Class 12 Chemistry
NCERT Solutions for Chapter 1 – The Solid State
Exercises Solutions

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

Sol. Amorphous solids are those substances, in which there is no regular arrangement of its constituent particles, (i.e., ions, atoms or molecules). The arrangement of the constituting particles has only short-range order, i.e., a regular and periodically repeating pattern is observed over short distances only, e.g., glass, rubber, and plastics.

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

Sol. Glass is a supercooled liquid and an amorphous substance. Quartz is the crystalline form of silica (SiO_2) in which tetrahedral units SiO_4 are linked with each other in such a way that the oxygen atom of one tetrahedron is shared with another Si atom. Quartz can be converted into glass by melting it and cooling the melt very rapidly. In the glass, SiO_4 tetrahedra are joined in a random manner.

1.3 Classify each of the following solids as ionic, metallic, modular, network (covalent), or amorphous:
(i) Tetra phosphorus decoxide (P_4O_{10}) (ii) Ammonium phosphate, ($NH_4)_3PO_4$ (iii) SiC (iv) I_2 (v) P_4 (vii) Graphite (viii), Brass (ix) Rb (x) LiBr (xi) Si
Sol.

Ionic	Metallic	Molecular	Network (covalent)	Amorphous
$(NH_4)_3PO_4$	Brass	P_4O_{10}	Graphite	Plastics
LiBr	Rb	I_2	SiC	
		P_4	Si	

1.4 (i) What is meant by the term 'coordination number'?
(ii) What is the coordination number of atom
(a) in a cubic close-packed structure?
(b) in a body centred cubic structure?
Sol. (i) The number of nearest neighbours of a particle are called its coordination number.
(ii) (a) 12 (b) 8

1.5. How can you determine the atomic mass of an unknown metal if you know its density and dimensions of its unit cell ? Explain your answer. (C.B.S.E. Outside Delhi 2011)

Sol.

$$\text{Atomic mass of element (M)} = \frac{\text{Density}(\rho) \times \text{Volume}(a^3) \times \text{Avogadro's no.}(N_0)}{\text{No. of atoms in unit cell (Z)}}$$

Consider a unit cell with edge length $= a$ pm $= a \times 10^{-10}$ cm.

($\because$ Because density is normally expressed in g cm^{-3})

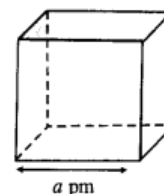Volume of the unit cell $= (a \times 10^{-10} \text{ cm})^3 = a^3 \times 10^{-30}$ cm^3

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

Now, mass of unit cell = No. of atoms in a unit cell × Mass of each atom

$$= Z \times \frac{\text{Atomic mass (M)}}{\text{Avogadro's number (No)}} \quad \ldots(ii)$$

By substituting the value of mass of unit cell in equation (i)

$$\text{Density of unit cell} = \frac{Z \times M(g)}{N_0 \times (a^3 \times 10^{-30} \text{cm}^3)} = \frac{Z \times M \ (g \ cm^{-3})}{N_0 \times a^3 \times 10^{-30}}$$

a pm

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

Sol. Higher the melting point, greater are the forces holding the constituent particles together and thus greater is the stability of a crystal. Melting points of given substances are following. Water = 273 K, Ethyl alcohol = 155.7 K, Diethylether = 156.8 K, Methane = 90.5 K.

The intermoleoilar forces present in case of water and ethyl alcohol are mainly due to the hydrogen bonding which is responsible for their high melting points. Hydrogen bonding is stronger in case of water than ethyl alcohol and hence water has higher melting point then ethyl alcohol. Dipole-dipole interactions are present in case of diethylether. The only forces present in case of methane is the weak van der Waal's forces (or London dispersion forces).

1.7. How will you distinguish between the following pairs of terms :
(a) Hexagonal close packing and cubic close packing
(b) Crystal lattice and unit cell
(c) Tetrahedral void and octahedral void.
Sol.
(a) In hexagonal close packing (hcp), the spheres of the third layer are

vertically above the spheres of the first layer (ABABAB……. type). On the other hand, in cubic close packing (ccp), the spheres of the fourth layer are present above the spheres of the first layer (ABCABC…..type).

