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Crystallography

The solid state : The physical state of matter in which the constituent molecules, atoms or ions have no translatory motion although they vibrate about the fixed position, that they occupy in a crystal lattice.

A solid is said to possess cohesion forces, remaining in the same shape unless changed by certain forces. Solids are of two types:

1. Crystalline solids : A crystalline solid has a definite melting point at which it becomes liquid, bounded by well defined plane faces, having same geometry irrespective of the source from which they have been obtained.

2. Amorphous solids : Amorphous solids have no precise melting point but when heated, become increasingly pliable until they assume the properties usually associated with liquids; they are super-cooled liquids in which the force of attraction holding the molecules together is so great that the material is rigid but there is **no regularity of structure.**

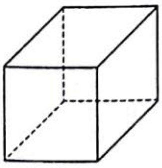
Crystal : A crystalline solid consists of a large number of unit cells, called crystal, each of which possess a definite geometric shape bounded by plane faces. The crystals of a given substance produced under a definite set of conditions are always of the same shape. On the change of condition, one crystalline form of a given substance may change into another altogether different crystalline form.

External features of crystals : The salient external features of crystals are given below :

1. Faces : Crystals are bounded by a number of surfaces which are generally perfect, flat. These are known as faces. Faces are of two types:

Like : All faces are alike, *e.g.*, Fluorspar.

Unlike : All faces are not alike, *e.g.*, Galena.



Fluorspar
Fig.1

Galena
Fig.2

2. Form : All the faces corresponding to a crystal are said to constitute a form.

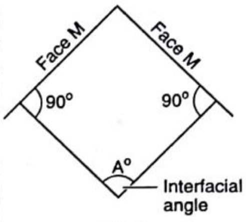


Fig. 3

3. Edges and interfacial angle : An edge is formed by the intersection of two adjacent faces where the angle between any two faces of crystal is known as interfacial angle.

The crystals are bounded by plane faces (F), straight edges (e) and interfacial angle (c). The relationship between these can be given as,

$$F + c = e + 2$$

4. Zone and zone axis : The faces of a crystal occur in sets called zones, which meet in parallel edges or would do so if the planes of the faces were extended. Each zone forms a complete belt around the crystal.

A line drawn through the centre of a crystal in a direction parallel to the edge of a zone is called the zone axis.

Elements of symmetry in crystals

(a) Plane of symmetry : A crystal is said to have a plane of symmetry when an imaginary plane passing through the centre of crystal can divide it into two parts such that one is the exact mirror image of the other.

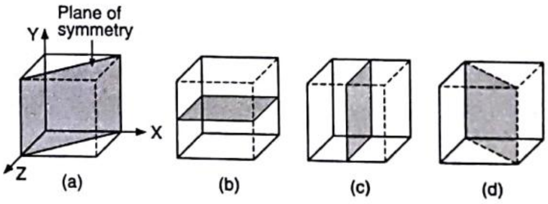


Fig. 4 Plane of symmetry

(b) Axis of symmetry : It is a line about which the crystal may be rotated so that it represents the same appearance more than once during a complete revolution. If the equivalent configuration occurs twice, thrice, four and six times, *i.e.*, after rotation of 180°, 120°, 90° and 60°, the axis of rotation are known as two-fold (diad), three-fold (triad), four-fold (tetrad) and six-fold (hexad), axes of symmetry respectively.

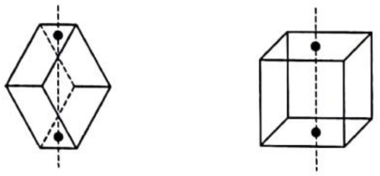

(a) (b)

Fig. 5 Axes of symmetry

(c) Centre of symmetry : It is a point when any line drawn through it meets the surface of the crystal at equal distances on either side. A crystal may possess a number of planes or axes of symmetry but it can have only one centre of symmetry.


(a) (b)

Fig. 6 Centre of symmetry

The total number of planes, axes and centres of symmetry possessed by a crystal is termed as elements of symmetry. A **cubic crystal possess a total of 23 elements of symmetry.**

$$\text{Plane of symmetry} = 3 + 6 = 9$$
$$\text{Axis of symmetry} = 3 + 4 + 6 = 13$$
$$\text{Centre of symmetry} = 1$$
$$\therefore \quad \text{Total elements of symmetry} = 9 + 13 + 1 = \mathbf{23}$$

Unit Cell : For every crystal lattice, it is possible to select a group of lattice points which sets the pattern for a whole lattice. This three dimensional group of points is called unit cell of a crystal and is characterised by the distances a, b and c and angles α, β and γ. The whole crystal can be developed by a step wise shifting of the unit cells in all the three dimensions. In simple cubic there is only one atom, in body-centred cubic (bcc) there are two atoms and in face-centred cubic (fcc) there are four atoms. The array of points showing how molecules, atoms or ions are arranged in different sites in three dimensional space is referred as **space** lattice.

In various unit cells, there are three kinds of **lattice points :** Points located at the corners; points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corners and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell :

(i) A point that lies at the corner of unit cell is shared among eight unit cells and thus, it contributes for 1/8 of each such point to unit cell.

(ii) A point along an edge is shared by four unit cells and thus contribute for 1/4 of each such point to unit cell.

(iii) A face-centred point is shared by two unit cells and thus contributes for 1/2 of each such point to unit cell.

(iv) A body-centred point lies entirely within the unit cell and thus contributes for one each such point to unit cell.

Note : (a) The simple cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} = 1$$

(b) The body centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore \qquad n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

(c) The face centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore \qquad n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

The coordination number : The number of nearest neighbours for any particular atom in a space lattice is called the coordination number. In diamond the coordination number is 4. In simple cubic crystal like NaCl it is 6. In bcc crystal like CsCl it is 8. Here Cs^+ is at the body-centre of a cube of Cl^- and Cl^- at the body-centre of cube of Cs^+. In cubic close packed and hexagonal close packed, the coordination number is 12.

The ratio of the radius of cation and anions (r^+/r^-) : The coordination number of an ion in closed packed structures depends on the ratio of the radius of ion with respect to the radius of the ions surrounding it. In case of ionic solids, the radius ratio $[r^+/r^-]$ is the ratio of the cation to anion radius.

Minimum ionic radius ratio	Geometry	Coordination number
0.225 to 0.414	tetrahedral	4
0.414 to 0.732	octahedral	6
0.732 to above	cubic	8

Usually cations are smaller than anions and hence the cations usually fill the voids and anions surrounds them.

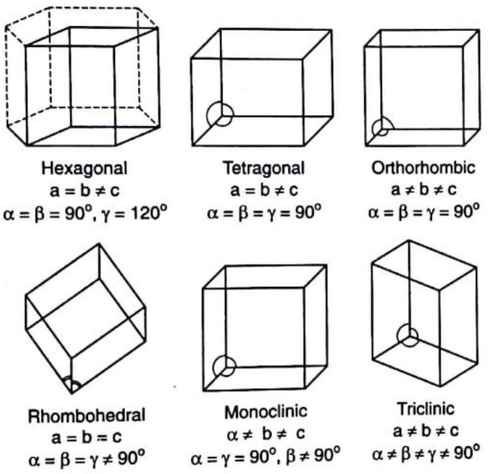
Crystal systems : The different possible geometrical shape of crystal lattice (or crystals) are called crystal systems.

On the basis of above facts and laws there are 230 crystal forms which are grouped on the basis of their symmetry into 32 classes. The 32 classes are then broadly referred to seven crystal systems (Fig. 7) given below in Table 1.

Table-1. Seven Crystal Systems

System	Axial distance	Axial angles	Maximum symmetry elements	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Nine planes, thirteen axes	NaCl, KCl, CaF_2, ZnS, diamond, alums
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Five planes, five axes	TiO_2, ZnO_2, SnO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Three planes, three axes	Rhombic Sulphur, $BaSO_4$, KNO_3
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	One plane, one axis	$Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, monoclinic sulphur
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Seven planes, seven axes	Mg, PbI_2, CdS, ZnO, HgS, Graphite
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	—do—	Calcite, $NaNO_3$, ICl
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	No plane, no axis	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3

Cubic crystals have three patterns of Bravais lattice in which crystals are formed:



Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

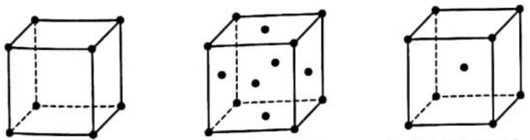
Monoclinic
$\alpha \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$

Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Fig. 7

(i) Simple cubic in which one atom (ion) is at the corner of a cube Fig. 8(a).

(ii) Face-centred cubic (fcc) in which the atoms are not only at the corner of the cube but there are atoms in the face of the cube also. Fig. 8 (b).



Simple cubic
(a)

Face-centred
(b)

Body-centred
(c)

Fig. 8

(iii) Body-centred cubic (bcc) in which one atom is placed at the centre which is not shared by any other cube. Fig. 8 (c).

One can think of the atoms (ions) as spheres which are arranged in two different ways:

(i) Cubic close packing (ccp) Fig. 9 (a), (ii) Hexagonal close packing (hcp) Fig. 9 (b), (iii) Body-centred cubic packing (bccp) Fig. 9 (c).

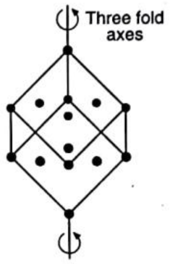


Fig. 9 (a) Cubic close packing

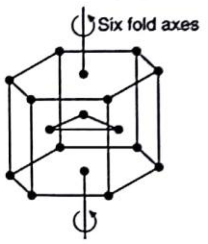


Fig. 9 (b) Hexagonal close packing

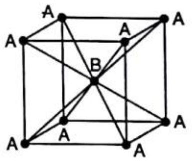


Fig. 9 (c) Body-centred close packing

Some Applications of Crystallographic Studies:

(i) Density of crystalline solids :

$$\text{Density of the unit cell} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell } (V)} \qquad ...(1)$$

Also, Mass of the unit cell

$$= \text{No. of atoms in unit cell } (n) \times \text{Mass of each atom}$$

$$= \text{No. of atoms in unit cell } (n) \times \frac{\text{Atomic mass}}{\text{Av. No.}} \qquad ...(2)$$

∴ By Eqs. (1) and (2),

$$\text{Density of unit cell} = \frac{n \times \text{atomic mass}}{\text{Av. no.} \times V} = \frac{n \times \text{atomic mass}}{\text{Av. no.} \times a^3} \qquad \ldots(3)$$

Where volume of cubic unit cell $= a^3$ and a is edge length of unit cell.

(ii) Radii of the ion : If the edge length of the cubic cell is known, ionic radii for the ion in the crystal lattice can be calculated.

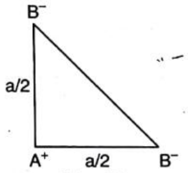


Fig. 10

Where a is edge length of cubic cell.

