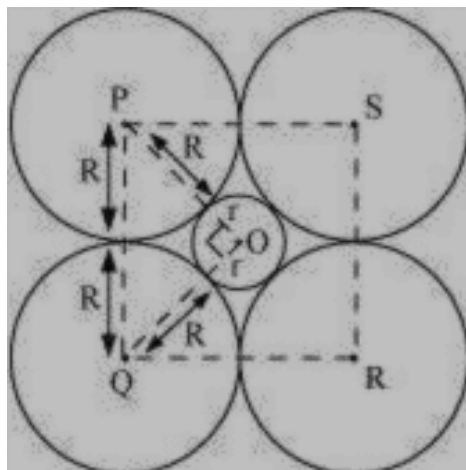
Therefore, $a = 3.306 \times 10^{-8} \text{ cm}$

For body-centred cubic unit cell,

$$\begin{aligned}
 r &= \frac{\sqrt{3}}{4} a \\
 &= \frac{\sqrt{3}}{4} \times 3.306 \times 10^{-8} \text{ cm} \\
 &= 1.432 \times 10^{-8} \text{ cm} \\
 &= 14.32 \text{ nm}
 \end{aligned}$$

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

Answer:



As shown in the figure above, a sphere with center O is fitted into an octahedral void. The figure clearly shows that POQ is right-angled triangle.

Now, applying Pythagoras theorem,

$$PQ^2 = PO^2 + OQ^2$$

$$(2R)^2 = (R+r)^2 + (R+r)^2$$

$$(2R)^2 = 2(R+r)^2$$

$$\sqrt{2}R = R+r$$

$$r = (\sqrt{2} - 1)R$$

$$= 0.414R$$

1.15. Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .

Answer:

Edge length, $a = 3.61 \times 10^{-8}$ cm.

Since the lattice is fcc type, the number of atoms per unit cell (z) is 4.

Atomic mass, $M = 63.5 \text{ g mol}^{-1}$

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

The density of the lattice is calculated as

$$\begin{aligned}
 d &= \frac{zM}{a^3 N_A} \\
 &= \frac{4 \times 63.5 \text{ g mol}^{-1}}{(3.61 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})} \\
 &= 8.97 \text{ g cm}^{-3}
 \end{aligned}$$

Therefore, the measured value of density is given as 8.92 g cm^{-3} .

Hence, the calculated density 8.97 g cm^{-3} is in agreement with its measured value.

1.16. Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

Answer:

The formula of nickel oxide is $\text{Ni}_{0.98}\text{O}_{1.00}$. So, the ratio of the number of Ni atoms to the number of O atoms,

Ni : O

0.98 : 1.00

98 : 100

Now, the total charge on 100 oxide ions is

$$= 100 \times (-2)$$

$$= -200$$

Let the number of Ni^{2+} ions be x . So, the number of Ni^{3+} ions is $98 - x$.

Now, the total charge on Ni^{2+} ions is

$$= x(+2)$$

$$= +2x$$

And, the total charge on Ni^{3+} ions is

$$= (98 - x)(+3)$$

$$= 294 - 3x$$

Since, the compound is neutral, it is written as

$$2x + (294 - 3x) + (-200) = 0$$

$$\Rightarrow -x + 94 = 0$$

$$\Rightarrow x = 94$$

Therefore, the number of Ni^{2+} ions is 94 and the number of Ni^{3+} ions is $98 - 94$ or 4.