(b) Crystal lattice: It deplicts the actual shape as well as size of the constituent particles in the crystal. It is therefore, called space lattice or crystal lattice.
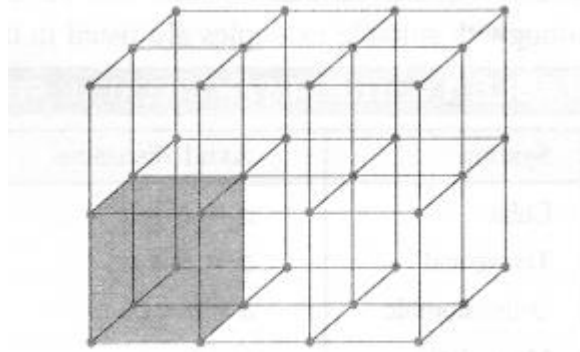

Figure 1.11. Representation of space lattice and unit cell.

Unit cell: Each bricks represents the unit cell while the block is similar to the space or crystal lattice. Thus, a unit cell is the fundamental building block of the space lattice.

(c) Tetrahedral void: A tetrahedral void is formed when triangular void made by three spheres of a particular layer and touching each other.
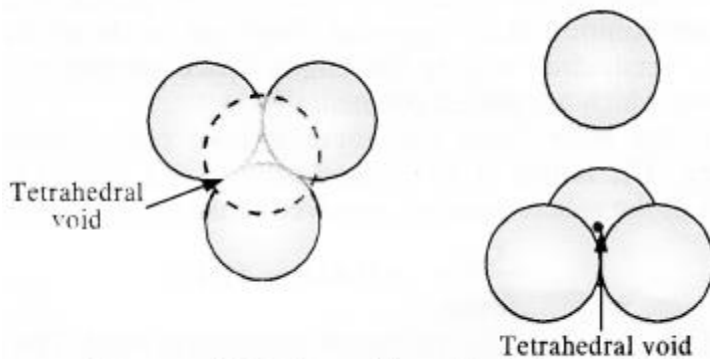

Figure 1.28. Formation of Tetrahedral Void.

Octahedral void: An octahedral void or site is formed when three spheres arranged at the corners of an equilateral triangle are placed over anothet set of
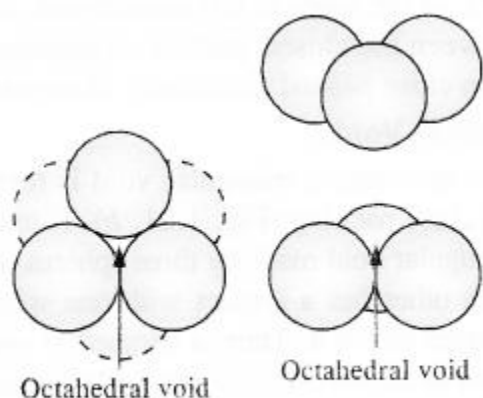
spheres.

Figure 1.30. Formation of Octahedral Void.

1.8 How many lattice points are there is one unit cell of each of the following lattices?
(i) Face centred cubic (if) Face centred tetragonal (iii) Body centred cubic
Sol.

Lattice points in face centred cubic
(*i*) and face centred tetragonal
(*ii*) = 8 (at corners) + 6 (at face centres) = 14

$$\text{Particle per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Lattice points in body centred cubic
(*iii*) = 8 (at corners) + 1 (at body centre) = 9

$$\text{Particles per unit cell} = 8 \times \frac{1}{2} + \frac{1}{8} \times 1 = 2.$$

1.9 Explain:
(i) The basis of similarities and differences between metallic and ionic crystals.
(ii) Ionic solids are hard and brittle.
Sol. (i) Metallic and ionic crystals
Similarities:
(a) There is electrostatic force of attraction in both metallic and ionic crystals.
(b) Both have high melting points.
(c) Bonds are non-directional in both the cases.
Differences:
(a) Ionic crystals are bad conductors of electricity in solids state as ions are not free to move. They can conduct electricity only in die molten state or in aqueous solution. Metallic crystals are good conductors of electricity in solid

state as electrons are free to move.

(b) Ionic bond is strong due to strong electrostatic forces of attraction. Metallic bond may be strong or weak depending upon the number of valence electrons and the size of the kernels.