Thus, radius of B^-

$$= \frac{\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}}{2} = \frac{a}{2\sqrt{2}}$$

(iii) Radii of metal atoms : If a is the length of unit cell, then

(a) For simple cubic lattice : Radius of metal atom $= \frac{a}{2}$

(b) For bcc lattice : Radius of metal atom $= \frac{\sqrt{3}a}{4}$

(c) For fcc lattice : Radius of metal atom $= \frac{a}{2\sqrt{2}}$

(iv) Packing density :

$$\text{Packing density} = \frac{\text{Volume of atom in unit cell}}{\text{Volume of unit cell}}$$

(a) In sc structure : Packing density $= 0.52$

(b) In fcc structure : Packing density $= 0.74$

(c) In bcc structure : Packing density $= 0.68$

The Bragg's equation : The diffraction pattern obtained during X-ray diffraction resulting from the scattering of X-rays by a regular arrangement of atoms or ions has been interpreted in terms of Bragg's equation :

$$n\lambda = 2d\sin\theta \qquad \ldots(1)$$

(Bragg's equation)

where n is an integer (1, 2, 3, ...); λ is the wavelength of X-rays used, d is the distance of separation between the planes of atoms, θ is the angle at which constructive interference occurs.

It is evident from Bragg's equation, if $2d < n\lambda$ then $\sin\theta > 1$ which is not possible.

• NUMERICAL PROBLEMS •

1. Calculate the number (n) of atoms contained within (a) cubic cell (b) a body-centred cubic cell (c) a face-centred cubic cell.

2. The figures given below show the location of atoms is three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **(IIT 2000)**

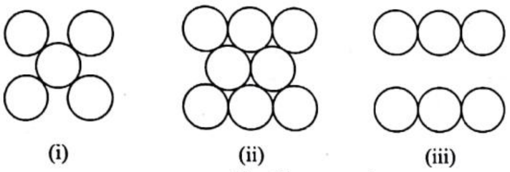

(i) (ii) (iii)

Fig. 11

3. A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?

4. A solid made up of A and B atoms has atoms A in ccp arrangement. Atoms of B occupy all the octahedral voids and half the tetrahedral voids. Suggest the formula of compound.

5. In an ionic oxide, oxide ions are arranged in hcp array and positive ion occupy two thirds of octahedral void. Suggest the formula assuming metal as M.

6. In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one eighth of tetrahedral voids are occupied by divalent cations while one half of octahedral voids are occupied by trivalent cations. What is the formula of the oxide?

7. In a crystal of an ionic compound, the anions B form a close packed lattice and the cations A occupy one half of the tetrahedral voids. What is the formula of the compound?

8. In a crystal of an ionic compound the ions B form the close packed lattice and the ions A occupy all the tetrahedral voids. What is the formula of the compound?

9. Calculate the coordination number of an atom is :

(a) A premitive cubic unit cell

(b) A bcc unit cell

(c) A fcc unit cell

10. A closed packed structure of uniform spheres has the cell edge = 0.8 mm. Calculate the radius of molecule if it has:

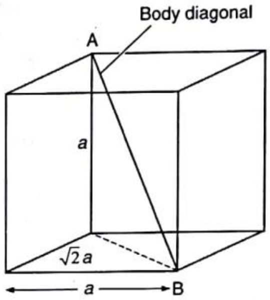
(a) single cubic lattice

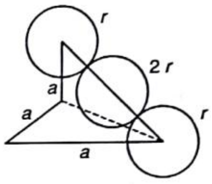
(b) bcc lattice

(c) fcc lattice

11. Sodium metal crystallizes in a body-centred cubic lattice with the cell edge $a = 4.29$ Å. What is the radius of sodium atom? **(IIT 1994)**

12. The length of the unit cell edge of a body-centred cubic metal crystal is 352 pm. Calculate the radius of an atom of the metal.





13. Chromium metal crystallizes with a body-centred cubic lattice. The length of the unit cell edge is found to be 287pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3? **(IIT July 1997)**

14. At room temperature, sodium crystallizes in a body-centred cubic lattice with $a = 4.24$ Å. Calculate theoretical density of sodium (Atomic mass of Na = 23).

15. Lithium borohydride crystallizes in an orthorhombic system with 4 molecule per unit cell. The unit cell dimensions are $a = 6.8$ Å, $b = 4.4$ Å and $c = 7.2$ Å. If the molar mass is 21.76, calculate the density of crystal.

16. An ionic compound AB has a rock salt structure with $A : B = 1 : 1$. The formula mass of AB is $6.023y$ amu and the closest $A - B$ distance is $y^{1/2}$ nm.

(a) Calculate the density of lattice.

(b) If the observed density of lattice is found to be 20 kg m^{-3}, then predict the type of defect. **(IIT 2004)**

17. A compound CuCl has face-centred cubic structure. Its density is 3.4 g cm^{-3}. What is the length of unit cell?

18. A fcc element (atomic mass = 60) has a cell edge of 400 pm. What is its density?

19. A metal crystallizes into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of fcc and bcc. **(IIT 1999)**

20. The density of KCl is 1.9893 g cm^{-3} and the length of a side unit cell is 6.29082 Å as determined by X-ray diffraction. Calculate the value of Avogadro's number.

21. The edge length of unit cell of a metal having molar mass 75 g mol^{-1} is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cm^3, calculate the radius of metal atom ($N_A = 6 \times 10^{23}$). **(IIT 2006)**

22. The density of solid argon is 1.65 g/mL at –233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon is apparently empty space? (Atomic mass of Ar = 40)

23. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? **(IIT May 1997)**

24. The unit cell edge length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.

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

26. An element crystallizes in fcc lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. **(IIT 2005)**

27. A solid compound AB has NaCl structure. If the radius of the cation is 100 pm (picometer) what is the radius of cation B ? 1 pm $= 10^{-12}$ m.

28. In a compound AB, the ionic radii of A^+ and B^- are 88 pm and 200 pm respectively. What is the coordination number of A^+?

29. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.

30. Calculate the concentration of cation vacancies if NaCl is doped with 10^{-3} mole % of $SrCl_2$.

31. In the cubic crystal of CsCl ($d = 3.97$ g cm^{-3}) the eight corners are occupied by Cl^- with a Cs^+ at the centre and *vice-versa*. Calculate the distance between the neighbouring Cs^+ and Cl^- ions. What is the radius ratio of the two ions? [Atomic mass of Cs = 132.91 and Cl = 35.45]

32. You are given marbles of diameter 10 mm. They are to be placed such their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area. **(IIT 2003)**

33. Calculate the wavelength of X-rays which produces a diffraction angle 2θ equal to 16.80° for a crystal. Assume first order diffraction with interparticle distance in crystal of 0.2 nm.

34. The angle of diffraction 2θ for a first order nature was found to be 27°8′ using X-rays of wavelength 2.29 Å. Calculate the distance between two diffracted planes.

35. In diamond lattice, all lattice points and alternate tetrahedral voids are occupied by the carbon atoms. If diamond crystallizes in fcc form with edge length 'a', find out the:

(a) number of next nearest neighbours in diamond lattice

(b) distance between the next nearest neighbours.

36. A metallic element crystallises into a lattice containing a sequence of layers of $AB\ AB\ AB$. Any packing of spheres leaves out voids in the lattice. Calculate?

(a) Coordination number.

(b) Packing fraction and % by volume of this empty lattice space. **(IIT 1996)**

(c) Base area of unit cell.

(d) Volume of unit cell.

SOLUTIONS (Numerical Problems)

1. (a) The cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore \quad n = 8\times\frac{1}{8} = \mathbf{1}$$

(b) The body-centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore \quad n = \left(8\times\frac{1}{8}\right) + 1 = \mathbf{2}$$

(c) The face-centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore \quad n = 8\times\frac{1}{8} + \left(6\times\frac{1}{2}\right) = \mathbf{4}$$

2. (i) Face plane
(ii) Face diagonal plane
(iii) Diagonal plane.

3. A atoms are at eight corners of the cube.

Therefore, the number of A atoms in the unit cell $= \frac{8}{8} = 1$

B atoms are at the face-centre of six faces

Therefore, its share in the unit cell $= \frac{6}{2} = 3$

The formula is $\boldsymbol{AB_3}$.

4. **For ccp or hcp array of A :**
No. of octahedral voids for each atom of $A = 1$
No. of tetrahedral voids for each atom of $A = 2$
Since, B occupy all the octahedral voids and half of the tetrahedral voids, thus one atom of B for octahedral void and one atom of B for tetrahedral void for each A atom is involved or the formula will be $\boldsymbol{AB_2}$.

5. **For ccp or hcp array of oxide ion :**
No. of octahedral voids for each oxide ion = 1

Since $\frac{2}{3}$ of octahedral voids are occupied by metal ion

Thus each oxide ion has $\frac{2}{3}$ metal ion or whole number ratio of oxide and metal ion is $1 : \frac{2}{3}$ or $3 : 2$. Thus formula is $\boldsymbol{M_3O_2}$.

6. Number of oxide ions (O) per unit cell = 1
Number of tetrahedral voids per ion in lattice = 2
Number of divalent cation $(A) = \frac{1}{8}\times 2 = \frac{1}{4}$
Number of octahedral voids per ion in lattice = 1
Number of trivalent cations $(B) = 1\times\frac{1}{2} = \frac{1}{2}$
Formula $= A_{1/4}B_{1/2}\text{O} = \boldsymbol{AB_2O_4}$

7. In a close packed array of B ion the number of tetrahedral voids per ion of B is **two.** Since, half of the tetrahedral voids is occupied by the cations A the number of cations is the same as that of the anion in the crystal and the formula of the compound is $\boldsymbol{AB}$.

8. In closed packed array of B ion the number of tetrahedral voids per ion of B is two. Since, tetrahedral voids are occupied by A ions, there are two A ions per B ion in the crystal. Therefore, the formula of the compound is $\boldsymbol{A_2B}$.