Hence, the fraction of nickel that exists as Ni^{2+} is

$$= \frac{94}{98}$$

$$= 0.959$$

And the fraction of nickel that exists as Ni^{3+} is

$$= \frac{4}{98}$$

$$= 0.041$$

1.17. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

Answer:

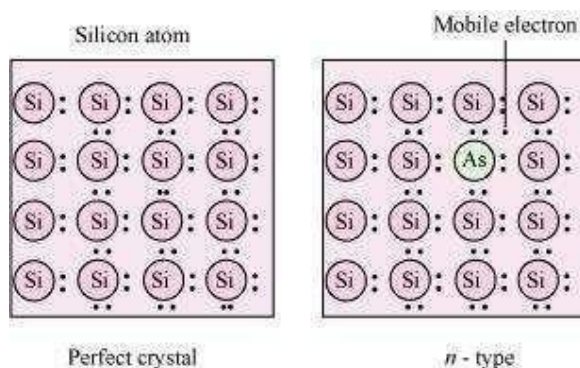
Semiconductors are substances that have conductance with the range of 10^{-6} to $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$.

The two main types of semiconductors are:

(i) n-type semiconductor

(ii) p-type semiconductor

n-type semiconductor: An n-type semiconductor is one that has increased conductivity as a result of negatively charged electrons. An n-type semiconductor is formed when a crystal of a group 14 element, such as Si or Ge, is doped with a crystal of a group 15 element, such as P or As. Si and Ge both have four valence electrons. Each atom forms four covalent bonds in their crystals. P and As, on the other hand, each have five valence electrons. When Si or Ge is doped with P or As, the latter occupies some of the crystal's lattice sites. Four of the five electrons are used to form four covalent bonds with four neighboring Si or Ge atoms. The remaining fifth electron becomes delocalised and increases the conductivity of the doped Si or Ge.

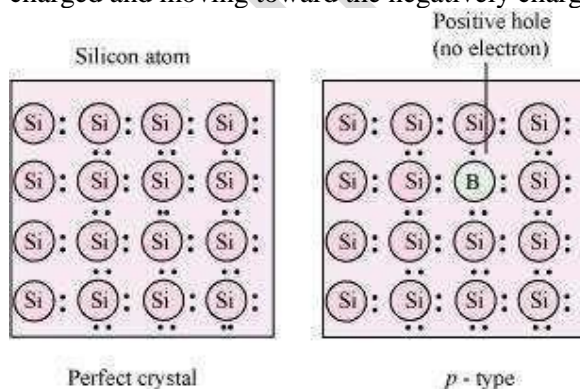


p-type semiconductor:

A p-type semiconductor is a semiconductor that has increased conductivity as a result of an electron hole. A p-type semiconductor is formed when a crystal of group 14 elements such as Si or Ge is doped with a crystal of group 13 elements such as B, Al, or Ga (which contains only three valence electrons).

When a Si crystal is doped with B, the three electrons of B are used to form three covalent bonds, resulting in the formation of an electron hole. An electron from a neighboring atom can come in and fill this electron hole, but it will leave an electron hole in its original location.

The process appears to have moved the electron hole in the opposite direction of the electron that filled it. As a result, when an electric field is applied, electrons will move through electron holes toward the positively charged plate. However, the electron holes will appear to be positively charged and moving toward the negatively charged plate.



1.18. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?

Answer:

The copper to oxygen ratio in laboratory-prepared cuprous oxide (Cu_2O) is slightly less than 2:1.

This means that the number of Cu^+ ions is slightly less than twice that of O_2 . This is due to some Cu^+ ions being replaced by Cu^{2+} ions. Every Cu^{2+} ion replaces two Cu^+ ions, resulting in the formation of holes. As a result of these positive holes, the substance conducts electricity. As a result, the substance is classified as a p-type semiconductor.

1.19. Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Answer:

Let the number of oxide (O^{2-}) ions be x . So, the number of octahedral voids be x .

It is known that two out of every three octahedral holes are filled by ferric ions.

So, the number of ferric (Fe^{3+}) ions is $\frac{2}{3}x$.

Therefore, the ratio of the number of ferric ions to the number of oxide ions is

$$\frac{2}{3}x : x$$

$$\frac{2}{3} : 1$$

$$2 : 3$$

Hence, the formula of the ferric oxide is Fe_2O_3 .

1.20. Classify each of the following as being either a p-type or an n-type semiconductor:

(i) Ge doped with In

(ii) B doped with Si.