(ii) Ionic solids are hard and brittle.Ionic solids are hard due to the presence of strong electrostatic forces of attraction. The brittleness in ionic crystals is due to the non- directional bonds in them.

1.10 Calculate the efficiency of packing in case **of a metal crystal for (i) simple cubic, (ii) body centred cubic, and (iii) face centred cubic (with the assumptions that atoms are touching each other).**

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

(i) In simple cubic lattice:

Here $a = 2r$

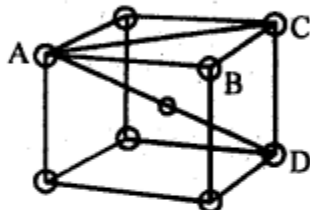No. of spheres per unit cell $= 1$

Volume of spheres $= \dfrac{4}{3}\pi r^3$

Volume of cube $= a^3 = (2r)^3 = 8r^3$

∴ Packing efficiency

$= \dfrac{4/3\,\pi r^3}{8\,r^3} = 0.524$, *i.e.,* 52.4%.

(ii) In *bcc* : $AD = 4r$

From right angled triangle ABC,

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

Body diagonal, AD

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

∴ $\sqrt{3}\,a = 4r \quad a = 4r/\sqrt{3}$

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

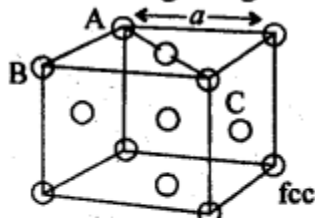No. of spheres per unit cell $= 2$

∴ Volume of two spheres $= 2 \times \dfrac{4}{3}\pi r^3 = \dfrac{8}{3}\pi r^3$

∴ Packing efficiency

$= \dfrac{8/3\,\pi r^3}{64r^3/3\sqrt{3}} = 0.68$, *i.e.,* 68%

(iii) In *fcc*: Let the edge length of unit cell $= a$

fcc
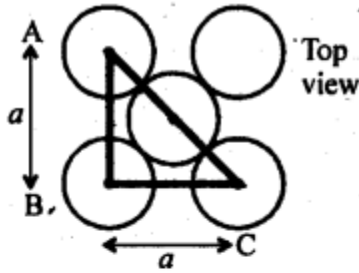
Let the radius of each sphere $= r$

∴ $AC = 4r$

From right angled triangle ABC,

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

Top view

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

$$\therefore \quad a = \frac{4r}{\sqrt{2}}$$

$\therefore$ Volume of the unit cell

$$= a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{64r^3}{2\sqrt{2}} = \frac{32r^3}{\sqrt{2}}$$

No. of unit cell in fcc = 4

$\therefore$ Volume of four spheres $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

$\therefore$ Packing efficiency

$$= \frac{16\pi r^3/3}{64r^3/3\sqrt{3}} \doteq 0.74, \ i.e., 74\%$$

1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07 x 10⁻⁸ cm and density is 10.5 g cm⁻³, calculate the atomic mass of silver.
Sol.

$$M = \frac{d \cdot a^3 \cdot N_a}{Z} = \frac{10.5 \times (4.07 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4}$$

$$= 107.09 \text{ g mol}^{-1}.$$

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

Sol. Contribution by atoms Q present at the eight corners of the cube = 18= x 8 = 1

Contribution by atom P present at the body centre = 1

Thus, P and Q are present in the ratio 1:1.

$\therefore$ Formula of the compound is PQ.

Co-ordination number of atoms P and Q = 8.

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

Sol.

$$a^3 = \frac{M \cdot Z}{d \cdot N_a \times 10^{-30}} = \frac{93 \times 2}{8.55 \times 6.02 \times 10^{23} \times 10^{-30}}$$
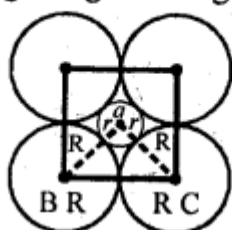
$$= 3.61 \times 10^7$$

$$\therefore \quad a = (3 \cdot 61 \times 10^7)^{1/3} = (36 \cdot 1 \times 10^6)^{1/3}$$
$$= 3 \cdot 304 \times 10^2 \text{ pm} = 330 \cdot 4 \text{ pm}$$

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.

Sol. A sphere is fitted into the octahedral void as shown in the diagram.