9. (a) In a primitive cubic unit cell, each atom has 6 equally spaced nearest neighbour atoms. Thus, coordination number = **6.**

(b) Considering the atom in the centre of the bcc unit cell, we find that it is surrounded by 8 nearest neighbour atoms situated at the corners of the cube. Thus, coordination number = **8.**

(c) Coordination number for a face-centred atom in an fcc unit cell is, evidently, equal to **12.**

10. (a) $$r = \frac{a}{2} = \frac{0.8}{2} = \mathbf{0.4\ mm}$$

(b) $$r = \frac{\sqrt{3}\,a}{4} = \frac{0.8\times\sqrt{3}}{4} = \mathbf{0.3464\ mm}$$

(c) $$r = \frac{a}{2\sqrt{2}} = \frac{0.8}{2\sqrt{2}} = \mathbf{0.2828\ mm}$$

11. Radius of Na (if bcc lattice) $= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}\times 4.29}{4} = \mathbf{1.8574\ \text{Å}}$

12. In a bcc unit cell, the atoms touch each other along the body diagonal. So, if the radius of the atom is r, then

$$\text{Body diagonal} = r + 2r + r = 4r$$

From the geometry of a cube

$$\text{Body diagonal} = \sqrt{3}\times\text{edge length} = \sqrt{3}\,a$$

Then, $4r = \sqrt{3}\times a$ or radius of metal atom $= \frac{\sqrt{3}}{4}\times a$

$$r = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times 352 = \mathbf{152.4\ pm}$$

13. For bcc lattice $r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4}\times 287 = \mathbf{124.27\ pm}$

Now, $\quad \text{Density} = \frac{n\times\text{atomic mass}}{V\times\text{Av. no.}} = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. no.}}$

$n = 2$ for bcc; $a = 287\times10^{-10}$ cm

$$\therefore \quad D = \frac{2\times 51.99}{(287\times10^{-10})^3\times 6.023\times10^{23}} = \mathbf{7.30\ g/mL}$$

14. A body-centred cubic unit cell contains 8 atoms at the 8 corners and one in the centre

$\because$ Total number of atoms per unit cell $= 8\times\frac{1}{8} + 1 = 2$

$$\therefore \text{Density} = \frac{n\times\text{atomic mass}}{\text{Av. no.}\times a^3}$$

$$= \frac{2\times 23}{6.023\times10^{23}\times(4.24\times10^{-8})^3}$$

$$= \mathbf{1.002\ g\ cm^{-3}}$$

15. $\because \quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}}$

$n = 4,\ M = 21.76\,\text{g mol}^{-1},$

Av. no. $= 6.023\times10^{23}$ and $V = a\times b\times c$

$$\therefore\quad V = 6.8\times10^{-8}\times4.4\times10^{-8}\times7.2\times10^{-8}$$
$$= 2.154\times10^{-22}\,\text{cm}^3$$
$$\therefore\ \text{Density} = \frac{4\times21.76}{2.154\times10^{-22}\times6.023\times10^{23}} = \mathbf{0.6709\ g\ cm^{-3}}$$

16. (a) AB has rock salt ($A : B = 1 : 1$) structure, *i.e.*, fcc structure ($n = 4$) and formula mass of BB is 6.023 y g having closest distance $A - B$ $y^{1/3}$ nm. Therefore edge length of unit cell

$$a = 2(A^+ + B^-) = 2\times y^{1/3}\times10^{-9}\ \text{m}$$
$$\therefore\ \text{Density of } AB = \frac{n\times\text{ molar mass}}{\text{Av. no.}\times V} = \frac{n\times\text{molar mass}}{6.023\times10^{23}\times a^3}$$
$$= \frac{4\times6.023\times y\times10^{-3}}{6.023\times10^{23}\times(2y^{1/3}\times10^{-9})^3}$$

(molar mass in kg mol^{-1})

$$= \mathbf{5.0\ kg\ m^{-3}}$$

(b) The observed density of AB is 20 kg m^{-3} which is higher than calculated density 5.0 kg m^{-3} and thus AB has either interstitial impurity defect or substitutional impurity defect.

17. Molecular mass of CuCl = 99

$n = 4$ for face-centred cubic cell

$$\because\quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}} = \frac{4\times99}{a^3\times6.023\times10^{23}}$$
$$\text{or}\quad 3.4 = \frac{4\times99}{a^3\times6.023\times10^{23}}$$
$$\therefore\quad a = 5.783\times10^{-8}\,\text{cm} = \mathbf{5.783\ Å}$$

18. $$\because\ \text{Density} = \frac{n\times\text{atomic mass}}{V\times\text{Av. no.}} = \frac{n\times\text{atomic mass}}{a^3\times\text{Av. no.}}$$

Given, Atomic mass = 60,

$$a = 4\times10^2\,\text{pm} = 4\times10^2\times10^{-12}\ \text{m}$$
$$= 4\times10^{-10}\times10^2\,\text{cm} = 4\times10^{-8}\ \text{cm}$$
$$(\because 1\,\text{pm} = 10^{-12}\ \text{m})$$

Also, $n = 4$ for face-centred cubic lattice

$$\therefore\quad \text{Density} = \frac{4\times60}{(4\times10^{-8})^3\times6.023\times10^{23}} = \mathbf{6.23\ g\ cm^{-3}}$$

19. fcc unit cell length = 3.5 Å

bcc unit cell length = 3.0 Å

$$\text{Density in fcc} = \frac{n_1\times\text{atomic mass}}{V_1\times\text{Av. no.}}$$
$$\text{Density in bcc} = \frac{n_2\times\text{atomic mass}}{V_2\times\text{Av. no.}}$$
$$\frac{D_{\text{fcc}}}{D_{\text{bcc}}} = \frac{n_1}{n_2}\times\frac{V_2}{V_1}$$

Now, n_1 for fcc = 4; Also, $V_1 = a^3 = (3.5\times10^{-8})^3$

n_2 for bcc = 2; Also, $V_2 = a^3 = (3.0\times10^{-8})^3$

$$\frac{D_{\text{fcc}}}{D_{\text{bcc}}} = \frac{4\times(3.0\times10^{-8})^3}{2\times(3.5\times10^{-8})^3} = \mathbf{1.259}$$

20. KCl has face-centred cubic structure $\therefore n = 4$

Given, Density = 1.9893 g cm^{-3}

$$a = 6.29082\times10^{-8}\ \text{cm}$$

$$\because\quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}} = \frac{n\times\text{molar mass}}{a^3\times\text{Av. no.}}$$
$$\therefore\quad 1.9893 = \frac{4\times74.5}{(6.29082\times10^{-8})^3\times N}$$
$$\therefore\quad N = \mathbf{6.017\times10^{23}}$$

21. $$\text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. No.}}$$

$a = 5\times10^{-8}\,\text{cm}$, $d = 2\,\text{g/cm}^3$

$$\therefore\quad 2 = \frac{n\times75}{(5\times10^{-8})^3\times6\times10^{23}}\quad \therefore n = 2$$

i.e., the metal crystallizes in bcc, thus,

$$\text{radius} = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times5 = 2.165\ \text{Å} = \mathbf{216.5\ pm}$$

22. Volume of one atom of Ar $= \frac{4}{3}\pi r^3$

Also, No. of atoms in 1.65 g or one mL $= \frac{1.65}{40}\times6.023\times10^{23}$

$\therefore$ Total volume of all atoms of Ar in solid state

$$= \frac{4}{3}\pi r^3\times\frac{1.65}{40}\times6.023\times10^{23}$$
$$= \frac{4}{3}\times\frac{22}{7}\times(1.54\times10^{-8})^3\times\frac{1.65}{40}\times6.023\times10^{23}$$
$$= 0.380\ \text{cm}^3$$

Volume of solid argon = 1 cm^3

$$\therefore\quad \%\ \text{empty space} = \frac{[1-0.380]}{1}\times100 = \mathbf{62\%}$$

23. $$\text{Density of NaCl} = \frac{n\times\text{atomic mass}}{\text{Av. no.}\times a^3}$$
$$= \frac{4\times58.5}{6.023\times10^{23}\times(5.64\times10^{-8})^3}$$
$$= \mathbf{2.16\ g/cm^3}$$

24. The distance between Li^+ and Cl^- ion can be derived as half of the edge length of cube

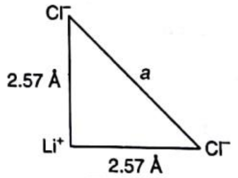


Fig. 12

$$\therefore\quad d_{\text{Li}^+-\text{Cl}^-} = \frac{5.14}{2} = 2.57\ \text{Å}$$
$$\therefore\quad d_{\text{Cl}^--\text{Cl}^-} = \sqrt{(2.57)^2+(2.57)^2} = 3.63\ \text{Å}$$
$$\text{The radius of Cl}^- = \frac{d_{\text{Cl}^--\text{Cl}^-}}{2} = \frac{3.63}{2}$$
$$= \mathbf{1.815\ Å}$$

25. Consider an octahedral void (Fig. 13) represented by the shaded portion (the spheres present below and above the void are not shown). Now suppose the length of each arm of the square will be $2R$ (R is radius of atom). Let r be the radius of void. For right angle triangle ABC.

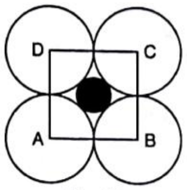


Fig. 13

$$AC = \sqrt{[(AB)^2 + (BC)^2]}$$
$$= \sqrt{[(2R)^2 + (2R)^2]} = \sqrt{8}R$$

Also, $AC = R + R + 2r = 2r + 2R = 2(r + R)$

or $\sqrt{8}R = 2\sqrt{2}R = 2(r+R)$ or $r = \sqrt{2}R - R$

$$r = [\sqrt{2} - 1]R = \mathbf{0.414 \times R}$$

26. Either octahedral voids $\left(\frac{r_1}{r_2} = 0.414\right)$ or tetrahedral voids $\left(\frac{r_1}{r_2} = 0.225\right)$ are occupied by interstitial sites in fcc where r_1 is radius of atom in interstitial sites and r_2 is radius of atom arranged in fcc.

Since in fcc atoms along face diagonal are touching, thus,

$$4r_2 = \sqrt{2}\,a$$

Required diameter of interstitial sites $= 2r_1 = 2 \times 0.414 r_2$

$$= \frac{2 \times 0.414 \times \sqrt{2}\,a}{4} = \frac{2 \times 0.414 \times \sqrt{2} \times 400}{4}$$

$$= \mathbf{117.1\ pm}$$

27. The number of units of AB in a unit cell (fcc) = 4

Radius of cation $A^+ = 100\,\text{pm} = 100 \times 10^{-10}$ cm

Radius of r^+/r^- for octahedral coordination = 0.414

Hence, Radius of the anion $(B^-) = \frac{100}{0.414} = \mathbf{241.5\ pm}$

28. Radius ratio $= \frac{r^+}{r^-} = \frac{88}{200} = 0.44$

The radius ratio lying in between 0.414 and 0.732 and thus represents for octahedral voids. Also B^- is larger than A^+ and thus B^- forms closed packed structure and A^+ occupies the void space. Thus, coordination number of cation A^+ in AB is **six.**

29. No. of atoms in unit cell = 1 + 2 = 3

Volume of unit cell $= 24 \times 10^{-24}\,\text{cm}^3$

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

$\because$ Density $= \frac{n \times \text{atomic mass}}{V \times \text{Av. no.}}$

$\therefore$ $7.2 = \frac{3 \times \text{atomic mass}}{24 \times 10^{-24} \times 6.023 \times 10^{23}}$

$\therefore$ Atomic mass = 34.69

$\because$ 34.69 g has no. of atoms $= 6.023 \times 10^{23}$

$\therefore$ 200 g has no. of atoms $= \frac{6.023 \times 10^{23} \times 200}{34.69}$

$$= \mathbf{3.4722 \times 10^{24}\ atoms}$$

30. Doping of $SrCl_2$ to NaCl brings in replacement of two Na^+ ion by each Sr^{2+} ion, but each Sr^{2+} occupies only one lattice point. This produces one cation vacancy.

