DAY NINTEEN

Solid State

Learning & Revision for the Day

- Classification of Solids
- Bragg's Equation
- Space Lattice or Crystal Lattice
- Unit Cell
- Packing in Solids
- Coordination Number
- Point Defects (Imperfections)
- Electrical and Magnetic Properties of Solids
- Band Theory

A **solid** is defined as that form of matter which has rigidity, due to which it possesses a definite volume and a definite shape. The rigidity of the solids is because, their constituent particles have fixed positions and can only oscillate about their mean positions.

Classification of Solids

- On the basis of the arrangement of their atoms or ions or molecules, solids are broadly classified into two groups:
  (i) **Crystalline Solids** They have systematic and regular arrangement of particles and sharp melting point. They have flat faces and sharp edges.
  (ii) **Amorphous Solids** They have unsystematic and irregular arrangement of particles.
- On the basis of different binding forces, they are divided into four groups:
  (i) Molecular crystal or van der Waals' crystals, e.g. $I_2(s)$, $H_2O\ (s)$, etc.
  (ii) Covalent crystals or atomic crystals, e.g. graphite, diamond, etc.
  (iii) Metallic crystals, e.g. all metallic solids, etc.
  (iv) Ionic crystals, e.g. NaCl, CsCl, ZnS, etc.

NOTE Crystalline solids are **anisotropic**, i.e. their physical properties have different values in different directions while amorphous solids are **isotropic**, i.e. their physical properties have same values in different directions.

Bragg's Equation

It is the fundamental equation, which gives a simple relation among the wavelength of the X-rays, the inter planar distance in the crystal and the angle of reflection.

$$\boxed{2d \sin\theta = n\lambda}$$

where,

λ = wavelength of X-ray used.
θ = angle between incident X-rays and the plane of the crystal.
d = distance between planes of the constituent particles in a crystal.
n = an integer (1, 2, 3, 4, ...) which represents the serial order of diffracted beams.

This equation has following applications :

(i) Structure of solids are determined by X-ray diffraction methods.

(ii) Structures of complex substances such as proteins and nucleic acids are also determined by this method.

Space Lattice or Crystal Lattice

- It is an array of lattice points showing arrangement of constituent particles in different position in three dimensional space.
- There are seven crystal lattice which can be tabulated with edge length and interfacial angles as:

System	Unit cell		Example
	Lengths	Angles	(Common name)
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl (Rock salt)
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2 (Rutile)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$MgSO_4 \cdot 7H_2O$ (Epsomite)
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	$CaSO_4 \cdot 2H_2O$ (Gypsum)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$ (Potassium dichromate)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	SiO_2 (Silica)
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (Calcite)

Unit Cell

It is the smallest group of lattice points which when repeated in all directions will develop the entire lattice. It can be :

(i) **Simple unit cell** or **primitive unit cell,** in which particles are present only at corners.

$$\therefore \text{Number of atoms per unit cell} = \frac{1}{8} \times 8 = 1$$

(ii) **Face centred unit cell,** in which the particles are present at the corners as well as at the centre of each face.

$$\therefore \text{Number of atoms per unit cell} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

(ii) **Body centred unit cell,** in which the particles are present at the corners of the cube as well as one particle is present at the centre within the body.

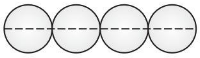
$$\therefore \text{Number of atoms per unit cell} = \frac{1}{8} \times 8 + 1 = 2$$

Packing in Solids

The packing of spheres of equal size takes place as follows:

1. One Dimensional Packing

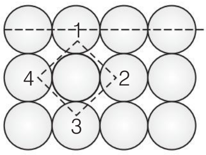
When the particles are placed in horizontal row, touching each other, an edge of the crystal is formed.



2. Two Dimensional Packing

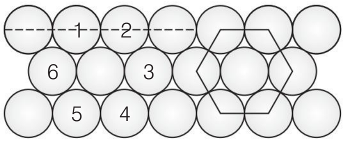
It is of two types

- **In Square Close Packing** (SCP) the particles, when placed in the adjacent rows, show a horizontal as well as vertical alignment and form squares.



Coordination number is 4 (scp)

- **In Hexagonal Close Packing** (HCP), the particles in every next row are placed in the depression between the particles of the first row. The particles in the third row will be vertically aligned with those in the first row.



Coordination number is 6 (hcp)

3. Three Dimensional Packing

It is of two types:

- **In Hexagonal Closed Packing** (HCP), the first layer is placed as layer *A* and second layer as layer *B* and the third layer becomes exactly indentical to the first layer, then the arrangement is called *AB AB* … pattern.
- **In Cubic Closed Packing** (CCP), the third layer is placed over the second layer in such a way that spheres cover the octahedral voids, a layer, different from layers *A* and *B* is produced. Let us call it as layer *C*. This pattern of stacking spheres is called *ABC ABC* … It is similar to Face Centred Cubic (FCC) packing.

Packing Efficiency

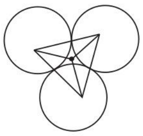
It is the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell. It is also known as packing fraction or density of packing.

$$\text{Packing fraction} = \frac{\text{volume occupied by particles of unit cell}}{\text{total volume of unit cell}}$$

The density of packing gives idea about how closely the atoms are packed in a unit cell. More be the packing efficiency, more compact is the lattice and has more force of attraction between the particles. It follows the following order fcc (74%)> bcc (68%)> simple cubic lattice (52%)> diamond (32%)

Voids

- In closely packed structures, the empty space is called interstitial site or void.