ΔABC is a right angled triangle.

$$\therefore \quad BC^2 = AB^2 + AC^2$$
$$(2R)^2 = (R+r)^2 + (R+r)^2$$
$$(2R)^2 = 2(R+r)^2$$

$$\Rightarrow \quad \frac{(2R)^2}{2} = (R+r)^2$$

$$\left(\sqrt{2}R\right)^2 = (R+r)^2$$

$$\Rightarrow \quad \sqrt{2}\,R = R + r$$
$$r = \sqrt{2}\,R - R \qquad\qquad r = R(\sqrt{2}-1)$$
$$r = R(1 \cdot 414 - 1) \qquad\qquad r = 0 \cdot 414\,R$$

1.15 Copper crystallises into a fee lattice with edge length 3.61 x 10⁻⁸ cm. Show that the calculated density is in agreement with its measured value of 8.92 gcm⁻³.

Sol.

$$d = \frac{Z \times M}{a^3 \times N_a}$$

$$= \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.023 \times 10^{23}} \quad \{M = 63.5 \text{ for Cu}\}$$

$$= 8.96 \text{ g cm}^{-3}.$$

This calculated value of density is closely in agreement with its measured value of 8.92 g cm³.

Question 16.

Analysis shows that nickel oxide has the formula $Ni_{0.98} O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

Solution:

98 Ni-atoms are associated with 100 O – atoms. Out of 98 Ni-atoms, suppose

Ni present as Ni^{2+} = x

Then Ni present as Ni^{3+} = 98 – x

Total charge on x Ni^{2+} and (98 – x) Ni^{3+} should

be equal to charge on 100 O^{2-} ions.

Hence, x × 2 + (98 – x) × 3 = 100 × 2 or 2x + 294 – 3x = 200 or x = 94

∴ Fraction of Ni present as Ni^{2+} = 9498 × 100 = 96%

Fraction of Ni present as Ni^{3+} = 498 × 100 = 4%

Question 17.

What are semi-conductors? Describe the two main types of semiconductors and contrast their conduction mechanisms.
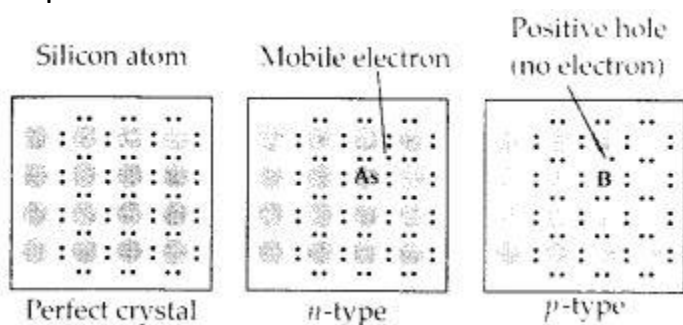
Solution:

Semi-conductors are the substances whose conductivity lies in between those of conductors and insulators. The two

main types of semiconductors are n-type and p-type.

(i) n-type semiconductor: When a silicon or germanium crystal is doped with group 15 element like P or As, the dopant atom forms four covalent bonds like Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and continues its share towards electrical conduction. Thus silicon or germanium doped with P or As is called H-type semiconductor, a-indicative of negative since it is the electron that conducts electricity.

(ii) p-type semiconductor: When a silicon or germanium is doped with group 13 element like B or Al, the dopant is present only with three valence electrons. An electron vacancy or a hole is created at the place of missing fourth electron. Here, this hole moves throughout the crystal like a positive charge giving rise to electrical conductivity. Thus Si or Ge doped with B or Al is called p-type semiconductor, p stands for positive hole, since it is the positive hole that is

responsible for conduction.

Silicon atom   Mobile electron   Positive hole (no electron)

Perfect crystal n-type p-type

Question 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?
Solution:
The ratio less than 2 : 1 in Cu_2O shows cuprous (Cu^+) ions have been replaced by cupric (Cu^{2+}) ions. For maintaining electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion thereby creating a hole. As conduction will be due to the presence of these positive holes, hence it is a p-type semiconductor.