Thus, doping of 10^{-3} mole of $SrCl_2$ in 100 mole NaCl will produce cation vacancies $= 10^{-3}$

$\therefore$ 100 mole NaCl will have cation vacancies after doping $= 10^{-3}$

$\therefore$ 1 mole NaCl will have cation vacancies $= \frac{10^{-3}}{100} = 10^{-5}$

$\therefore$ Total cationic vacancies $= 10^{-5} \times$ Av. no. $= \mathbf{6.02 \times 10^{18}}$

31. In a unit cell, there are one Cs^+ and $\frac{1}{8} \times 8 = 1Cl^-$, *i.e.*, one CsCl molecule

$\because$ Density $= \frac{n \times \text{molar mass}}{V \times \text{Av. no.}} = \frac{n \times \text{molar mass}}{a^3 \times \text{Av. no.}}$

$\therefore$ $3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$

$a = 4.13 \times 10^{-8}$ cm

$\therefore$ $a = 4.13$ Å

For a cube of side length 4.13 Å, diagonal

$= \sqrt{3} \times 4.13 = 7.15$ Å

As it is a bcc with Cs^+ at centre (radius r^+) and Cl^- at corners (radius r^-) so,

$2r^+ + 2r^- = 7.15$ or $r^+ + r^- = 3.57$ Å

i.e., Distance between neighbouring Cs^+ and Cl^- = 3.57 Å

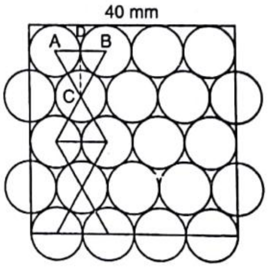
Now assume two Cl^- ions touch each other so,

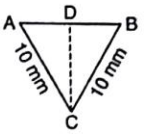
Length of unit cell $= 2r^- = 4.13$ Å $\therefore r^- = 2.06$ Å

$\therefore$ $r^+ = 3.57 - 2.06 = 1.51$

$\therefore$ $r^+/r^- = 1.51/2.06 = \mathbf{0.73}$

32.





$\text{CD} = 10\ \text{Sin}\ 60 = 10\frac{\sqrt{3}}{2}$

$= 5\sqrt{3}$

Area of square having spherical marbles in it

$$= 40 \times 10^{-1} \times 40 \times 10^{-1}\,\text{cm}^2 = 16\,\text{cm}^2$$

The maximum number of spheres of 10 mm diameter in hcp packing can be seen in Fig. 1.

Total length covered by spheres

$= 5 + 4 \times \text{CD} = 5 + 4 \times 10 \sin 60$

$= 5 + 4 \times 5\sqrt{3} = 40$ mm

Maximum number of spheres $(s) = \underset{\text{(Full)}}{14} + \underset{\text{(Half)}}{8} = 18$

$\therefore$ Number of spheres per cm^2 $= \frac{18}{16} = \mathbf{1.125}$

33. $\because \quad n\lambda = 2d\sin\theta$.

Given, $n = 1$; $d = 0.2\times10^{-9}$ m, $\theta = \frac{16.80}{2} = 8.40°$

Thus, $\lambda = \frac{2\times0.2\times10^{-9}\times\sin 8.4}{1} = \mathbf{5.84\times10^{-11}\,m}$

34. $\because \quad n\lambda = 2d\sin\theta$

Given, $n = 1$; $\lambda = 2.29\times10^{-10}$ m; $\theta = \frac{27°8'}{2} = 13°34'$

$\therefore \quad 1\times2.29\times10^{-10} = 2\times d\times\sin 13°34'$

$\therefore \quad \mathbf{d = 4.88\times10^{-10}\,m}$

35. (a) Nearest neighbours are atoms at lattice points and tetrahedral voids.

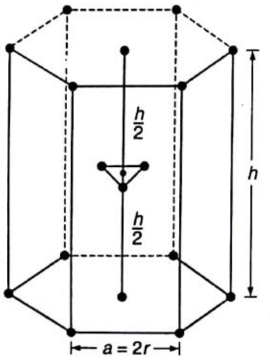
Thus, next nearest neighbours are atoms at **lattice points.**

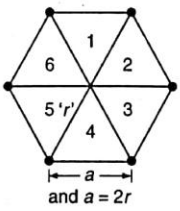
$\therefore$ Number of next nearest neighbours = 12

(b) Distance between next nearest neighbour (for fcc)

$$= \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} = \mathbf{0.707a}$$

36. (a) The given packing ($AB\ AB\ AB\ldots$) is three dimensional close packing as shown in given figure. In this arrangement three atoms are arranged in the body centred position in such a way, so that it forms equilateral triangle and twelve atoms are placed at 12 corners and two atoms at two face centres.





(i) $\therefore$ **No. of atoms per unit cell** $= \frac{1}{6}\times12+\frac{1}{2}\times2+3 = 6$

(ii) Thus, **coordination number** of three dimensional hcp lattice becomes 12, *i.e.*, 6 from own layer and 3 from above and 3 from lower layer.

(b) Packing fraction : Each corner atom would be common to 6 other unit cells. If r is the radius of each sphere, then

$$\text{packing fraction} = \frac{6\times\frac{4}{3}\pi r^3}{V}$$

where V = volume of hexagon = Area of base (A) $\times$ height (h)

$$\therefore \text{ Packing fraction} = \frac{6\times\frac{4}{3}\pi r^3}{6\sqrt{3}r^2\times4r\times\sqrt{\frac{2}{3}}} = \frac{\pi}{3\sqrt{2}}$$

$$= \mathbf{0.74} \quad \text{or} \quad \mathbf{74\%}$$

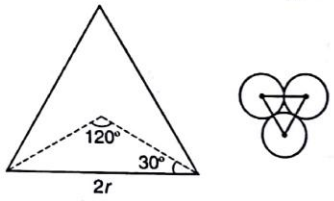
(c) Base Area (A) of unit cell : Base area of hcp-unit cell is given by :

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

$$A = \frac{3\sqrt{3}}{2}a^2$$

$$A = \frac{3\sqrt{3}}{2}\times4r^2 = 6\sqrt{3}r^2$$

(d) Calculation of height : $\cos 120° = \frac{x^2+x^2-(2r)^2}{2x^2}$



or $\quad -\frac{1}{2} = \frac{2x^2-4r^2}{2x^2} = \frac{x^2-2r^2}{x^2}$ or $3x^2 = 4r^2$

$\therefore \quad x = \frac{2r}{\sqrt{3}}$

Now $\quad \left(\frac{h}{2}\right)^2 = a^2 - x^2$

$$\frac{h^2}{4} = (2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2 \text{ or } \frac{h^2}{4} = \frac{8r^2}{3}$$

$\therefore \quad h^2 = \frac{32r^2}{3}$ or $h = 4r\times\sqrt{\frac{2}{3}}$

• SINGLE INTEGER ANSWER PROBLEMS •

1. If radius ratio is less than 0.155, the co-ordination no. is ......
2. In pentagonal bipyramidal structure, the co-ordination no. is ......
3. Number of second nearest neighbours in body centred lattice is ......
4. Co-ordination no. of Cs^+ in CsCl is ......
5. Number of Al atoms per unit cell of Al in its crystal lattice is ......
6. The ratio of co-ordination no. of Al and no. of Al atoms per unit cell in fcc lattice is ......
7. FeO crystallises in NaCl type lattice. The crystal is however non-stoichiometric as $Fe_{0.96}O$ and deficient in iron. Some cation sites are vacant and some contain Fe^{3+} so that it becomes electrically neutral. The % of cation sites vacant are ......
8. A crystal of sodium hydride has fcc unit cell of H^- ions with Na^+ ions at the body centres of unit cell and in the centre of edges. The no. of H^- that touch each Na^+ is ......
9. In HCP arrangement of atoms, co-ordination no. of atoms in the middle layer is ......
10. The number of tetrahedral voids present in bcc lattice is ......
11. If the distance between $Cs^+ - Cl^-$ in CsCl lattice is $2\sqrt{3}$ Å, the edge length of cube is ......
12. The no. of octahedral sites per square are in a ccp (fcc) structure ......
13. If edge length of a bcc crystallized Fe is $8\sqrt{3}$, the atomic radius is ......
14. A mineral having the formula AB_2 crystallises in cubic close packed lattice, with A atoms occupying the lattice point. The ratio of co-ordination no. of A and B is ......
15. Lattice energy of NaCl is −186 kcal/mol and solution enthalpies of cation and anion respectively are −97 and −85 kcal / mol. The enthalpy of solution of NaCl in kcal is ......
16. Number of regular hexagonal faces in a truncated tetrahedron is ......
17. Number of regular trigonal faces in a truncated tetrahedron is ......
18. Number of square faces in a truncated octahedron is :
19. A compound AB has rock salt structure with $A : B = 1:1$. The formula mass of AB is 6.023 Y amu and the closest A-B distance is $y^{1/3}$ nm. The density of lattice in 5×10^{-a} g / cm^3. The value of a is ......
20. A metal crystallises in two cubic faces fcc and bcc, where unit cell lengths are 4.0 and 2.0Å respectively. The ratio of density in bcc and fcc is ......
21. The ratio of co-ordination no. of A and B is 1 : 3, then the ratio of no. of atoms of A and B in unit cell is ......
22. The number of nearest neighbours in an atom/ion for an octahedral hole of a closed packed structure is ......
23. The ratio of number of nearest neighbour and no. of atoms per unit cell in a simple cubic structure is ......
24. The ratio of number of nearest neighbour and no. of atoms per unit cell in a fcc structure is ......
25. The ratio of number of nearest neighbour and no. of atoms per unit cell in a bcc structure is ......
26. The ratio of co-ordination number of cation and anion in fluorite CaF_2 is ......
27. The ratio of co-ordination number of anion and cation in antifluorite Na_2O is ......
28. Ice crystallises in a hexagonal lattice having volume of the unit cell as 132×10^{-24} cm^3. If density of ice is 0.92 g cm^{-3} at a given temperature, then number of H_2O molecule per unit cell is ......
29. When the radius ratio of r_M / r_X of a crystal lies in the range of $0.414 - 0.732$, the co-ordination number of M is ......
30. Silver (atomic mass = 108 g mol^{-1}) has a density of 10.5 g/cm^3. The number of silver atoms on a surface area of 10^{-12} m^2 can be expressed in scientific notations as $Y \times 10^X$. The value of X is : **(IIT 2010)**
31. Co-ordination number of Al in the crystalline state of $AlCl_3$ is : **(IIT 2009)**
32. Number of hexagonal faces that are present in a truncated octahedron. **(IIT 2011)**
33. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8g cm^{-3}, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is : **[JEE (Main) 2017]**