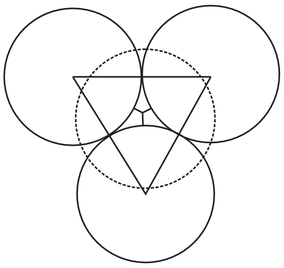


Trigonal void

- This can be a simple triangular space in the case of two dimensional packing and called the **trigonal void.**

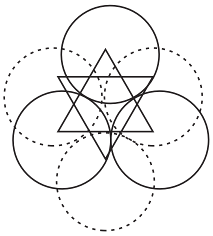
  In three dimensional close packing patterns, the voids can be of two types:

  (i) **Tetrahedral void** is a simple triangular space surrounded by 4 spheres as shown below:



Tetrahedral void

  (ii) **Octahedral void** is a double triangular void surrounded by 6 spheres as shown below:



Octahedral void

- Increasing order of void size

  Trigonal < Tetrahedral < Octahedral

- In CCP structure, number of octahedral voids $= 4$, and number of tetrahedral voids $= 8$

  $\therefore$ In general, if in a closed packed (ccp or hcp) there are N sphere (atoms or ions) in the packing then,

  Number of octahedral voids $= N$

  Number of tetrahedral voids $= 2N$

Calculations Involving Unit Cell Parameters

Relation between edge length and radius of sphere of different unit cells given below:

(i) **Simple cubic** $r = a/2$

Percentage of packing fraction $= 52\%$.

(ii) **Face centred cubic** $r = \dfrac{a}{2\sqrt{2}}$

Percentage of packing fraction $= 74\%$

(iii) **Body centred cubic** $r = \dfrac{\sqrt{3}}{4}a$

Percentage of packing fraction $= 68\%$

(iv) **Density of unit cell**

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

where, d = density

M = molecular weight

Z = number of atoms per unit cell

N_A = Avogadro number

a = edge length of unit cell

Coordination Number

It is defined as the number of atoms in a crystal which surrounds a particular atoms as its nearest atoms in its neighbour.

Structures of Some Ionic Solids

Structures of some ionic solids with their coordination numbers are given below:

(i) **Rock salt** (NaCl) fcc arrangement, coordination number $Na^+ = 6, Cl^- = 6$, e.g. LiCl, AgF,AgCl, NH_4Br, etc.

(ii) **CsCl type** (bcc arrangement) coordination number $Cs^+ = 8, Cl^- = 8$, e.g. CsCN, TiCl, TiCN, etc.

(iii) **Zinc blende** (ZnS) (ccp or fcc arrangement) coordination number $Zn^{2+} = 4, S^{2-} = 4$

e.g. CuCl, AgI, etc.

(iv) **Fluorite** (CaF_2) **type** (ccp arrangement) coordination number $Ca^{2+} = 8$, $F^- = 4$,

e.g. CdF_2, PbF_2, $BaCl_2$, $SrCl_2$.

(v) **Antifluorite** (A_2B) **type** (ccp arrangement)

coordination number $Na^+ = 4, O^{2-} = 8$, e.g. Na_2O.

NOTE On applying pressure, NaCl structure (6 : 6 coordination) changes into CsCl (8 : 8 coordination) and reverse of this occur at high temperature.

The shapes of solids can be determined by radius ratio as given in following table :

Radius ratio $\left(\frac{r_+}{r_-}\right)$	Coordination number	Structure	Example
< 0.155	2	linear	—
0.155 – 0.225	3	planar triangular	B_2O_3
0.225 – 0.414	4	tetrahedral	CuCl, CuBr
0.414 – 0.732	6	octahedral	NaBr, KBr
0.732 – 1	8	cubic	CsI, CsBr

Point Defects (Imperfections)

It is defined as any departure from perfectly ordered arrangement of atoms around a point in a crystal.

These are broadly divided into three classes :

(i) **Stoichiometric defects** are those in which imperfection in crystals are such that the ratio between the cations and the anions remain the same as described in its molecular formula. These defects are found as Schottky and Frenkel defects.

Schottky defect	Frenkel defect
It is due to equal number of cations and anions missing from the lattice sites.	It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
This results, decrease in density of crystal.	It has no effect on the density of crystal.
This type of defect is found in highly ionic compounds with high coordination number, e.g. NaCl, CsCl, AgBr, etc.	This type of defect is found in crystals, where the difference in the size of cations and anions is very large, e.g. AgCl, AgBr, ZnS, etc.

(ii) **Non-stoichiometric defects** arise when the ratio of cations and anions, due to imperfection, differ from that indicated by their molecular formula. These defects result in either excess of metal atom or excess of non-metal atom.

A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, thereby maintaining the electrical balance. The electrons, thus trapped in the anion vacancies are called ***F*-centres** because they are responsible for imparting colour to the crystals.

Doping

Addition of small amount of foreign impurity in the host crystal is known as doping. It increases the electrical conductivity.

(iii) **Impurity defects** are the defects in ionic crystals that arise due to the presence of some impurity ions in the lattice site.

- These foreign atoms are present at lattice site in substitutional solids and at vacant interstitial sites in interstitial solids.
- These defects are important in *n*-type and *p*-type semiconductors.

Electrical and Magnetic Properties of Solids

Many of the solids show electrical and magnetic properties, which can be as follows :

Electrical Properties of Solids

Solids are classified into three groups on the basis their conductivity. These are as follows:

(i) **Conductors** are the solids with conductivity range of the order of 10^4 to $10^7\ \Omega^{-1}\text{m}^{-1}$, e.g. metals.

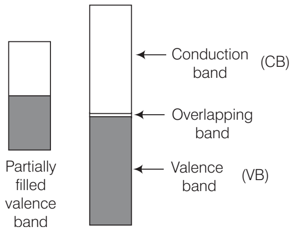
(ii) **Semiconductors** are the solids with conductivity range $10^{-6} - 10^4\ \Omega^{-1}\ \text{m}^{-1}$, e.g. semi-metals.

(iii) **Insulators** are the solids with conductivity range $10^{-20} - 10^{-10}\ (\Omega\ \text{m})^{-1}$, e.g. non-metals.

