8

Solid State

Objective Questions I (Only one correct option)

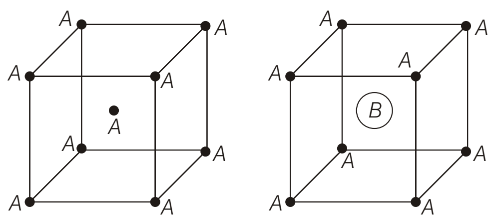
1. The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are, respectively. **(2019 Main, 12 April II)**

(a) 8 : 1 : 6 (b) 1 : 2 : 4
(c) 4 : 2 : 1 (d) 4 : 2 : 3

2. An element has a face-centred cubic (fcc) structure with a cell edge of a. The distance between the centres of two nearest tetrahedral voids in the lattice is **(2019 Main, 12 April I)**

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

3. Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more is solid 2 than in 1. What is the approximate packing efficiency in solid 2? **(2019 Main, 8 April II)**



Solid 1 Solid 2

(a) 65% (b) 90%
(c) 75% (d) 45%

4. The statement that is incorrect about the interstitial compounds is **(2019 Main, 8 April II)**

(a) they are very hard
(b) they have metallic conductivity
(c) they have high melting points
(d) they are chemically reactive

5. Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is **(2019 Main, 8 April I)**

(a) A_2BO_4 (b) AB_2O_4
(c) A_2B_2O (d) A_4B_2O

6. The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is (Edge length is represented by 'a') **(2019 Main, 11 Jan II)**

(a) 0.134 a (b) 0.027 a (c) 0.047 a (d) 0.067 a

7. A solid having density of $9\ \ 10^3\ \text{kg m}^{\ 3}$ forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid?
[Avogadro constant $6\ \ 10^{23}\ \text{mol}^{\ 1}$, $\ \ 3$]
(2019 Main, 11 Jan I)

(a) 0.03050 kg mol ^{1} (b) 0.4320 kg mol ^{1}
(c) 0.0432 kg mol ^{1} (d) 0.0216 kg mol ^{1}

8. A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms ? **(2019 Main, 10 Jan II)**

(a) hcp lattice- A, $\frac{2}{3}$ tetrahedral voids-B

(b) hcp lattice-A, $\frac{1}{3}$ tetrahedral voids-B

(c) hcp lattice-B, $\frac{1}{3}$ tetrahedral voids-A

(d) hcp lattice-B, $\frac{2}{3}$ tetrahedral voids-A

9. Which primitive unit cell has unequal edge lengths ($a\ \ b\ \ c$) and all axial angles different from 90°? **(2019 Main, 10 Jan I)**

(a) Hexagonal (b) Monoclinic
(c) Tetragonal (d) Triclinic

10. At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm ^{3}) at this temperature?
[Atomic mass of Cu 63.55 u] **(2019 Main, 9 Jan II)**

(a) $\frac{211}{x^3}$ (b) $\frac{205}{x^3}$
(c) $\frac{105}{x^3}$ (d) $\frac{422}{x^3}$

11. The one that is extensively used as a piezoelectric material is **(2019 Main, 9 Jan I)**

(a) quartz (b) tridymite
(c) amorphous silica (d) mica

12. Which type of 'defect' has the presence of cations in the interstitial sites? **(2018 Main)**

(a) Schottky defect (b) Vacancy defect

(c) Frenkel defect (d) Metal deficiency defect

13. 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 **(2017 Main)**

(a) $2\,a$ (b) $2\sqrt{2}\,a$

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

14. Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately **(2015 Main)**

(a) 1.86Å (b) 3.22Å

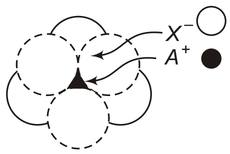
(c) 5.72Å (d) 0.93Å

15. CsCl crystallises in body centred cubic lattice. If 'a' its edge length, then which of the following expressions is correct? **(2014 Main)**