ANSWERS

1. Two **2.** Seven **3.** Six **4.** Eight **5.** Four **6.** Three **7.** Four **8.** Six **9.** Six **10.** Four **11.** Four **12.** One
13. Six **14.** Two **15.** Four **16.** Four **17.** Four **18.** Six **19.** Three **20.** Four **21.** Three **22.** Six **23.** Six **24.** Three
25. Four **26.** Two **27.** Two **28.** Four **29.** Six **30.** Seven **31.** Four **32.** Eight **33.** Two

OBJECTIVE PROBLEMS (One Answer Correct)

1. Na and Mg crystallise in bcc and fcc type crystals, the ratio of number of atoms present in unit cell of their respective crystal is :

(a) 1 (b) 0.5
(c) 3 (d) 4

2. In a closed packed structure of mixed oxides, the lattice is composed of mixed oxides ions. One eighth of tetrahedral voids are occupied by divalent cations (A^{2+}) while one half of octahedral voids are occupied by trivalent cation (B^{3+}). The formula of mixed oxide is :

(a) A_2BO_3 (b) AB_2O_3
(c) A_2BO_4 (d) AB_2O_4

3. An ionic solid A^+B^- crystallises as a bcc structure. The distance between cation and anion in the lattice is 338 pm. The edge length of cell is :

(a) 338 pm (b) 390.3 pm
(c) 292.7 pm (d) 507 pm

4. An ionic solid A^+B^- crystallises as a fcc structure. If the edge length of cell is 508 pm and radius of anion is 144 pm, the radius of cation is :

(a) 110 pm (b) 364 pm
(c) 220 pm (d) 288 pm

5. The density of an ionic compound (molar mass 58.5) is 2.165 kg m^{-3} and the edge length of unit cell is 562 pm, then the closest distance between A^+B^- and rank of unit cell is:

(a) 281 pm, 4 (b) 562 pm, 2
(c) 562 pm, 4 (d) 281 pm, 2

6. The γ-form of iron has fcc structure (edge length 386 pm) and β-form has bcc structure (edge length 290 pm). The ratio of density in γ-form and β-form is :

(a) 0.9788 (b) 1.02
(c) 1.57 (d) 0.6344

7. The internuclear distance in NaCl is 0.282 nm and density of solid NaCl (molar mass 58.5) is 2.17×10^3 kg m^{-3}. If a unit cell of NaCl has 4 formula units, the Avogadro's number is :

(a) 6.01×10^{23} (b) 6.02×10^{23}
(c) 6.03×10^{23} (d) 6.04×10^{23}

8. The bcc structure of an element has density 7.12 kg/m^3 and edge length of unit cell is 2.88 Å. The number of atoms present in 288 g of element is :

(a) 3.4×10^{22} (b) 3.4×10^{23}
(c) 3.4×10^{24} (d) 3.4×10^{21}

9. The edge length of unit cell of a metal (molar mass 24) having cubic structure 4.53 Å. If the density of metal is 1.74 g/cm^3, the radius of metal is : (Av. No. $= 6 \times 10^{23}$)

(a) 180 pm (b) 160 pm
(c) 140 pm (d) 190 pm

10. The ratio of packing density in fcc, bcc and cubic structure is respectively :

(a) 1 : 0.92 : 0.70 (b) 0.70 : 0.92 : 1
(c) 1 : 0.70 : 0.92 (d) 0.92 : 0.70 : 1

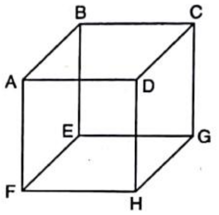
11. If R is the radius of the octahedral voids and r is the radius of the atom in close packing, then :

(a) $\frac{r}{R} = 2.41$ (b) $\frac{r}{R} = 4.76$
(c) $\frac{r}{R} = 3.22$ (d) $\frac{r}{R} = 9.1$

12. A metal crystallises in bcc lattice. The % fraction of edge length not covered by atom is:

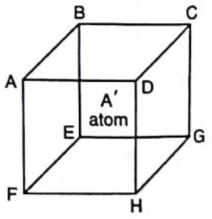
(a) 10.4% (b) 13.4%
(c) 12.4% (d) 11.4%

13. In the cubic lattice given below the three distances between the atoms $A - B$, $A - C$ and $A - G$ are respectively :



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

14. In body-centred cubic lattice given below, the three distances AB, AC and AA' are:



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

15. Two ionic solids AB and CB crystallise in the same lattice. If $\frac{r_{A^+}}{r_{B^-}}$ and $\frac{r_{C^+}}{r_{B^-}}$ are 0.50 and 0.70 respectively, then the ratio of edge length of AB and CD is :

(a) 0.68 (b) 0.78
(c) 0.88 (d) 0.98

16. A molecule A_2B (molar mass $= 166.4$) occupies triclinic lattice with $a = 5$ Å, $b = 8$ Å and $c = 4$ Å. If density of AB_2 is 5.2 g cm^{-3}, the number of molecules present in one unit cell is:

(a) 2 (b) 3
(c) 4 (d) 5

17. Silicon dopped with gp. 13 and gp. 15 members elements is respectively called ... semiconductor.
(a) *p*-type, *n*-type (b) *n*-type, *p*-type
(c) *p*-type (d) *n*-type

18. Na and Mg crystallise in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respectively crystal is:
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

19. How many unit cells are present in a cubic shaped ideal crystal of NaCl of mass 1.0 g?
(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

20. What type of crystal defect is indicated in the diagram given below?

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-	□	Cl^-	Na^+	□	Cl^-
Na^+	Cl^-	□	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+	□	Na^+

(a) Frenkel and Schottky defects
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel defect

21. The volume of atoms present in a face-centred cubic unit cell of a metal (r is atomic radius) is:
(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

22. In a *p*-type semiconductor, the majority carriers of current are:
(a) protons (b) electrons
(c) holes (d) neutrons

23. Among which the magnetic susceptibility does not depend upon temperature?
(a) Diamagnetism (b) Paramagnetism
(c) Ferromagnetism (d) Ferrite

24. Copper and silicon are cooled from 300 K to 60 K, the conductivity:
(a) decrease in Cu but increase in Si
(b) increase in Cu but decrease in Si
(c) increase in both
(d) decrease in both

25. Zn converts from molten state to its solid state in hcp structure. The number of nearest atoms is:
(a) 4 (b) 6
(c) 8 (d) 12

26. Forbidden energy gap for Si is approximately:
(a) 1 eV (b) 6 eV
(c) 0 eV (d) 3 eV

27. In a semiconductor at room temperature:
(a) the valence band is partially empty and conduction band is partially filled
(b) the valence band is completely filled and the conduction band is partially filled
(c) the valence band is completely filled
(d) the conduction band is completely filled

28. Si is used more as semiconductor than Ge because:
(a) Si is cheaper than Ge
(b) It is found in abundance
(c) Less leakage of current in Si
(d) All of the above

29. Above Curic temperature:
(a) A ferromagnetic substance becomes ferromagnetic
(b) A ferromagnetic substance becomes paramagnetic
(c) A paramagnetic substance becomes diamagnetic
(d) A diamagnetic substance becomes paramagnetic

30. 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) $\frac{\pi}{4}$

31. Percentage of free space in a body centred cubic unit cell is:
(a) 34% (b) 28%
(c) 30% (d) 32%

32. In which of the following pairs of structures, tetrahedral as well as octahedral voids are noticed?
(a) hc, fcc (b) hcp, sc
(c) hcp, ccp (d) bcc, hcp

33. In a cubic unit cell 7 of the 8 corners are occupied by atom A and centres of faces are occupied by atom B. The general formula of compound is:
(a) A_7B_6 (b) A_7B_{24}
(c) $A_{24}B_7$ (d) A_6B_7

34. Anions A form hexagonal closest packing and cation B occupy only 2/3 of octahedral voids in it, the general formula of compound is:
(a) BA (b) BA_2
(c) B_2A_3 (d) B_3A_2

35. In NaCl crystal, the number of next nearest neighbours of each Na^+ is:
(a) $8Cl^-$ (b) $12Na^+$
(c) $12Cl^-$ (d) $24Cl^-$

36. When anion leaves the normal sites an electron occupies interstitial sites in a crystal lattice it is called:
(a) Schottky defect (b) Frenkel defect
(c) Metal excess defect (d) Metal deficiency

37. Certain crystals produce electric signals on applying pressure. This phenomenon is:
(a) Ferro electricity (b) Ferri electricity
(c) Piezo electricity (d) Pyro electricity

38. Co-ordination no. of $AlCl_3$ in crystalline state is:
(a) 4 (b) 6
(c) 5 (d) 8

39. Carbon, Silicon and Germanium have four valency electrons each. These are characterised by conduction bond separated by energy bond gaps respectively equal to $(E_g)_C$, $(E_g)_{Si}$ and $(E_g)_{Ge}$. The correct statement is:
(a) $(E_g)_C = (E_g)_{Si} = (E_g)_{Ge}$
(b) $(E_g)_C > (E_g)_{Si} > (E_g)_{Ge}$
(c) $(E_g)_C < (E_g)_{Ge} > (E_g)_{Si}$
(d) $(E_g)_{Si} < (E_g)_{Ge} > (E_g)_C$

40. In a solid lattice, the cation left a lattice site and is located at an interstitial position. The lattice defect is:
(a) Interstitial defect (b) Vacancy defect
(c) Frenkel defect (d) Schottky defect

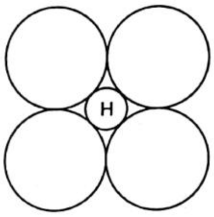
41. Schottky defect in crystals is observed when:
(a) unequal no. of cations and anions are missing from crystal lattice
(b) equal no. of cations and anions are missing from crystal lattice
(c) an atom leaves its normal site and occupies an interstitial site
(d) density of crystal is increased

42. The metallic lustre exhibited by sodium is explained by:
(a) diffusion of sodium ions
(b) oscillation of loose electrons
(c) excitation of free protons
(d) existence of body centred cubic lattice

43. CsBr has bcc structure with edge length 4.3Å. The shortest interionic distance in between Cs^+ and Br^- (in Å) is:
(a) 3.72 (b) 1.86
(c) 7.44 (d) 4.3

44. The co-ordination number of a metal crystallizing in a hexagonal close-packed structure is: .
(a) 12 (b) 4
(c) 8 (d) 6

45. The radius (R) of atoms forming a closed packed structure in the given figure is 2×10^{-8} cm.



The maximum radius of atom occupying the octahedral hole (H) is :
(a) 8.28×10^{-9} cm (b) 0.414×10^{-8} cm
(c) 0.225×10^{-8} cm (d) 4.5×10^{-8} cm

46. Which of the following crystal does not possess any symmetry ?
(a) $K_2Cr_2O_7$ (b) $CuSO_4 \cdot 5H_2O$
(c) H_3BO_3 (d) Either of these

47. The energy gap between conduction band and valence band is zero in :
(a) Na (b) Diamond
(c) Si (d) Ge

48. Which one is the incorrect statement ?
(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 piezo electric crystal
(d) Frenkel defect is favoured in those ionic compounds in which sizes of cations and anions are almost equal

SOLUTIONS (One Answer Correct)