Answer:

(i) Ge (an element of group 14) is doped within (a group 13 element). As a result, a hole will be formed, and the resulting semiconductor will be a p-type semiconductor.

(ii) Si is doped into B (a group 13 element) (a group 14 element). As a result, there will be an extra electron, and the resulting semiconductor will be an n-type semiconductor.

1.21. Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

Answer:

For a face-centred unit cell:

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

It is given that the atomic radius, $r = 0.144$ nm.

So,

$$\begin{aligned}
 a &= 2\sqrt{2} \times 0.144 \text{ nm} \\
 &= 0.407 \text{ nm}
 \end{aligned}$$

Therefore, the length of a side of the cell is 0.407 nm.

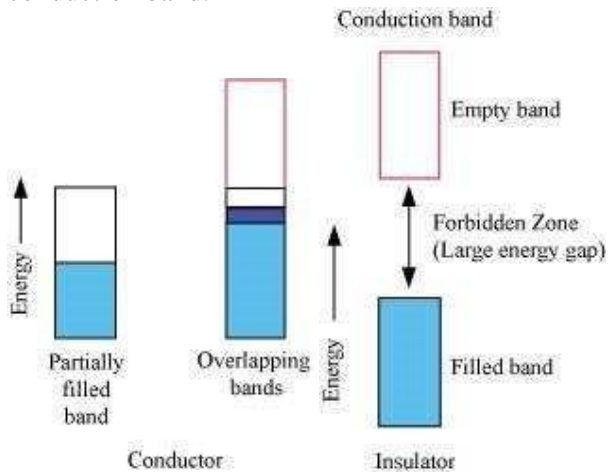
1.22. In terms of band theory, what is the difference

(i) Between a conductor and an insulator

(ii) Between a conductor and a semiconductor

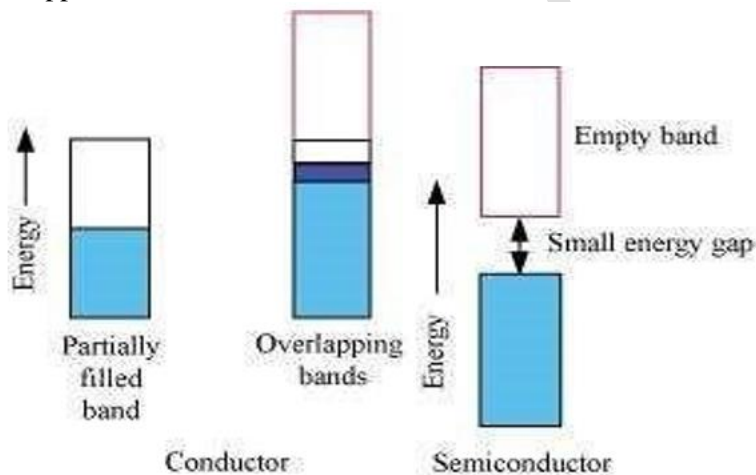
Answer:

(i) A conductor's valence band is partially filled or overlaps with a higher energy, unoccupied conduction band.



In the case of an insulator, on the other hand, the valence band is completely filled and there is a large gap between the valence band and the conduction band.

(ii) In the case of a conductor, the valence band is either partially or completely occupied by a higher energy, unoccupied conduction band. As a result, electrons can easily flow in the presence of an applied electric field.



A semiconductor's valence band, on the other hand, is completely filled, with only a small gap between it and the next higher conduction band. As a result, some electrons can conduct electricity by jumping from the valence band to the conduction band.