Band Theory

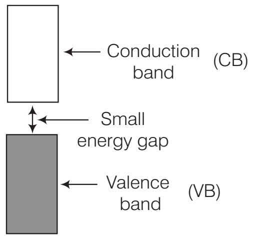
According to band theory the energy gap between the valence band and conduction band is responsible for the conduction of electricity. This can described as follows:

1. In **conductors**, the conduction band is almost overlapping with the valence band, i.e. there is no energy gap present between these two bands or valence band is not completely filled. Therefore, electrons can flow easily under the influence of electric field, in both the cases.



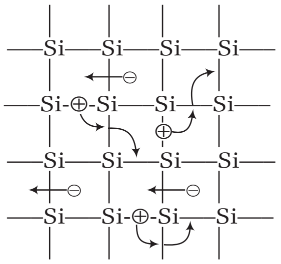
NOTE Graphite a non-metal is a good conductor of electricity because of presence of free electrons in its structure.

2. In **semiconductors**, the gap between valence band and conduction band is small and therefore, some of the electrons may jump from valence band to conduction band and some conductivity is observed. The conductivity here increases with increase in temperature due to lowering of energy gap as shown in the figure.

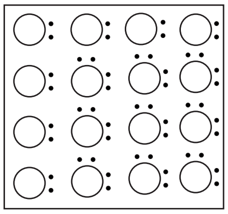


Semi-conductors are classified into following types:

- **Intrinsic Semiconductors**. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called intrinsic semiconductor (undoped).

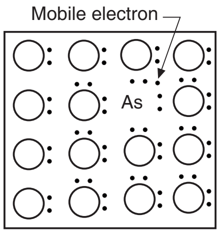


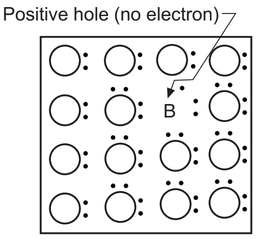
- **Extrinsic Semiconductors** For increasing conductivity of pure Si and Ge, it is doped with elements of 13 and 15 group (periodic table). Such type of conductance is called extrinsic conductance. These can be of two types, *viz*, *n*-type semiconductors and *p*-type semiconductors.



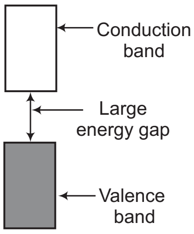
(i) **In *n*-type Semiconductor**, Group 14 elements are doped with group 15 elements. Here, *n* specifies that negative charge flows in them.

(ii) **In *p*-type Semiconductor**, Group 14 elements when doped with elements of group 13. Here, *p* specifies that conduction is passed through positive holes in them.





3. In **insulators**, the energy gap between valence band and conduction band is so large that it cannot even covered up by supplying energy in the form of heat.



Magnetic Properties of Solids

Solids can be divided into different classes depending on their response to magnetic field.

(i) **Diamagnetic substances** are weakly repelled by the magnetic field and do not have any unpaired electron.
e.g. TiO_2, V_2O_5, C_6H_6, NaCl, etc.

(ii) **Paramagnetic substances** are attracted by the magnetic field and have unpaired electrons. These lose magnetism in the absence of magnetic field. e.g. O_2, Cu^{2+}, Fe^{3+}, etc.

(iii) **Ferromagnetic substances** are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field, e.g. Fe, Co and Ni, etc.

(iv) **Antiferromagnetic substances** have net magnetic moment zero due to compensatory alignment of magnetic moments, e.g. MnO, MnO_2, Mn_2O, FeO, etc.

(v) **Ferrimagnetic substances** have a net dipole moment due to unequal parallel and antiparallel alignment of magnetic moments, e.g. Fe_3O_4, ferrites, etc.

Dielectric Properties

These are seen in insulators. They show generation of dipoles in them, when they are placed in an electric field.

These dipoles are given below:

- May align themselves in an ordered manner so that there is a net dipole moment in the crystal.
- May align themselves in such a manner that dipole moments may cancel each other.
- It is also possible that there are no dipoles in the crystal but only ions are present.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 The first order diffraction of X-rays from a certain set of crystal planes occur at an angle of 11.8° from the planes. If the planes are 0.281 nm apart, what is the wavelengths of X-rays?

(a) – 0.2180 nm (b) – 0.2044 nm
(c) – 0.1180 nm (d) – 0.3897 nm

2 Example of unit cell with crystallographic dimensions, $a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$ is

(a) calcite (b) rhombic sulphur
(c) graphite (d) monoclinic sulphur

3 In a face centred cubic lattice, atom *A* occupies the corner positions and atom *B* occupies the face centre positions. If one atom of *B* is missing from one of the face centred points, the formula of the compound is

(a) A_2B (b) AB_2
(c) A_2B_2 (d) A_2B_5

4 In a compound, atoms of element *Y* form ccp lattice and those of element *X* occupy 2/3rd of tetrahedral voids. The formula of the compound will be

(a) X_4Y_3 (b) X_2Y_3
(c) X_2Y (d) X_3Y_4

5 Iron oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by iron ions. What would be the formula of the iron oxide?

(a) FeO (b) Fe_2O_3
(c) Fe_3O_4 (d) All are possible

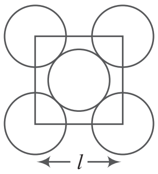
6 In a face centred cubic lattice, a unit cell is shared equally by how many unit cells?