1. (b) No. of atoms in bcc = 2

No. of atoms in fcc = 4

$\therefore \quad \text{Ratio} = \frac{2}{4} = 0.5$

2. (d) Number of tetrahedral voids per ion in lattice = 2

Number of $A^{2+} = \frac{1}{8} \times 2 = \frac{1}{4}$

Number of octahedral voids per ion in lattice = 1

Number of $B^{3+} = 1 \times \frac{1}{2} = \frac{1}{2}$

$\therefore$ Formula AB_2O_4

3. (b) $r^+ + r^- = \sqrt{3} \times \frac{a}{2}$

$\therefore \quad a = \frac{2}{\sqrt{3}} \times 338 = 390.3\ \text{pm}$

4. (a) $r^+ + r^- = \frac{a}{2}$ for fcc

5. (a) $d = \frac{n \times \text{atomic mass}}{a^3 \times \text{Av. No.}}$ or

$$2.165 = \frac{n \times 58.5}{(562 \times 10^{-10})^3 \times 6 \times 10^{23}}$$

$\therefore$ $n = 4$ rank of unit cell

$\therefore$ AB has fcc structure,

$\therefore \quad d_{A^+-B^-} = \frac{a}{2}$

6. (a) $\frac{d_r}{d_B} = \frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{n_r \times (a_B)^3}{n_B \times (a_r)^3} = \frac{4}{2} \times \left(\frac{290}{386}\right)^3 = 0.9788$

7. (a) $d = \frac{n \times \text{atomic mass}}{a^3 \times \text{Av. No.}}$ and $r^+ + r^- = \frac{a}{2}$

8. (c) $\text{Density} = \frac{n \times \text{atomic mass}}{a^3 \times \text{Av. No.}}$

$\therefore \quad \text{Atomic mass} = \frac{\text{Density} \times a^3 \times \text{Av. No.}}{n}$

$$= \frac{7.12 \times (2.88 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{2} = 51.22$$

$\therefore$ No. of atoms $= \frac{6.023 \times 10^{23} \times 2.88}{51.22} = 3.386 \times 10^{24}$

9. (b) $d = \frac{n \times \text{atomic mass}}{a^3 \times \text{Av. No.}}$

$\therefore$ $n = 4$ and metal crystallises in fcc. Then $r = \frac{a}{2\sqrt{2}}$

10. (a) Packing density in fcc, bcc and sc are 0.74, 0.68 and 0.52 respectively.

11. (a)
$$AC = \sqrt{AB^2 + BC^2} = \sqrt{(2r)^2 + (2r)^2}$$

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

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

$$R = (\sqrt{2} - 1)r, \quad \frac{R}{r} = 0.41, \quad \therefore \frac{r}{R} = 2.41$$

12. (b) In bcc $r = \frac{\sqrt{3}a}{4}$

Also, edge length of unit cell = a

radius of atom = r

$\therefore$ Edge length not covered by atom $= a - 2r$

or $= a - \frac{\sqrt{3}}{2} \cdot a = a\left[\frac{2-\sqrt{3}}{2}\right]$

$\therefore$ Percentage fraction not covered

$$= \frac{a\left[\frac{2-\sqrt{3}}{2}\right]}{a} \times 100 = 0.134 \times 100 = 13.4\%$$

13. (a) Edge length $= AB = AD = BC = CD = a$

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

$AG = \sqrt{AC^2 + CG^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

14. (a) Edge length $= AB = AD = BC = CD = a$

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

Now, $AA'^2 + A'G^2 = \left(\frac{\sqrt{3}a}{2}\right)^2$

$\therefore \quad 2AA'^2 = \frac{3a}{4}$ or $AA' = \frac{\sqrt{3}a}{2}$

15. (c) $\frac{r_{A^+}}{r_{B^-}} = 0.50$ and $\frac{r_{C^+}}{r_{B^-}} = 0.70$

$\therefore \quad \frac{r_{A^+} + r_{B^-}}{r_{B^-}} = 1 + 0.5 = 1.5 \quad \frac{r_{C^+} + r_{B^-}}{r_{B^-}} = 1.70$

$\therefore \quad \frac{r_{A^+} + r_{B^-}}{r_{C^+} + r_{B^-}} = \frac{1.5}{1.7}$

$\therefore \quad a_{AB} = 2(r_{A^+} + r_{B^-})$

$a_{CB} = 2(r_{C^+} + r_{B^-})$

$\therefore \quad \frac{a_{AB}}{a_{CB}} = \frac{1.5}{1.7} = 0.88$

16. (b) Volume of unit cell

$= a \times b \times c = 5 \times 10^{-8} \times 8 \times 10^{-8} \times 4 \times 10^{-8}$

$= 1.6 \times 10^{-22}\ \text{cm}^3$

Mass of unit cell $= 1.6 \times 10^{-22} \times 5.2 = 8.32 \times 10^{-22}$ g

Number of molecules in one unit cell

$$= \frac{8.32 \times 10^{-22} \times 6 \times 10^{23}}{166.4} = 3$$

17. (a) Follow text.

18. (d) No. of unit cell in bcc is 2 and fcc is 4.

19. (c) $n = 4$ for fcc;

Also, no. of atoms in 1g NaCl $= \frac{6.023 \times 10^{23}}{58.5}$

No. of unit cell present in 1g NaCl

$$= \frac{6.023\times10^{23}}{58.5\times4} = 2.57\times10^{21}\text{ unit cell}$$

20. (b) These defect are produced when one +ve and one –ve ion are missing from their respective position removed.

21. (d) Volume of atom in a cell $= \frac{4}{3}\pi r^3 \times n$ ($n = 4$ for fcc)

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

22. (c) In *p*-type semiconductors, conduction occurs by "+ve" majority carriers (*i.e.*, by holes).

23. (a) Diamagnetism is independent of temperature.

24. (b) Copper is conductor and thus resistance decreases (conductance increase) and silicon is semiconductor and so resistance increases (conductance decreases) on cooling.

25. (d) In hcp, unit cell is hexagonal and co-ordination number 12.

26. (a) E_g for Si = 1.1 eV ; E_g for Ge = 0.7 eV

27. (a) In semiconductors at room temperature, some of the electrons of valence bond gain sufficient energy to go in conduction bond.

28. (d) All are facts.

29. (b) It is a fact.

30. (a) — do —

31. (d) — do —

32. (c) These are facts.

33. (b) No. of atoms A at corners $= 7\times\frac{1}{8} = \frac{7}{8}$

No. of atoms B at faces $= 6\times\frac{1}{2} = 3$

$\therefore\ A_{7/8}B_3$ or A_7B_{24}

34. (c) No. of anion A^- in unit cell $= 6$

No. of cation B^- in unit cell $= 6\times\frac{2}{3} = 4$

$\therefore\ B_4A_6$ or B_2A_3

35. (b) It is a fact.

36. (c) — do —

37. (c) — do —

38. (a) In solid state it exists as Al_2Cl_6.

39. (b) Carbon is insulator, Si is semiconductor with higher energy bond gap, while Ge is semiconductor with smaller energy bond gap.

40. (c) It is a fact.

41. (b) — do —

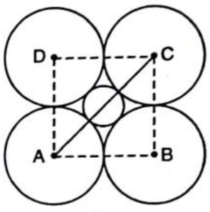
42. (b) Follow metallic bonding.

43. (a) For bcc : $r = \frac{\sqrt{3}}{4}\times a = \frac{\sqrt{3}}{4}\times 4.3 = 1.86\,\text{Å}$

$\therefore$ shortest inter ionic distance $= 2r = 3.72\,\text{Å}$.

44. (a) In hcp structure co-ordination no. of metal is 12.

45. (a) Given radius of spheres is $R(2\times10^{-8}\text{cm})$. Let radius of void be r.



The octahedral void.

In the triangle ABC

$$AC^2 = (AB)^2 + (BC)^2 = (2R)^2 + (2R)^2$$

$$[R + 2r + R]^2 = 8R^2$$

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

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

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

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

$$\therefore \quad r = 0.414R = 0.414\times2\times10^{-8} = 8.28\times10^{-9}$$

46. (d) All are triclinic crystals having no symmetry.

47. (a) Conduction bond and valence bonds overlaps in metals.

48. (a,d) $FeO_{0.98}$ has a non-stoichiometric molecule having metal excess defect (compare this molecule with FeO) and not metal deficiency defect. Frenkel defect is favoured in those ionic compounds if there is a large difference between sizes of cation and anions.

• PREVIOUS YEARS PROBLEMS •

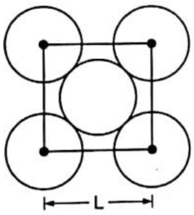
1. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axis are removed, then the resultant stoichiometry of the solid is : **(IIT 2001)**
(a) AB_2 (b) A_2B
(c) A_4B_3 (d) A_3B_4

2. A substance A_xB_y crystallises in face-centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centre of each face of the cube. The composition of A_xB_y is : **(IIT 2002)**
(a) AB_3 (b) A_4B_3
(c) A_3B (d) cannot be specified

3. The pyknometer density of NaCl crystal is $2.165 \times 10^3\ \text{kg m}^{-3}$ while its X-ray density is $2.178 \times 10^3\ \text{kg m}^{-3}$. The fraction of unoccupied sites in NaCl crystal is: **(IIT 2003)**
(a) 5.96×10^{-2} (b) 5.96×10^{-1}
(c) 5.96×10^{-3} (d) 5.96

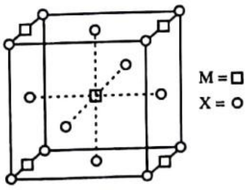
4. In which of the following crystals alternate tetrahedral voids are occupied? **(IIT 2005)**
(a) NaCl (b) ZnS
(c) CaF_2 (d) Na_2O

5. The packing efficiency of the two dimensional square unit cell shown below is : **(IIT 2010)**



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

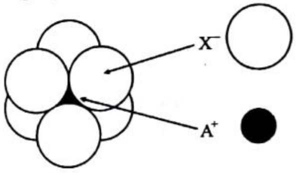
6. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown in figure. The empirical formula of the compound is : **(IIT 2012)**



(a) MX (b) MX_2
(c) M_2X (d) M_5X_{14}

7. Which of the following exists as covalent crystals in the solid state? **[JEE (Main) 2013]**
(a) Sulphur (b) Phosphorus
(c) Iodine (d) Silicon

8. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is :



[JEE (Advanced-I) 2013]
(a) 104 pm (b) 125 pm
(c) 183 pm (d) 57 pm

9. CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? **[JEE (Main) 2014]**
(a) $r_{Cs^+} + r_{Cl^-} = 3a$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
(c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3a}$

10. Sodium metal crystallizes in a body-centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately : **[JEE (Main) 2015]**
(a) 1.86 Å (b) 3.22 Å
(c) 5.72 Å (d) 0.93 Å

11. If the unit cell of a mineral has cubic packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holed occupied by magnesium ions m and n respectively, are : **[JEE (Advanced) I 2015]**
(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$
(c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

12. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be : **[JEE (Main) 2017]**
(a) $2a$ (b) $2\sqrt{2}a$
(c) $\sqrt{2}a$ (d) $\frac{a}{\sqrt{2}}$

SOLUTIONS (Previous Year Problems)

1. (d) Na in NaCl has 8 corner and 6 face atoms. If we remove face-centred atom of one axis, two face atoms are removed. Thus, A is at 8 corner and B is at 4 faces.