(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} $\sqrt{3}a$

16. 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 **(2013 Adv.)**



(a) 104 pm (b) 125 pm

(c) 183 pm (d) 57 pm

17. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3} would be

(a) 7.01% (b) 4.08% **(2013 Main)**

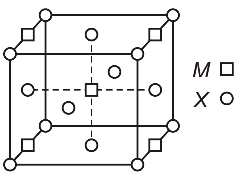
(c) 6.05% (d) 5.08%

18. Which of the following exists as covalent crystals in the solid state? **(2013 Main)**

(a) Iodine (b) Silicon

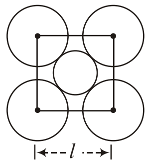
(c) Sulphur (d) Phosphorus

19. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound, is **(2012)**



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

20. The packing efficiency of the two-dimensional square unit cell shown below is **(2010)**



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

21. Which of the following fcc structure contains cations in alternate tetrahedral voids? **(2005, 1M)**

(a) NaCl (b) ZnS (c) Na_2O (d) CaF_2

22. A substance A_xB_y crystallises in a face centred cubic (fcc) lattice in which atoms A occupy each corner of the cube and atoms B occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y **(2002, 1M)**

(a) AB_3

(b) A_4B_3

(c) A_3B

(d) composition cannot be specified

23. 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 axes are removed, then the resultant stoichiometry of the solid is **(2001, S, 1M)**

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

24. The coordination number of a metal crystallising in a hexagonal close-packed structure is **(1999, 2M)**

(a) 12 (b) 4 (c) 8 (d) 6

Objective Questions II

(One or more than one correct option)

25. The correct statement(s) for cubic close packed (ccp) three dimensional structure is (are) **(2016 Adv.)**

(a) The number of the nearest neighbours of an atom present in the topmost layer is 12

(b) The packing efficiency of atom 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

26. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n respectively, are **(2015 Adv.)**

(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

27. The correct statement(s) regarding defects in solids is/are

(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion **(1999)**

(b) Frenkel defect is a dislocation defect

(c) Trapping of an electron in the lattice leads to the formation of F-centre

(d) Schottky defects have no effect on the physical properties of solids

28. Which of the following statement(s) is/are correct?

(a) The coordination number of each type of ion in CsCl crystal is 8 **(1998, 2M)**

(b) A metal that crystallises in bcc structure has a coordination number of 12

(c) A unit cell of an ionic crystal shares some of its ions with other unit cells

(d) The length of the unit cell in NaCl is 552 pm.
(r_{Na} 95 pm; r_{Cl} 181 pm)

Numerical Value

29. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instruction given below. Neglect the charge balance. **(2018 Adv.)**

(a) Remove all the anions (X) except the central one

(b) Replace all the face centered cations (M) by anions (X)

(c) Remove all the corner cations (M)

(d) Replace the central anion (X) with cation (M)

The value of $\frac{\text{Number of anions}}{\text{Number of cations}}$ in Z is ___

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct Statement II is correct Statement II is the correct explanation of Statement I

(b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I

(c) Statement I is correct Statement II is incorrect

(d) Statement I is incorrect Statement II is correct

30. **Statement I** In any ionic soid (MX) with Schottky defects, the number of positive and negative ions are same.

Statement II Equal numbers of cation and anion vacancies are present. **(2001, 1M)**

Passage Based Questions

Passage

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 close-packed (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'.

31. The number of atoms in one of this hcp unit cell is **(2008, 3 4M = 12M)**

(a) 4 (b) 6 (c) 12 (d) 17

32. 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) $\frac{64r^3}{3\sqrt{3}}$

33. The empty space in this hcp unit cell is

(a) 74 % (b) 47.6 % (c) 32 % (d) 26 %

Match the Columns

34. Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. **(2007, 6M)**

	Column I		Column II
A.	Simple cubic and face centred cubic	p.	have these cell parameters a b c and 90
B.	Cubic and rhombohedral	q.	are two crystal systems
C.	Cubic and tetragonal	r.	have only two crystallographic angles of 90°
D.	Hexagonal and monoclinic	s.	belong to same crystal system