Question 19.
Ferric oxide crystallises in a hexagonal dose- packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.
Solution:
Suppose the number of oxide ions (O^{2-}) in the packing = 90
∴ Number of octahedral voids = 90
As $2/3^{rd}$ of the octahedral voids are occupied by ferric ions, therefore, number of ferric ions 2 present = 23 × 90 = 60
∴ Ratio of Fe^{3+} : O^{2-} = 60 : 90 = 2 : 3
Hence, the formula of ferric oxide is Fe_2O_3.

Question 20.
Classify each of the following as being either a p-type or n-type semiconductor :

1. Ge doped with In

2. B doped with Si.

Solution:

1. Ge is group 14 element and In is group 13 element. Hence, an electron deficient hole is created and therefore, it is a p – type semiconductor.

2. B is group 13 element and Si is group 14 element, there will be a free electron, So, it is an n-type semiconductor.

Question 21.
Gold (atomic radius = 0.144 nm) crystallises in a face centred unit cell. What is the length of the side of the unit cell ?

Solution:
For a face centred cubic unit cell (fcc)
Edge length (a) = $2\sqrt{2}r$ = 2 x 1.4142 x 0.144 mm = 0.407 nm

Question 22.
In terms of band theory, what is the difference

1. between a conductor and an insulator

2. between a conductor and a semiconductor?

Solution:
In most of the solids and in many insulating solids conduction takes place due to migration of electrons under the influence of electric field. However, in ionic solids, it is the ions that are responsible for the conducting behaviour due to their movement.

(i) In metals, conductivity strongly depends upon the number of valence electrons available in an atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other, as to form a band. If this band is partially filled or it overlaps with the higher energy unoccupied conduction band, then electrons can flow easily under an applied

electric field and the metal behaves as a conductor.

Fig. 1.33
Distinction among
(a) metals
(b) insulators and
(c) semiconductors.
In each case, an
unshaded area
represents a
conduction band.
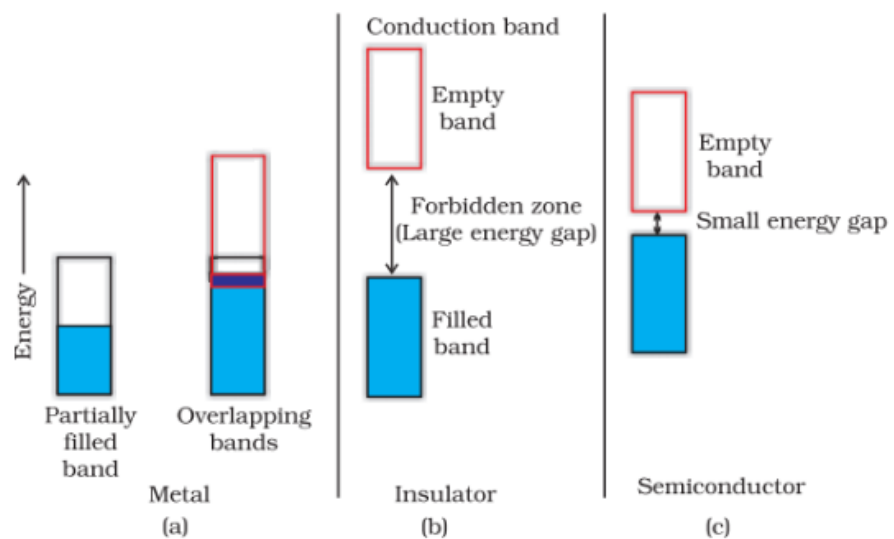
If the gap between valence band and next higher unoccupied conduction band is large, electrons cannot jump into it and such a substance behaves as insulator.

(ii) If the gap between the valence band and conduction band is small, some electrons may jump from valence band to the conduction band. Such a substance shows some conductivity and it behaves as a semiconductor. Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump to the conduction band. Silicon and germanium show this type of behaviour and are called intrinsic semiconductors. Conductors have no forbidden band.

**Question 23.**
Explain the following terms with suitable examples :

1. Schottky defect

2. Frenkel defect

3. Interstitial defect

4. F-centres.

Solution:
(i) Schottky defect : In Schottky defect a pair of vacancies or holes exist in the crystal lattice due to the absence of equal number of cations and anions from their lattice points. It is a common defect in ionic compounds of high coordination number where both cations and anions are of the same size, e.g.,

KCl, NaCl, KBr, etc. Due to this defect density of crystal decreases and it begins to conduct electricity to a smaller extent.