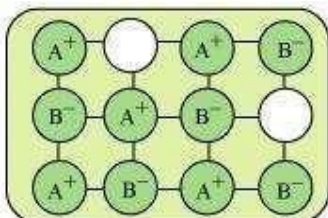
1.23. Explain the following terms with suitable examples:

- (i) Schottky defect
- (ii) Frenkel defect
- (iii) Interstitials and
- (iv) F-centres

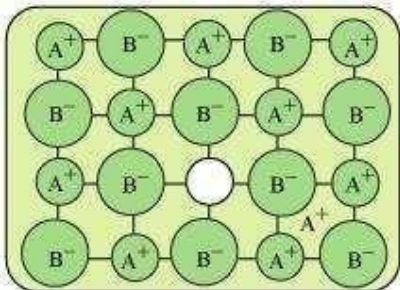
Answer:

(i) **Schottky defect:** The Schottky defect is essentially a vacancy defect observed in ionic solids. To

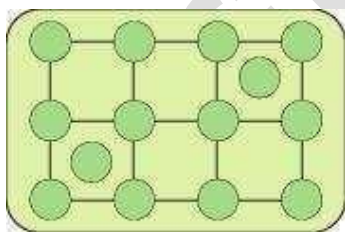
maintain electrical neutrality, an equal number of cations and anions are missing in this defect. It reduces a substance's density. Ionic solids contain a significant number of Schottky defects. At room temperature, for example, there are approximately 10^6 Schottky pairs per cm^3 in NaCl. This type of defect occurs in ionic substances containing similarly sized cations and anions. For example, NaCl, KCl, CsCl, AgBr, and so on.



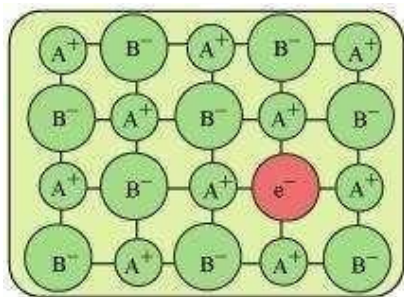
(ii) Frenkel defect: This type of defect can be found in ionic solids with large differences in ion size. Frenkel defect occurs when a smaller ion (usually a cation) is dislocated from its normal site to an interstitial site. It causes both a vacancy defect and an interstitial defect. The Frenkel defect is also referred to as the dislocation defect. This type of defect can be found in ionic solids such as AgCl, AgBr, AgI, and ZnS.



(iii) Interstitials: Non-ionic solids exhibit interstitial defects. When some constituent particles (atoms or molecules) occupy an interstitial site of the crystal, this type of defect occurs. Because of this flaw, the density of a substance increases.



(iv) F-centres: When unpaired electrons occupy the anionic sites of a crystal, the ionic sites are referred to as F-centres. These unpaired electrons give the crystals their color. When NaCl crystals are heated in an atmosphere of sodium vapour, sodium atoms are deposited on the crystal's surface. Cl ions diffuse to the crystal's surface and combine with Na atoms to form NaCl. During this process, the Na atoms on the crystal's surface lose electrons. These liberated electrons diffuse into the crystal and occupy the vacant anionic sites, resulting in the formation of F-centres.



1.24. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

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

(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

Answer:

(i) For cubic close-packed structure:

$$\begin{aligned}
 a &= 2\sqrt{2}r \\
 &= 2\sqrt{2} \times 125 \text{ pm} \\
 &= 353.55 \text{ pm} \\
 &\approx 354 \text{ pm}
 \end{aligned}$$

(ii) Volume of one unit cell is $(354 \text{ pm})^3$

$$\begin{aligned}
 &= 4.4 \times 10^7 \text{ pm}^3 \\
 &= 4.4 \times 10^7 \times 10^{-30} \text{ cm}^3 \\
 &= 4.4 \times 10^{-23} \text{ cm}^3
 \end{aligned}$$

Therefore, the number of unit cells in 1.00 cm^3 is $\frac{1.00}{4.4 \times 10^{-23} \text{ cm}^3}$ or 2.27×10^{22} .

1.25. If NaCl is doped with 10^{-3} mol % of SrCl_2 , what is the concentration of cation vacancies?

Answer:

It is given that NaCl is doped with 10^{-3} mol % of SrCl_2 . It means that 100 mol of NaCl is doped with 10^{-3} mol % of SrCl_2 .