Integer Answer Type Questions

35. 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 8 g cm ^{3}, then the number of atoms present in 256 g of the crystal is N 10^{24}. The value of N is **(2017 Adv.)**

36. The number of hexagonal faces that are present in a truncated octahedron is **(2011)**

37. Silver (atomic weight 108 g mol ^{1}) has a density of 10.5 g cm ^{3}. The number of silver atoms on a surface of area 10 ^{12} m^2 can be expressed in scientific notation as y 10^x. The value of x is **(2010)**

Subjective Questions

38. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. (N_A 6 10^{23}). Give the answer in pm. **(2006, 3M)**

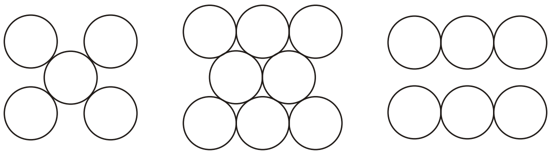
39. An element crystallises in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure. **(2005, 2M)**

40. The crystal AB (rock salt structure) has molecular weight 6.023y u. Where, y is an arbitrary number in u. If the minimum distance betweeen cation and anion is $y^{1/3}$ nm and the observed density is 20 kg/m^3. Find the (i) density in kg/m^3 and (ii) type of defect. **(2004, 2M)**

41. (i) Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centres are within this area.

(ii) Find the maximum number of marbles per unit area and deduce an expression for calculating it. **(2003, 4M)**

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



43. A metal crystallises 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. **(1999, 3M)**

44. Chromium metal crystallises with a body centred cubic lattice. The length of the unit edge is found to be 287 pm. Calculate the atomic radius . What would be the density of chromium in g/cm^3? **(1997, 3M)**

45. A metallic element crystallises into a lattice containing a sequence of layers of $ABABAB\ldots\ldots$ Any packing of layers leaves out voids in the lattice. What percentage of this lattice is empty space? **(1996, 3M)**

46. Sodium crystallises in a bcc cubic lattice with the cell edge, a 4.29 Å. What is the radius of sodium atom? **(1994, 2M)**

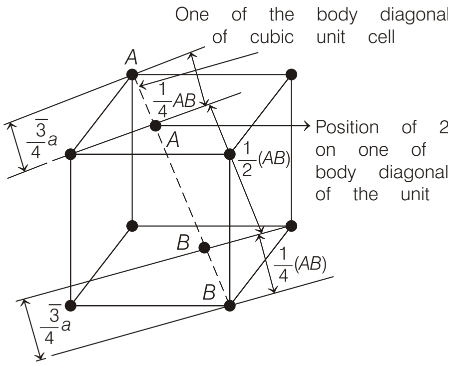
Answers

1. (b)	**2.** (c)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (d)	**7.** (a)	**8.** (c)	**9.** (d)
10. (d)	**11.** (a)	**12.** (c)	**13.** (d)	**14.** (a)	**15.** (c)	**16.** (a)	**17.** (b)	**18.** (b)
19. (b)	**20.** (d)	**21.** (b)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (b,c,d)	**26.** (a)	**27.** (b,c)
28. (a,c,d)	**29.** (3)	**30.** (a)	**31.** (b)	**32.** (a)	**33.** (d)	**34.** A p, s; B q; C q; D q, r		
35. (2)	**36.** (8)	**37.** (7)	**38.** (217 pm)	**39.** (117 pm)	**43.** (1.26)	**44.** (7.3 g/cm^3)		
45. (0.74)	**46.** (1.86 Å)							

Hints & Solutions

1. The ratio of number of atoms present in simple cubic, body centred cubic and face centered cubic structure are 1 : 2 : 4 respectively.

2. In fcc unit cell, two tetrahedral voids are formed on each of the four non-parallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.