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

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

Thus, formula is A_3B_4.

2. (a) A at fcc thus $A=\frac{8}{8}=1$ and B at centre thus $B=\frac{1}{2}\times 6=3$. Thus formula is AB_3.

3. (c) Fraction not occupied $=\frac{(m/e_1)-(m/e_2)}{(m/e_2)}$

$$=\frac{\left(\frac{1}{e_1}\right)-\left(\frac{1}{e_2}\right)}{\left(\frac{1}{e_2}\right)}=\frac{e_1-e_2}{e_1}=\frac{e_2}{e_1}-1$$

$$=\frac{2.178}{2.165}-1=0.006$$

4. (b) In ZnS structure, sulphide ions occupy all the lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.

5. (d) Packing efficiency $=\frac{u}{V}=\frac{2\pi r^2}{L^2}$

$\because \quad r=\frac{L}{2\sqrt{2}}$

$\therefore \quad \text{P.E.}=\frac{2\pi L^2}{(2\sqrt{2})^2\cdot L^2}=\frac{\pi}{4}=0.7854$

6. (b) M_pX_q has ccp structure, therefore,

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

$M=4\times\frac{1}{4}+1=2$

So, unit cell formula of the compound is M_2X_4 and the empirical formula of the compound is MX_2.

7. (d) Silicon (Si) : Covalent solid
Sulphur : Molecular solid
Phosphorus (P_4) : Molecular solid
Iodine (I_2) : Molecular solid

8. (a) The figure represents an octahedral void

$$\frac{r_{A^+}}{r_{X^-}}=0.414$$

$$r_{A^+}=0.414\times 250=104\text{ pm}$$

9. (c) For bcc if edge length is a, then

$$r_{Cs^+}+r_{Cl^-}=\frac{\sqrt{3}}{2}a$$

10. (a) For bcc unit cell : $r=\frac{\sqrt{3}}{4}.a$

$\therefore \quad r=\frac{\sqrt{3}}{4}\times 4.29=1.85\text{ Å}$

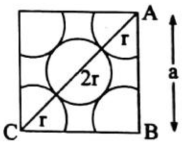
11. (a) Effective number of $O^{-2}=4$
Effective number of $Al^{+3}=4m$
Effective number of $Mg^{+2}=8m$
$\Rightarrow$ By charge balance $12m+16n=8$
$3m+4n=2$

Possible value of m and n which satisfy the above equation are

$$m=\frac{1}{2};\ n=\frac{1}{8}$$

i.e., $3\times\frac{1}{2}+4\times\frac{1}{8}=2$

12. (d) In fcc, one of the face is like



From ΔABC,

$$2a^2=16r^2$$

or $\quad r^2=\frac{1}{8}a^2$

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

Distance of closest approach $=2r=\frac{a}{\sqrt{2}}$.

OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. In which of the following systems primitives $a \neq b \neq c$?
(a) Orthorhombic (b) Monoclinic
(c) Triclinic (d) Hexagonal

2. In which of the following systems interfacial angles $\alpha = \gamma = 90°$ but $\beta \neq 90°$?
(a) Monoclinic (b) Rhombohedral
(c) Triclinic (d) Hexagonal

3. The space in which atoms are not present in unit cell is?
(a) In sc 48% (b) In fcc 26%
(c) In bcc 32% (d) In hexagonal 26%

4. Which of the following having their radius ratio between 0.414 to 0.732, *i.e.*, for NaCl structure have their radius ratio not in this range but possess NaCl type structure?
(a) LiBr (b) KCl
(c) RbCl (d) BaO

5. If radius of anion is 0.20 nm, the maximum radius of cations which can be filled in respective voids are correctly matched in :
(a) $r^+ = 0.0828$ nm for tetrahedral void
(b) $r^+ = 0.045$ triangular void
(c) $r^+ = 0.1464$ nm for octahedral void
(d) none of the above

6. Which of the following statements are correct?
(a) Dislocation of ion from lattice site to interstitial site is called Frenkel defect
(b) Missing of +ve and –ve ions from their respective position producing a pair of holes is called Schottky defect
(c) Presence of ions in the vacant interstitial sites along with lattice point is called interstitial defect
(d) Non stoichiometric NaCl is yellow solid

7. Select the correct statements :
(a) The conductance through electrons is called *p*-type conduction
(b) The conductance through positive holes is called *p*-type conduction
(c) The conductance through electrons is called *n*-type conduction
(d) The band gap in Germanium is small

8. Select the correct statements :
(a) Solid with F-centres are paramagnetic
(b) Ferrimagnetic character of Fe_3O_4 at room temperature changes to paramagnetic character at 850 K
(c) Anti ferrimagnetic V_2O_3 changes to paramagnetic at 150 K
(d) Non stoichiometric Cu_2O is *p*-type semiconductor

9. Which of the following statements are correct ?
(a) The coordination number of each type of ion in CsCl crystal is 8
(b) A metal that crystallises in bcc structure has a coordination number of 12
(c) A unit cell of ionic crystal shares some of its ion with other unit cells
(d) The length of the unit cell in NaCl is 552 pm
($\gamma_{Na^+} = 95\,\text{pm}, \gamma_{Cl^-} = 181\,\text{pm}$)

10. Select the correct statements about three dimensional hcp system :
(a) Number of atoms in hcp unit cell is six
(b) The volume of hcp unit cell is $24\sqrt{2}\,r^3$
(c) The empty space in hcp unit cell is 26%
(d) The base area of hcp unit cell is $6\sqrt{3}\,r^2$

11. If the limiting radius ratio $\left(\frac{r^+}{r^-}\right)$ lies in the range 0.225 to 0.414, there is:
(a) tetrahedral void (b) coordination no. 4
(c) zinc blene structure (d) NaCl type structure

12. The correct statement(s) regarding defects in solids is(are): **(IIT 2009)**
(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
(b) Frenkel defect is a dislocation defect
(c) Trapping of an electron in the lattice leads to the formation of F-center
(d) Schottky defects have no effect on the physical properties of solids

13. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is(are) : **[JEE (Advanced) II 2016]**
(a) The number of the nearest neighbours of an atom present in the topmost layer is 12
(b) The efficiency of atom packing is 74%
(c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
(d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

SOLUTIONS (More Than One Answer Correct)

1. (a,b,c) Follow text.
2. (a,b) —do—
3. (a,b,c,d) —do—
4. (a,b,c,d) $\frac{r^+}{r^-}$ for LiBr, KCl, RbCl and BaO are 0.34, 0.38, 0.77 and 0.83 respectively.
5. (a,b,c) $\frac{r^+}{r^-} = 0.732, 0.414, 0.225$ Maximum for octahedral, tetrahedral and triangular voids.
6. (a,b,c,d) Non stoichiometric NaCl has F-centres due to anion vacancy defect.
7. (b,c,d) Follow text. **Concepts of Physical Chemistry** by **P. Bahadur**, Prakash publications, Muzaffarnagar.
8. (a,b,c,d) —do—
9. (a,c,d) In bcc coordination number is 8.
10. (a,b,c,d) Follow solution of Numerical problem 36 on page 623?
11. (a,b,c) These are facts.
12. (b,c) Frenkel defect is created when an ion leaves its correct lattice site and occupies an interstitial site, *i.e.*, dislocation. The holes left due to Schottky defect when negative ions are apart from their lattice are occupied by electrons and are called F-centres.
13. (b, c, d)
For any atom in top most layer, coordination number is not 12 since there is no layer above top most layer and thus (a) is wrong. (b) and (c) are facts

$\because$ $\sqrt{2}a = 4R$

So $a = 2\sqrt{2}R$

COMPREHENSION BASED PROBLEMS

Comprehension 1: In crystalline solids atoms or molecules are arranged in a regular and long range order fashion in a three dimensional pattern. These have sharp melting point, flat faces, sharp edges, bounded by well defined planes. A large number of unit cells, each of which possess a definite geometry bounded by plane faces give rise to the formation of a crystal. A point at the corner of unit cell contributes for 1/8 of each such point to unit cell. A point along an edge contribute for 1/4 of each such point to unit cell. A body centred point contributes for 1 each such points to unit cell. Co-ordination number is the number of nearest neighbours that each ion is surrounded by an oppositely charged ions. Radius of unit cell in sc, fcc and bcc is $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ and $\frac{\sqrt{3}a}{4}$ where a is edge length of cell.

[1] A mineral having the formula AB_2 crystallises in the cubic closed packed lattice, with A^{2+} atoms occupying the lattice points and B^- tetrahedral voids. The co-ordination number of A, B and fraction of the tetrahedral sites occupied by B atom respectively are:
(a) 8, 4, 100% (b) 4, 8, 100%
(c) 8, 6, 57% (d) 6, 8, 57%

[2] An alloy of Cu and gold crystallises in a cubic lattice in which the gold atoms occupy the lattice points at the corners of cube and copper atoms occupy the centre of each face. The formula of this compound is:
(a) $AuCu_3$ (b) AuCu
(c) $AuCu_2$ (d) $CuAu_3$

[3] Packing factors for a body centred cubic and simple cubic structure are:
(a) 0.68, 0.524 (b) 0.524, 0.68
(c) 0.48, 0.52 (d) 0.52, 0.48

[4] In solid NH_3, each NH_3 molecule has six other NH_3 molecules as nearest neighbours. ΔH of sublimation of NH_3 at the melting point is 30.8 kJ/mol and the estimated ΔH of sublimation in absence of H-bonding is 14.3 kJ/mol. The strength of H-bond in NH_3 ion kJ/mol is:
(a) 5.5 (b) 11.0
(c) 16.5 (d) 2.75

[5] The fraction of Ni^{2+} and Ni^{3+} ions in $Ni_{0.98}O_{100}$ is:
(a) 96, 4 (b) 90, 10
(c) 4, 96 (d) 10, 90

[6] An element (density 6.8 g/cm^3) occurs in bcc structure with cell edge of 290 pm. The number of atoms present in 200 g of element is:
(a) 24×10^{23} (b) 24×10^{24}
(c) 24×10^{22} (d) 24×10^{20}

Comprehension 2: In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal closepacked (hcp), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

[1] The number of atoms in this hcp unit cell is: **(IIT 2008)**
(a) 4 (b) 6
(c) 12 (d) 17

[2] The volume of this hcp unit cell is :
(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$
(c) $12\sqrt{2}r^3$ (d) $\frac{64}{3\sqrt{3}}r^3$

[3] The empty space in this hcp unit cell is:
(a) 74% (b) 47.6%
(c) 32% (d) 26%

SOLUTIONS

Comprehension 1

[1] (a) AB_2 has bcc structure, A^{2+} possess face centred cubic lattice. B^- ions occupy all the (100%) tetrahedral voids. Thus each A^{2+} is in contact with $8B^-$ and each B^- with $4A^{2+}$ ions.