(a) 8 (b) 4 (c) 2 (d) 6

7 An alloy of copper, silver and gold is found to have copper constituting the ccp lattice. If silver atoms occupy the edge centres and gold is present at body centre, the alloy has a formula

(a) CuAgAu (b) Cu_4Ag_2Au
(c) $CuAg_3Au$ (d) Cu_4Ag_4Au

8 The packing efficiency of the two dimensional square unit cell shown below is



(a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

9 The correct order of the packing efficiency in different types of unit cell is

(a) fcc < bcc < simple cubic (b) fcc > bcc > simple cubic
(c) fcc < bcc > simple cubic (d) bcc < fcc > simple cubic

10 If Z is the number of atoms in the unit cell that represents the closest packing sequence $ABC\ ABC$, the number of tetrahedral voids in the unit cell is equal to

(a) Z (b) $2Z$ (c) $\frac{Z}{2}$ (d) $\frac{Z}{4}$

11 What is the coordination number in a square close-packed structure in two dimensions?

(a) 2 (b) 3 (c) 4 (d) 6

12 The vacant space in bcc lattice cell is **→ CBSE-AIPMT 2015**

(a) 26% (b) 48%
(c) 23% (d) 32%

13 The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3}, while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is

(a) 5.96×10^{-1} (b) 5.96×10^{-3}
(c) 5.96 (d) 5.96×10^{-2}

14 If AgI crystallises in zinc blende structure with I^- ions at lattice points, what fraction of tetrahedral voids is occupied by Ag^+ ions?

(a) 25% (b) 50%
(c) 100% (d) 75%

15 The fraction of total volume occupied by the atoms present in a simple cube is

(a) $\frac{\pi}{6}$ (b) $\frac{\pi}{3\sqrt{2}}$ (c) $\frac{\pi}{4\sqrt{2}}$ (d) $\frac{\pi}{4}$

16 Total volume of atoms present in a face centred cubic unit cell of a metal is (r is atomic radius)

(a) $\frac{16}{3}\pi r^3$ (b) $\frac{20}{3}\pi r^3$
(c) $\frac{24}{3}\pi r^3$ (d) $\frac{12}{3}\pi r^3$

17 The edge lengths of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cell respectively are

(a) $2\sqrt{2}r, \frac{4r}{\sqrt{3}}, 2r$ (b) $\frac{4r}{\sqrt{3}}, 2\sqrt{2}r, 2r$
(c) $2r, 2\sqrt{2}r, \frac{4r}{\sqrt{3}}$ (d) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2}r$

18 AB crystallises in a body centred cubic lattice with edge length a equal to 387 pm. The distance between two oppositely charged ions in the lattice is **→ CBSE-AIPMT 2010**

(a) 335 pm (b) 250 pm
(c) 200 pm (d) 300 pm

19 CsBr crystal has bcc structure. It has an edge length of 4.3 Å. The shortest interionic distance between Cs^+ and Br^- ions is

(a) 1.86 Å (b) 2.86 Å
(c) 3.72 Å (d) 4.72 Å

20 If a is the length of the side of a cube, the distance between the body centred atom and one corner atom in the cube will be **→ CBSE-AIPMT 2014**

(a) $\frac{2}{\sqrt{3}}a$ (b) $\frac{4}{\sqrt{3}}a$
(c) $\frac{\sqrt{3}}{4}a$ (d) $\frac{\sqrt{3}}{2}a$

21 A metal crystallises with a face centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is **→ CBSE-AIPMT 2012**

(a) 288 pm (b) 408 pm (c) 144 pm (d) 204 pm

22 A given metal crystallises out with a cubic structure having edge length of 361 pm. If there are four metal atoms in one unit cell, what is the radius of one atom? **→ CBSE-AIPMT 2015**

(a) 40 pm (b) 127 pm
(c) 80 pm (d) 108 pm

23 A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-2}. The molar mass of the metal is
$[N_A = 6.02 \times 10^{23}\ mol^{-1}]$ **→ NEET 2013**

(a) 30 g mol^{-1} (b) 27 g mol^{-1}
(c) 20 g mol^{-1} (d) 40 g mol^{-1}

24 A metallic element has a cubic lattice. Each edge of the unit cell is 2Å. The density of the metal is 2.5 gcm^{-3}. The unit cells in 200 g of metal are

(a) 1×10^{24} (b) 1×10^{20}
(c) 1×10^{22} (d) 1×10^{25}

25 The following crystallographic data were obtained for a protein. Volume of unit cube $= 1.50 \times 10^{-19}$ cm^3.
Density = 1.35 gcm^3, Z = 4 and protein fraction=0.75. Thus, molar mass of protein is

(a) 2.3×10^4 g mol^{-1} (b) 3.048×10^4g mol^{-1}
(c) 1.725×10^4g mol^{-1} (d) None of these

26 Lithium has a bcc structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal.
$(N_A = 6.02 \times 10^{23} \text{ mol}^{-1})$ → **NEET 2016, Phase I**

(a) 352 pm
(b) 527 pm
(c) 264 pm
(d) 154 pm

27 In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are → **NEET 2016, Phase II**

(a) 4 and 2
(b) 6 and 6
(c) 8 and 4
(d) 4 and 8

28 The Ca^{2+} and F^- are located in CaF_2 crystal respectively at body centred cubic lattice points and in

(a) tetrahedral voids
(b) half tetrahedral voids
(c) octahedral
(d) half of octahedral voids

29 The structure of TlCl is similar to CsCl. What would be the radius ratio in TlCl?

(a) 0.155-0.225
(b) 0.225-0.414
(c) 0.414-0.732
(d) 0.732-1.00

30 The ionic radii of Rb^+ and I^- are 1.46 Å and 2.16 Å. The most probable type of structure exhibited by it is

(a) CsCl type
(b) ZnS type
(c) NaCl type
(d) CaF_2 type

31 The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is → **NEET 2016, Phase I**

(a) 4
(b) 8
(c) 2
(d) 6

32 The correct statement regarding defects in the crystalline solid is → **CBSE-AIPMT 2015**

(a) Schottky defects have no effect on the density of crystalline solids
(b) Frenkel defects decreases the density of crystalline solids
(c) Frenkel defect is a dislocation defect
(d) Frenkel defect is found in halides of alkaline metals

33 Which is the incorrect statement? → **NEET 2017**

(a) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect
(b) Density decreases in case of crystals with Schottky's defect
(c) NaCl(s) is insulator, silicon is semiconductor, silver is conductor, quartz is piezoelectric crystal
(d) Frenkel defect is favoured in those ionic compounds in which sizes of cation and anions are almost equal