Therefore, 1 mol of NaCl is doped with $\frac{10^{-3}}{100}$ mol of SrCl_2 . That is, 10^{-5} mol of SrCl_2 .

The cation vacancies produced by one Sr^{2+} ion is 1.

$$\begin{aligned}
 &\text{Therefore, the concentration of the cation vacancies produced by } 10^{-5} \text{ mol of } \text{Sr}^{2+} \text{ ions is} \\
 &= 10^{-5} \times 6.022 \times 10^{23} \\
 &= 6.022 \times 10^{18} \text{ mol}^{-1}
 \end{aligned}$$

Therefore, the concentration of cation vacancies created by SrCl_2 is 6.022×10^{18} per mol of NaCl.

1.26. Explain the following with suitable examples:

- (i) Ferromagnetism
- (ii) Paramagnetism
- (iii) Ferrimagnetism
- (iv) Antiferromagnetism
- (v) 12-16 and 13-15 group compounds.

Answer:

(i) Ferromagnetism: Ferromagnetic substances are those that are strongly attracted by a magnetic field. Even in the absence of a magnetic field, ferromagnetic substances can be permanently magnetized. Iron, cobalt, nickel, gadolinium, and CrO_2 are examples of ferromagnetic substances.

The metal ions of ferromagnetic substances are grouped together into small regions called domains in solid state, and each domain acts as a tiny magnet. The domains in an unmagnetised piece of a ferromagnetic substance are randomly oriented, and thus their magnetic moments cancel. When the substance is placed in a magnetic field, however, all of the domains become oriented in the magnetic field's direction. As a result, there is a strong magnetic effect. This domain ordering persists even after the magnetic field is removed. As a result, the ferromagnetic substance transforms into a permanent magnet.



Magnetic moment alignment in ferromagnetic substances is depicted schematically.

(ii) Paramagnetism: Paramagnetic substances are those that are attracted by a magnetic field.

O_2 , Cu^{2+} , Fe^{3+} , and Cr^{3+} are examples of paramagnetic substances.

Paramagnetic substances are magnetized in the same direction by a magnetic field, but lose magnetism when the magnetic field is removed. A substance must have one or more unpaired electrons in order to undergo paramagnetism. This is due to the fact that unpaired electrons are attracted by a magnetic field, resulting in paramagnetism.

(iii) Ferrimagnetism: Ferrimagnetic substances are those in which the magnetic moments of the domains are aligned in unequal numbers in parallel and anti-parallel directions. Fe_3O_4 (magnetite) and ferrites such as MgFe_2O_4 and ZnFe_2O_4 are examples.

In comparison to ferromagnetic substances, ferrimagnetic substances are weakly attracted by a magnetic field. These substances become paramagnetic when heated.



Schematic alignment of magnetic moments in ferrimagnetic substances

(iv) Antiferromagnetism: Antiferromagnetic substances have domain structures that are similar to ferromagnetic substances but are oriented in the opposite direction. The magnetic moments of the oppositely oriented domains cancel each other out.



Magnetic moment alignment in antiferromagnetic substances is depicted schematically.

(v) Compounds from the 12-16 and 13-15 groups: The 12-16 group compounds are made by combining elements from groups 12 and 16, while the 13-15 group compounds are made by combining elements from groups 13 and 15. These compounds are designed to stimulate the average valence of four, as found in Ge or Si. Groups 13-15 compounds include indium (III)

antimonide (IrSb), aluminum phosphide (AlP), and gallium arsenide (GaAs).

GaAs semiconductors have a very fast response time and have revolutionized semiconductor device design. Zinc sulphide (ZnS), cadmium sulphide (CdS), cadmium selenide (CdSe), and mercury (II) telluride are examples of group 12-16 compounds (HgTe). These compounds' bonds are not perfectly covalent. The electronegativities of the two elements determine the ionic character of the bonds.

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