[2] (a) An atoms/unit cell $= \frac{1}{8} \times 8 = 1$

Cu atoms/unit cell $= \frac{1}{2} \times 6 = 3$

$\therefore$ empirical formula is $AuCu_3$.

[3] (a) **Body centred cubic :** $r = \frac{\sqrt{3}a}{4}$;

The unit cell of body centred cubic has 2 atoms on the average

$\therefore$ Volume of atoms $= 2 \times \frac{4}{3}\pi r^3$

$$= 2 \times \frac{4}{3} \times \pi \times \left[\frac{\sqrt{3}a}{4}\right]^3 = \frac{\sqrt{3}}{8}\pi a^3$$

Volume of unit cell $= a^3$

$\therefore$ Packing factor $= \frac{\sqrt{3}}{8}\frac{\pi a^3}{24} = 0.68$

Simple cubic : $r = \frac{a}{2}$; The unit cell of sc has one atom.

$\therefore$ Volume of atoms $= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{4\pi a^3}{24}$

Volume of unit cell $= a^3$

$\therefore$ Packing factor $= \frac{4}{24}\frac{\pi a^3}{a^3} = 0.524$

[4] (a) Total strength of H-bonds = 30.8 − 14.4 = 16.4 kJ/mol. There are 6 nearest neighbours, but each H-bond involves 2 molecules. Thus, total H-bond $= \frac{6}{2} = 3$

$\therefore$ H-bond energy $= \frac{16.4}{3} = 5.5$ kJ

[5] (a) Let Ni^{2+} be a and Ni^{3+} be $(100 - a)$, then

$a \times 2 + (1 - a) \times 3 = \frac{2 \times 1.0}{0.98}$

$\therefore$ $a = 95.9\%$

[6] (a) Density $= \frac{n \times \text{atomic mass}}{\text{Av. no.} \times a^3}$ or

$$\frac{2 \times A}{6.023 \times 10^{23} \times (290 \times 10^{-10})^3} = 6.8$$

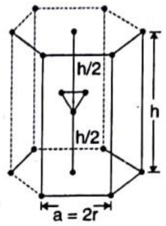
$\therefore$ $A = 50$

$\therefore$ no. of atoms in 200 g $= \frac{6.023 \times 10^{23} \times 200}{50}$

$= 24 \times 10^{23}$

Comprehension 2

In three dimensional closest packing of hcp or ccp (although both are different) only 74% of the available space is occupied by spheres. The remaining 26% space which is vacant, constitutes **interstitial voids** or **interstices sites** or **interstices**. The given packing (*AB AB AB*...) is three dimensional close packing as shown in given figure. In this arrangement three atoms are arranged in the body centred position in such a way, so that it forms equilateral triangle an twelve atoms are placed at 12 corners and two atoms at two face centres.

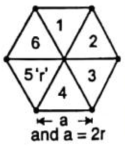


(i) **No. of atoms per unit cell**

$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 = 6$

(ii) Thus **co-ordination number** of three dimensional hcp lattice becomes 12, *i.e.*, 6 from own layer and 3 from above and 3 from lower layer.

(iii) **Base Area (*A*) of unit cell :** Base area of hcp unit cell is given by:



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

$A = \frac{3\sqrt{3}}{2}a^2$

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

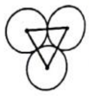
(iv) **Height of unit cell:**

$\cos 120° = \frac{x^2 + x^2 - (2r)^2}{2x^2}$

or $-\frac{1}{2} = \frac{2x^2 - 4r^2}{2x^2} = \frac{x^2 - 2r^2}{x^2}$

or $3x^2 = 4r^2$

$\therefore$ $x = \frac{2r}{\sqrt{3}}$



Now $\left(\frac{h}{2}\right)^2 = a^2 - x^2$

$\frac{h^2}{4} = (2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2$ or $\frac{h^2}{4} = \frac{8r^2}{3}$

$\therefore$ $h^2 = \frac{32r^2}{3}$ or $h = 4r \times \sqrt{\frac{2}{3}}$

(v) **Packing fraction :** Each corner atom would be common to 6 other unit cell. If r is the radius of each sphere, then

Packing fraction $= \frac{6 \times \frac{4}{3}\pi r^2}{v}$

where, v = volume of hexagon

= Area of base $(A) \times$ height (h)

$\therefore$ **Packing fraction** $= \frac{6 \times \frac{4}{3}\pi r^2}{6 \times \sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}}} = \frac{\pi}{3 \times \sqrt{2}}$

= 0.74 or 74%

(vi) $V = h \times \text{area} = 6\sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}} = 24\sqrt{2}r^3$

[1] (b), [2] (a), [3] (d)

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but **E** is wrong
(b) S is wrong but **E** is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and **E** are correct but **E** is not correct explanation of S

1. S : Initially the term pseudo solid was given for solids, which were easily distorted by bending and compression forces. They even tend to flow slowly under its own mass and lose shape.
E : These characteristics are shown by pseudo solids as in pitch, glass and thus, the name pseudo solid was replaced by super cooled liquids.

2. S : The close packing of atoms in cubic structure is in the order fcc > bcc > sc.
E : Packing density $= \dfrac{\text{Volume of unit cell}}{a^3}$

3. S : In hexagonal close packing voids are between three touching spheres whose centres lie at the corners of an equilateral triangle.
E : In hexagonal close packing voids are called square voids.

4. S : Bragg's equation has no solution, if $n = 2$ and $\lambda > d$.
E : Bragg's equation is: $n\lambda = 2d \sin\theta$.

5. S : 6 : 6 co-ordination at normal temperature and pressure changes to 8 : 8 co-ordination at high pressure.
E : Pressure influences the structure of solids.

6. S : 8 : 8 co-ordination of CsCl at low temperature changes to 6 : 6 co-ordination at 760 K.
E : Temperature also influences the structure of solids.

7. S : Solids containing F-centres are paramagnetic.
E : F-centres solids possess holes occupied by unpaired electrons.

8. S : Solids having more F-centres possess intense colours.
E : Excess of Na^+ in NaCl solid having F-centres makes it appear to pink.

9. S : The conductance through electrons is called *n*-type conduction and if through positive holes, it is called *p*-type conduction.
E : Doping involves preparation of semi-conductors by the presence of impurities in the intrinsic semi-conductor.

10. S : A crystal having fcc structure is more closely packed than a crystal having bcc structure.
E : Packing fraction for fcc structure is double that of bcc structure.

11. S : In any ionic solid (*MX*) with Schottky defects, number of positive and negative ions are same.
E : Equal number of cation and anion vacancies are present.

12. S : bcc arrangement is less closely packed than ccp arrangement.
E : In ccp 74% of the available space is occupied by spheres but in bcc only 68% of the space is occupied by spheres.

13. S : Ferromagnetic substances are strongly attracted by magnetic field.
E : Ferromagnetism arises due to spontaneous alignment magnetic moments of ions or atoms in the same direction.

14. S : For ionic solids exhibiting Frenkel defects, the density remains unaltered.
E : Doping of group 14 elements with suitable elements of group 13 produces *p*-type of semiconductors.

15. S : In rock salt structure, all the octahedral voids in the close packing of anions are occupied by cations.
E : In rock salt structure, the distance of closest approach between two anions equal to half the face diagonal of unit cell.

16. S : Co-ordination number of CsCl changes from 8 : 8 to 6 : 6 on heating.
E : The crystal structure of CsCl changes to NaCl on heating.

17. S : Equivalent conducting power of H^+ and OH^- ion is maximum and abnormally high among all the ions.
E : There occurs a proton jump from one water molecule to other leading to grothus type conductance.

18. S : Band gap in germanium is small.
E : The energy spread of each germanium atomic energy level is infinitesimally small. **[IIT 2007]**

ANSWERS (Statement Explanation Problems)

1. (d) Both are facts.
2. (c) Explanation is correct reason for statement.
3. (a) In hexagonal close packing voids are triangular voids.
4. (c) If $n = 2$ and $\lambda > d$, then $\sin\theta > 1$, which is not possible.
5. (c) Explanation is correct reason for statement.
6. (c) —do—
7. (c) —do—
8. (a) Excess Na^+ in NaCl solid at F-centres develops yellow colour.
9. (d) Both are facts.
10. (a) Packing fraction in fcc = 74%
Packing fraction in bcc = 67.9%
11. (c) Explanation is correct reason for statement.
12. (d) Both statement and explanation are correct but the reason is different.
13. (c) Explanation is correct reason for statement.
14. (d) Both statement and explanation are correct but reason for the statement is different.
15. (d) Both statement and explanation are correct but reason for the statement is different.
16. (c) Explanation is correct reason for statement.
17. (c) The given statement and its explanation are correct.
18. (a) Follow text.

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

1.

List A	List B
(A) Schottky defect	1. NaCl and $SrCl_2$
(B) Frenkel defect	2. Defects produced by heating Na in Cl_2
(C) F-centres	3. NaCl
(D) Metal deficiency	4. AgCl

Type II : More Than One Match Are Possible

2.

List A	List B
(A) Simple cubic and face-centred cubic parameters	(P) have these cell
(B) Cubic and rhombohedral	(Q) are two crystal system
(C) Cubic and tetragonal	(R) have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	(S) belong to same crystal system

Type III : Only One Match From Each List

3.

List A	List B	List C
1. Cubic	a. $a = b \neq c$	A. $\alpha = \beta = \gamma = 90°$
2. Tetragonal	b. $a \neq b \neq c$	B. $\alpha = \gamma = 90° \neq \beta$
3. Orthorhombic	c. $a = b = c$	C. $\alpha \neq \beta \neq \gamma \neq 90°$
4. Monoclinic		D. $\alpha = \beta = 90°; \gamma = 120°$
5. Triclinic		
6. Rhombohedral		
7. Hexagonal		

4.

List A	List B	List C
1. sc	a. $a = 2.31r$	A. $\frac{\pi}{6}$
2. fcc	b. $a = 2.828r$	B. $\frac{\pi}{3\sqrt{2}}$
3. bcc	c. $a = 2r$	C. $\frac{\sqrt{3}\pi}{8}$

5.

List A	List B
(A) Cubic	1. Simple or primitive
(B) Tetragonal	2. Body centred
(C) Orthorhombic	3. Face centred
(D) Monoclinic	4. End centred

ANSWERS

1. A– 3; B–4; C–2; D–1
2. A – P, S; B – P, Q; C – Q; D – Q,R
3. 1– c–A; 2–a –A; 3–b–A; 4 –b–B; 5–b – C; 6 – c–B; 7–a–D
4. 1– c–A; 2–b–B; 3–a– C
5. A– 1,2,3; B–1,2; C–1,2; D–4