34 Which one of the following has Frenkel defect?

(a) NaCl
(b) AgBr
(c) Graphite
(d) Diamond

35 If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be
$(N_A = 6.02 \times 10^{23} \text{mol}^{-1})$

(a) $6.02 \times 10^{22} \text{ mol}^{-1}$
(b) $6.02 \times 10^{15} \text{ mol}^{-1}$
(c) $6.02 \times 10^{17} \text{ mol}^{-1}$
(d) $6.02 \times 10^{14} \text{ mol}^{-1}$

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The number of hexagonal faces that are present in truncated octahedron is

(a) 2
(b) 4
(c) 6
(d) 8

2 An element occurring in the bcc structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cells will be

(a) 6.04×10^{23}
(b) 12.08×10^{23}
(c) 24.16×10^{23}
(d) 36.18×10^{23}

3 Which of the following statements is not true?

(a) Paramagnetic substances are weakly attracted by magnetic field
(b) Ferromagnetic substances cannot be magnetised permanently
(c) The domains in anti-ferromagnetic substances are oppositely oriented with respect to one another
(d) Pairing of electrons cancles their magnetic moment in the diamagnetic substances

4 In a solid AB having the NaCl structure, 'A'-atom occupies the corners of the cubic unit cell. If all the face centred atom along one of the axis are removed, then the resultant stoichiometry of the solid is

(a) AB_2
(b) A_2B
(c) A_4B_3
(c) A_3B_4

5 How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?
(atomic masses; Na = 23, Cl = 35.5)

(a) 1.28×10^{21} unit cells
(b) 1.71×10^{21} unit cells
(c) 2.57×10^{21} unit cells
(d) 5.14×10^{21} unit cells

6 Each rubidium halide crystallising in the NaCl-type lattice has a unit cell length 0.30 Å greater than that for corresponding potassium salt ($r_{(K^+)} = 1.33$ Å) of the same holagen. Hence, ionic radius of Rb^+ is

(a) 1.18 Å
(b) 1.48 Å
(c) 1.63 Å
(d) 1.03 Å

7 The cubic unit cell of a metal (molar mass = 63.55 g mol^{-1}) has an edge length of 362 pm. Its density is 8.92 g cm^{-3}. The type of unit cell is

(a) primitive
(b) face centred
(c) body centred
(d) end centred

8 Which of the following statements about amorphous solids is not true?

(a) On heating, they may become crystalline at a certain temperature
(b) They may become crystalline on keeping for a long time
(c) Amorphous solids can be moulded by heating
(d) They are anisotropic in nature

9 The unit cell of a binary alloy composed of *A* and *B* metals has a ccp structure with *A* atoms occupying the corners and *B* atoms occupying centres of each face of the cube. If during the crystallisation of this alloy, in the unit cell, two *A* atom are missing, the overall composition per unit cell is

(a) AB_8
(b) AB_6
(c) A_6B_{24}
(d) AB_4

10 Sodium crystallises in bcc arrangement with the interfacial separation between the atoms at the edge 53 pm. The density of the soild is

(a) 1.23 g/cc
(b) 485 g/cc
(c) 4.85 g/cc
(d) 123 g/cc

11 Ferrous oxide has cubic structure. The edge length of the unit cell is 5Å. The density of the oxide is 4.0 gcm^{-3}. The number of Fe^{2+} and O^{2-} ions present in each unit cell will be

(a) two Fe^{2+} and two O^{2-}
(b) two Fe^{2+} and four O^{2-}
(c) four Fe^{2+} and four O^{2-}
(d) four Fe^{2+} and two O^{2-}

12 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) A_2B
(b) AB_2
(c) AB_4
(d) AB

13 Iron exhibits bcc structure at room temperature. Above 900° C, it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900° C (assuming molar mass and atomic radii of iron remains constant with temperature) is **→ NEET 2018**

(a) $\frac{3\sqrt{3}}{4\sqrt{2}}$
(b) $\frac{4\sqrt{3}}{3\sqrt{2}}$
(c) $\frac{\sqrt{3}}{\sqrt{2}}$
(d) $\frac{1}{2}$

14 In which of the following structures coordination number for cations and anions in the packed structure will be same?

(a) Cl^- ions form fcc lattice and Na^+ ions occupy all octahedral voids of the unit cell
(b) Ca^{2+} ions form fcc lattice and F^- ions occupy all the eight tetrahedral voids of the unit cell
(c) O^{2-} ions form fcc lattice and Na^+ ions occupy all the eight tetrahedral voids of the unit cell
(d) S^{2-} ions form fcc lattice and Zn^{2+} ions go into alternate tetrahedral voids of the unit cell

ANSWERS

SESSION 1	**1** (d)	**2** (d)	**3** (d)	**4** (a)	**5** (b)	**6** (d)	**7** (c)	**8** (d)	**9** (b)	**10** (b)
	11 (c)	**12** (d)	**13** (b)	**14** (b)	**15** (a)	**16** (a)	**17** (a)	**18** (a)	**19** (c)	**20** (d)
	21 (a)	**22** (b)	**23** (b)	**24** (d)	**25** (a)	**26** (a)	**27** (c)	**28** (a)	**29** (d)	**30** (c)
	31 (d)	**32** (c)	**33** (a,d)	**34** (b)	**35** (c)					

SESSION 2	**1** (d)	**2** (c)	**3** (b)	**4** (a)	**5** (c)	**6** (b)	**7** (b)	**8** (d)	**9** (c)	**10** (a)
	11 (c)	**12** (b)	**13** (a)	**14** (a,d)						

Hints and Explanations

SESSION 1

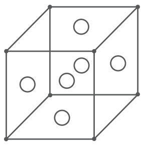
1 From Bragg's equation,

$$\lambda = \frac{2d\sin\theta}{n} = \frac{2 \times 0.281 \times \sin 11.8}{1}$$
$$= 2 \times 0.281 \times -0.6935$$
$$= -0.3897\,\text{nm}$$

2 Monoclinic sulphur is an example of monoclinic crystal system.
(i.e. $a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$).