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

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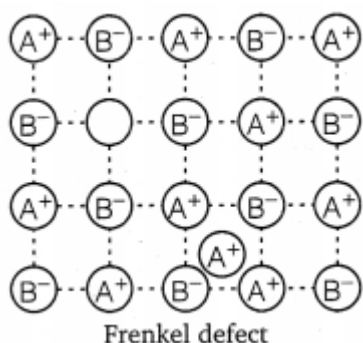
(iii) Interstitial defect : When some constituent particles (atoms or molecules) occupy an interstitial site of the crystal, it is said to have interstitial defect. Due to this defect the density of the substance increases.

(iv) F-Centres : These are the anionic sites occupied by unpaired electrons. F-centres impart colour to crystals. The colour results by the excitation of electrons when they absorb energy from the visible light falling on the crystal.

Question 24.
Aluminium crystallises in a cubic close packed structure. Its metallic radius is 125 pm.

1. What is the length of the side of the unit cell?

2. How many unit cells are there in 1.00 cm³ of aluminium?

Solution:
(i) For an fee unit cell, $r = \frac{a}{2\sqrt{2}}$ (given, r = 125 pm)
$a = 2\sqrt{2}\, r = 2\sqrt{2} \times 125$ pm
= 353.55 pm
≅354 pm

(ii) Volume of one unit cell = a^3 = (354 pm)³
= 4.4 × 10⁷ pm³
= 4.4 × 10⁷ × 10⁻³⁰ cm³

= 4.4×10^{-23} cm^3

Therefore, number of unit cells in 1.00 cm^3 = $\frac{1.00 \text{ cm}^3}{4.4 \times 10^{-23} \text{ cm}^3}$

= 2.27×10^{22}

Question 25.

If NaCl is doped with 10^{-3} mol % SrCl$_2$, what is the concentration of cation vacancies?

Solution:

Let moles of NaCl = 100

∴ Moles of SrCl$_2$ doped = 10^{-3}

Each Sr^{2+} will replace two Na+ ions. To maintain electrical neutrality it occupies one position and thus creates one cation vacancy.

∴ Moles of cation vacancy in 100 moles NaCl = 10^{-3}

Moles of cation vacancy in one mole

NaCl = $10^{-3} \times 10^{-2} = 10^{-5}$

∴ Number of cation vacancies

= $10^{-5} \times 6.022 \times 10^{23} = 6.022 \times 10^{18}$ mol^{-1}

Question 26.

Explain the following with suitable example:

1. Ferromagnetism

2. Paramagnetism

3. Ferrimagnetism

4. Antiferromagnetism

5. 12-16 and 13-15 group compounds.

Solution:

(i) Ferromagnetic substances : Substances which are attracted very strongly by a magnetic field are called ferromagnetic substances, e.g., Fe, Ni, Co and CrO$_2$ show ferromagnetism. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetic moments are due to unpaired electrons in the same direction.

Schematic alignment of magnetic moments
in ferromagnetic

The ferromagnetic material, CrO_2, is used to make magnetic tapes used for audio recording.

(ii) Paramagnetic substances : Substances which are weakly attracted by the external magnetic field are called paramagnetic substances. The property thus exhibited is called paramagnetism. They are magnetised in the same direction as that of the applied field. This property is shown by those substances whose atoms, ions or molecules contain unpaired electrons, e.g., O_2, Cu^{2+}, Fe^{3+}, etc. These substances, however, lose their magnetism in the absence of the magnetic field.

(iii) Ferrimagnetic substances : Substances which are expected to possess large magnetism on the basis of the unpaired electrons but actually have small net magnetic moment are called ferrimagnetic substances, e.g., Fe_3O_4, ferrites of the formula $M^{2+}Fe_2O_4$ where M = Mg, Cu, Zn, etc. Ferrimagnetism arises due to the unequal number of magnetic moments in opposite direction resulting in some net magnetic moment.

Schematic alignment of magnetic moments in ferrimagnetic

(iv) Antiferromagnetic substances : Substances which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called antiferromagnetic substances, e.g., MnO. Antiferromagnetism is due to the presence of equal number of magnetic moments in the opposite directions

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

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