3 Number of atoms (A) per unit cell

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



Number of atoms (B) per unit cell

$$= (6-1) \times \frac{1}{2} = \frac{5}{2}$$

(one atom B is missing)
Thus, formula is $A_1B_{5/2} = A_2B_5$.

4 Suppose atoms of element Y in ccp $= 100$
Number of tetrahedral voids $= 2 \times 100$
Number of atoms of element

$$X = \frac{2}{3} \times 200 = \frac{400}{3}$$
$$\frac{X}{Y} = \frac{400}{300}$$

and Formula $= X_4Y_3$

5 There is one octahedral hole for each atom in hexagonal close packed arrangement. If the number of oxide ions (O^{2-}) per unit cell is 1, then the number of Fe^{3+} ions $= 2/3 \times$ octahedral holes $= 2/3 \times 1 = 2/3$. Thus, the formula of the compound $= Fe_{2/3}O_1$ or Fe_2O_3.

6 In a face centred cubic lattice, a unit cell is shared equally by six unit cells.

7 Number of Cu-atoms at corners

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

Number of Ag-atoms at edge centres

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

Number of Au-atoms at body centre

$$= 1 \times 1 = 1$$

$\therefore$ Formula is $CuAg_3Au$.

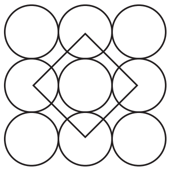
8 $a = (2\sqrt{2}r)$, Packing fraction

$$= \frac{2 \times \pi r^2}{(2\sqrt{2}r)^2} = \frac{2\pi r^2}{8r^2}$$
$$= \frac{\pi}{4} = \frac{3.14}{4} = 0.7854 = 78.54\%$$

9 Packing efficiency
For sc unit cell $= 52\%$
For bcc unit cell $= 68\%$
For fcc unit cell $= 74\%$
Thus, the order of packing efficiency is fcc > bcc > sc

10 Number of tetrahedral voids
$= 2 \times$ number of spheres in unit cell
$= 2 \times Z = 2Z$

11 Square close-packing in two dimension can be shown as



Thus, coordination number is 4 as each atom is surrounded by four other atoms.

12 $\because$ Packing efficiency in bcc lattice $= 68\%$
$\therefore$ Vacant space in bcc lattice $= 100 - 68 = 32\%$

13 The fraction of unoccupied site in sodium chloride crystal

$$= \frac{\text{X-ray density} - \text{pyknometric density}}{\text{X-ray density}}$$
$$= \frac{2.178 \times 10^3 - 2.165 \times 10^3}{2.178 \times 10^3}$$
$$= \frac{0.013 \times 10^3}{2.178 \times 10^3} = \frac{13}{2178} = 5.96 \times 10^{-3}$$

14 In AgI crystal, number of Ag^+ ions is equal to I^- ions. However, the number of tetrahedral voids are twice the number of atoms forming the cubic lattice.
Number of tetrahedral voids occupied by Ag^+ ion $= 50\%$.

15 Radius $(r) = \frac{a}{2}$

$$\text{Volume of atom} = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3$$
$$\text{Packing fraction} = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6}$$

16 In fcc, number of unit cells $= 4$
$\therefore$ Volume occupied by sphere

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

17 For fcc, $a = 2\sqrt{2}r$, for bcc, $a = \frac{4r}{\sqrt{3}}$ and for scc, $a = 2r$.

18 For body centred cubic (bcc) lattice, distance between two oppositely charged ions,

$$d = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 387}{2}\ \text{pm}$$
$$= 335.15\ \text{pm}$$

19 Closest approach in bcc lattice

$$= \frac{1}{2}\ \text{of body diagonal}$$
$$= \frac{1}{2} \times \sqrt{3}a = \frac{\sqrt{3}}{2} \times 4.3$$
$$= 3.72\ \text{Å}$$

20 Half of body diagonal $= \frac{\sqrt{3}a}{2}$

21 For fcc lattice,

$$4r = \sqrt{2}a$$
$$r = \frac{\sqrt{2}}{4}a = \frac{a}{2\sqrt{2}} = \frac{408}{2\sqrt{2}} = 144\,\text{pm}$$

Diameter $(d) = 2r = 2 \times 144\,\text{pm}$
$= 288\,\text{pm}$

22 Given, edge length $= 361\,\text{pm}$
Four metal atoms in one unit cell, i.e. effective number in unit cell (Z)
$= 4$ (given)
$\therefore$ It is a fcc structure
$\therefore$ Face diagonal $= 4r$

$$\sqrt{2}a = 4r$$
$$r = \frac{\sqrt{2} \times 361}{4} = 127\ \text{pm}$$

23 The density of a unit cell,

$$d = \frac{Z \times M}{N_A \times a^3}$$
$$M = \frac{d \times N_A \times a^3}{Z}$$
$$= \frac{2.72 \times 6.02 \times 10^{23} \times (404 \times 10^{-10})^3}{4}$$
$$= 26.99 \approx 27\ \text{g/mol}$$

24 Number of unit cells

$$= \frac{\text{Mass of metal}}{\text{Mass of one unit cell}}$$

Given, edge length of unit cell

$$= 2\text{Å} = 2 \times 10^8\text{cm}$$

Mass of metal = 200 g

Density of metal = 2.5 g cm^{-3}

Volume of unit cell

$$= (\text{edge length})^3 = (2 \times 10^{-8})^3$$
$$= 8 \times 10^{-24} \text{ cm}^3$$

Mass of one unit cell

$$= \text{volume} \times \text{density}$$
$$= 8 \times 10^{-24} \times 2.5 = 20 \times 10^{-24}$$

$\therefore$ Number of unit cells in 200 g metal

$$= \frac{\text{mass of metal}}{\text{mass of one unit cell}}$$
$$= \frac{200}{20 \times 10^{-24}}$$
$$= 10 \times 10^{24} = 1.0 \times 10^{25}$$

25 Density $(d) = \dfrac{MZ}{N_0 a^3}$

$$\therefore \quad M = \frac{dN_0 a^3}{Z}$$
$$= 3.048 \times 10^4 \text{ g mol}^{-1}$$

Since, protein fraction is 0.75, hence M (protein) $= 3.048 \times 10^4 \times 0.75$

$$= 2.286 \times 10^4$$
$$= 2.3 \times 10^4 \text{ g mol}^{-1}$$

26 Given, Li has a bcc structure.

Density $(\rho) = 530 \text{ kg-m}^{-3}$

Atomic mass $(M) = 6.94 \text{ g mol}^{-1}$

Avogadro's number (N_A)

$$= 6.02 \times 10^{23} \text{ mol}^{-1}$$

We know that, number of atoms per unit cell in bcc $(Z) = 2$.

$\therefore$ We have the formula for density,

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

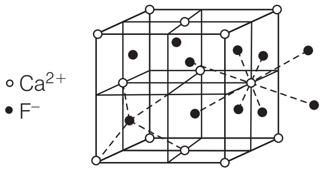
where, a = edge-length of a unit cell.

or $a = \sqrt[3]{\dfrac{ZM}{\rho N_A}}$

$$= \sqrt[3]{\frac{2 \times 6.94 \text{ g mol}^{-1}}{0.53 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1}}}$$
$$= \sqrt[3]{4.35 \times 10^{-23} \text{ cm}^{-3}} = 3.52 \times 10^{-8} \text{ cm}$$

a = 352 pm

27 In CaF_2 (Fluorite structure), Ca^{2+} ions are arranged in ccp arrangement (Ca^{2+} ions are present at all corners and at the centre of each face of the cube), while F^- ions occupy all the tetrahedral sites.



From the above figure, you can clearly see that coordination number of F^- is 4, while that of Ca^{2+} is 8.

28 In CaF_2, radius ratio = 0.73

It indicates that CaF_2 belongs to body centred cubic. But in fluorite, the Ca^{2+} ions are too small to touch each other, hence the structure is not strictly close packed structure. Relative positions of Ca^{2+} ions are like ions in cubic close packed structure, in which all the tetrahedral voids are occupied by F^- ions.

29 Radius ratio in TlCl is 0.732 – 1.000 and coordination number is 8 and arrangement is body centred cubic.

30.

Radius ratio	Coordination number	Example
0.155 - 0.225	3	B_2O_3
0.225 - 0.414	4	ZnS
0.414 - 0.732	6	NaCl
0.732-1	8	CsCl

In ionic solids, the shape of crystal depends upon relative size of ions.

Given, $r_{c^+}(\text{Rb}^+) = 1.46$ Å

$$r_{a^-}(\text{I}^-) = 2.16 \text{ Å}$$
$$\therefore \quad \frac{r_{c^+}}{r_{a^-}} = \frac{1.46}{2.16} = 0.676$$

$\therefore$ It will have coordination number 6 and structure will be same as NaCl.

31 Given, ionic radius of cation (A^+)

$$= 0.98 \times 10^{-10} \text{ m}$$

Ionic radius of anion (B^-)

$$= 1.81 \times 10^{-10} \text{ m}$$

Coordination number of each ion in AB = ?

Now, we have

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$
$$= \frac{0.98 \times 10^{-10} \text{ m}}{1.81 \times 10^{-10} \text{ m}} = 0.541$$

If radius ratio range is in between 0.441 – 0.732, ion would have octahedral structure with coordination number 'six'.

32 In Frenkel defect, ions in solids dislocate from their positions. Hence, Frenkel defect is a dislocation defect.

33 (a) $\text{FeO}_{0.98}$ has non-stoichiometric metal excess defect. It occurs due to missing of a negative ion from its lattice site, thus leaving a hole which is occupied by an electron. Non-stoichiometric ferrous oxide is $\text{FeO}_{0.93-0.96}$ and it is due to metal deficiency defect. Thus, statement (a) is incorrect.

(d) In an ionic crystal, when an ion is missing from its lattice site and occupies interstitial site, the defect is called Frenkel' defect. This type of defect is seen in those crystals where the difference in the size of cations and anions is very large and their coordination number is low. Thus, statement (d) is incorrect.

34 AgBr exhibits Frenkel-defect due to large difference in the size of Ag^+ and Br^- ions.

35 Due to addition of SrCl_2, each Sr^{2+} ion replaces two Na^+ ions, but occupies only one Na^+ lattice point. This makes one cation vacancy.

Number of moles of cation vacancies in 100 mol of NaCl $= 10^{-4}$

Number of moles of cation vacancies in

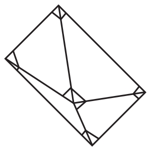
$$1 \text{ mol} = \frac{10^{-4}}{100} = 10^{-6}$$

The total cation vacancies

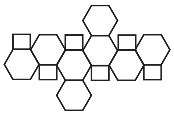
$$= 6.02 \times 10^{23} \times 10^{-6}$$
$$= 6.02 \times 10^{17} \text{mol}^{-1}$$

SESSION 2

1 The truncated octahedron is the 14 faced archimedean solid, with 14 total faces : 6 squares and 8 regular hexagons. The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron.



Truncated octahedron



Truncated octahedron unfolded in two dimensions

2 There are two atoms in a bcc unit cell so, number of atoms in 12.08×10^{23} unit cells

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

3 Ferromagnetic substances can be magnetised by applying magnetic field to it and magnetic property persist within it even after removal of magnetic field. Hence, choice (b) is not the correct answer, while other. three choices are correct

4 AB has fcc type structure.

Atoms at corner $(A) = \frac{8}{8} = 1$

Atoms at face $= \frac{4}{2} = 2$

Since, atoms B at face B removed Hence AB_2

5 Number of formula units of NaCl

$$= \frac{1}{58.5} \times 6.023 \times 10^{23}$$
$$= 1.029 \times 10^{22}$$

A unit cell contains $4Na^+$ and $4Cl^-$ ions.

$$\text{Unit cell} = \frac{1.029 \times 10^{22}}{4}$$
$$= 2.57 \times 10^{21} \text{ unit cells.}$$

6 There is increase in 0.30Å unit length. This is due to two atoms at the corners.

Thus, $r^+_{Rb} = 1.33\text{Å} + \frac{0.30\text{Å}}{2} = 1.48\text{Å}$

7 Density $(d) = \frac{z \times M}{N_a \times a^3}$

Given, $a = 362$ pm

$$= 362 \times 10^{-12} \text{ m}$$
$$= 362 \times 10^{-10} \text{ cm}$$
$$M = 63.55 \text{ g mol}^{-1},$$
$$d = 8.92 \text{ g cm}^{-3},$$
$$z = ?$$

$$\therefore \quad z = \frac{d \times N_a \times a^3}{M}$$

$$= \frac{8.92 \times 6.023 \times 10^{23} \times (362 \times 10^{-10})^3}{63.55}$$

$= 4$

i.e., the metal crystallises in fcc.

8 Amorphous solids are isotropic in nature, because it has no long range order and any physical property will be same for all characteristic feature of crystalline solids.

Hence, option 'd' is not true.

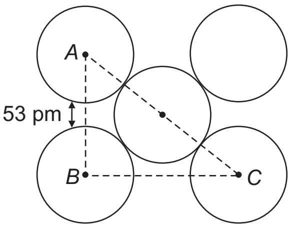
9 Permitted coordination number for ccp is 8, but $2A$ atoms are missing

$\therefore$ Contribution of $A = 6 \times \frac{1}{8} = \frac{6}{8}$

Contribution of $B = 6 \times \frac{1}{2} = 3$

So, $A_{6/8} B_3$ or $A_6 B_{24}$

10 Given, $(a - 2r) = 53$ pm ...(i)



The spheres at the corners are not touching each other.

For bcc structure,

$$4r = \sqrt{3}a \text{ or } 2r = \frac{\sqrt{3}}{2} a$$

$$\Rightarrow a - \frac{\sqrt{3}}{2} a = 53$$

$$\therefore \quad a = 395.6 \text{ pm}$$
$$395.6 \times 10^{-12} \text{ m}$$
$$= 395.6 \times 10^{-10} \text{ cm}$$
$$= 3.956 \times 10^{-8} \text{ cm}$$

Density $(d) = \frac{zM}{Na^3}$

$$d = \frac{2 \times 23}{6.023 \times 10^{23} \times (3.956)^3 \times 10^{-24}}$$
$$= 1.23 \text{ g/cc}$$

11 We have, $d = \frac{Z \times M}{N_0 \times V}, Z = ?$

$$\therefore \quad Z = \frac{d \times N_0 \times V}{M}$$

$a = 5\text{Å} = 5 \times 10^{-8}$cm

Molecular mass, $M = 56 + 16$

$= 72$ g/mol,

$N_0 = 6.023 \times 10^{23}$

$V = a^3 = 125 \times 15^{-24}$cm, $d = 4$ g/cm^3

$$\therefore Z = \frac{4 \times 6.023 \times 10^{23} \times 125 \times 10^{-24}}{72}$$
$$= 4.16 = 4$$

$Z = 4$, i.e four molecules of ferrous oxide (FeO) are present, which gives four Fe^{2+} and four O^{2-} ions. Hence, the correct answer is (c).

12 No. of B^- ions in unit cell

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

Now, A^+ ion occupies 25% of octahedral holes $= \frac{8 \times 25}{100} = 2$

Thus, ratio of B^- to A^+ is 2 : 1 or formula is AB_2.

13 Density of unit cell $d = \frac{Z \times M}{N_A \times a^3}$

where, Z = Number of atoms per unit cell

M = Molar mass

a^3 = Volume of unit cell

[a = edge length]

N_A = Avogadro's number

$= 6.022 \times 10^{23}$

For bcc, $Z = 2$, radius $(r) = \frac{\sqrt{3}a}{4}$

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

For fcc, $Z = 4$, $r = \frac{a}{2\sqrt{2}}$

$$\Rightarrow \quad a = 2\sqrt{2}\, r$$

According to question.

$$\frac{d_{\text{room temp.}}}{d_{900°\text{C}}} = \frac{\left(\frac{ZM}{N_A a^3}\right)_{\text{bcc}}}{\left(\frac{ZM}{N_A a^3}\right)_{\text{fcc}}}$$

On substituting the given values, we get $\frac{d_{\text{room temp.}}}{d_{900°\text{C}}}$

$$= \frac{2 \times M}{N_A \times \left(\frac{4r}{\sqrt{3}}\right)^3} \Bigg/ \frac{4 \times M}{N_A \times (2\sqrt{2}r)^3}$$

[$\because$ Given, M and r of iron remains constant with temperature]

$$= \frac{2 \times 3\sqrt{3}}{64 r^3} \times \frac{16\sqrt{2}\, r^3}{4}$$

$$\frac{d_{\text{bcc}}}{d_{\text{fcc}}} = \frac{3}{4}\sqrt{\frac{3}{2}}$$

14 NaCl crystal have rock salt structure having fcc lattice in which Cl^- ions are present at fcc lattice point and at face centres and Na^+ occupies all the octahedral void of given unit cell.

Where, coordination number of $Na^+ = 6$

coordination number of $Cl^- = 6$

Similarly, co-ordination for Zn^{2+} and S^{2-} are 4.