The angle between body diagonal and an edge is $\cos^{-1}(1/\sqrt{3})$. So, the projection of the line on an edge is $a/4$. Similarly, other tetrahedral void also will be $a/4$ away. So, the distance between these two is $a \quad \frac{a}{4} \quad \frac{a}{4} \quad \frac{a}{2}$.

3. **Key Idea** Packing efficiency

$$\frac{\text{Volume occupied by sphere}}{\text{Volume of cube}} \quad 100$$

Given,

$$r_B \quad 2r_A$$

$$a_2 \quad a_1 \quad \frac{50}{100}a_1 \quad 1.5\,a_1$$

For bcc lattice

$$4r_A \quad \sqrt{3}\,a_1$$

$$r_A \quad \frac{\sqrt{3}\,a_1}{4}$$

$$a_1 \quad \frac{4r_A}{\sqrt{3}}$$

$$a_2 \quad 1.5 \quad \frac{4r_A}{\sqrt{3}}$$

$$\frac{3}{2} \quad \frac{4r_A}{\sqrt{3}}$$

$$a_2 \quad 2\sqrt{3}\, r_A$$

Packing efficiency $\dfrac{\dfrac{4}{3} \quad r_A^3 \quad z_A \quad \dfrac{4}{3} \quad r_B^3 \quad z_B}{a_2^3}$

[As the atoms A are present at the edges only $z_A \quad \dfrac{1}{8} \quad 8 \quad 1$, atom B is present only at the body centre $z_B \quad 1$]

$$\text{PE}_2 \quad \frac{\dfrac{4}{3} \quad r_A^3 \quad 1 \qquad \dfrac{4}{3} \quad r_B^3 \quad 1}{a_2^3}$$

$$\frac{\dfrac{4}{3} \quad r_A^3 \quad \dfrac{4}{3} \quad (2r_A)^3}{(2\sqrt{3}\, r_A)^3} \qquad \frac{\dfrac{4}{3} \quad r_A^3 \quad 9}{8 \quad 3\sqrt{3}\, r_A^3} \qquad \overline{2\sqrt{3}}$$

$$90.72\% \quad 90\%$$

4. Interstitial compounds are formed when a neutral atom with a small radius occupies in an interstitial hole (tetrahedral or octahedral voids) in a transition metal's hcp or ccp lattices (host lattice). Examples of small atoms (guest atom) are H, B, C and N.

Interstitial compounds are non-stoichiometric (Birtholide) in composition. They are very hard with very high melting points. The electrical conductivity of interstitial compounds are comparable to that of the pure metal. These are chemically unreactive in nature.

5. The number of element 'B' in the crystal structure = 4 N

Number of tetrahedral voids = $2N$

Number of octahedral voids = N

Number of 'A' in the crystal $\dfrac{N}{2} \quad \dfrac{4}{2} \quad 2$

Number of oxygen (O) atoms $\quad 2N \quad 2 \quad 4 \quad 8$

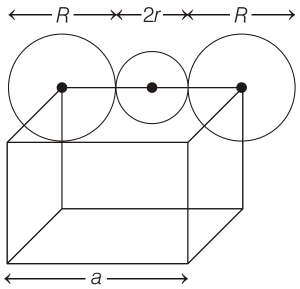
The structure of bimetallic oxide $\quad A_2\, B_4\, O_8 \quad AB_2\, O_4$

6. For body centred cubic bcc structure,

radius (R) $\dfrac{\sqrt{3}}{4}a$ ...(i)

Where, a edge length

According to question, the structure of cubic unit cell can be shown as follows:



$$a \quad 2(R \quad r) \qquad \text{...(ii)}$$

On substituting the value of R from Eq. (i) to Eq. (ii), we get

$$\frac{a}{2} \quad \frac{\sqrt{3}}{4}a \quad r$$

$$r \quad \frac{a}{2} \quad \frac{\sqrt{3}}{4}\, a \quad \frac{2a \quad \sqrt{3}a}{4}$$

$$r \quad \frac{a(2 \quad \sqrt{3})}{4}$$

$$r \quad 0.067a$$

7. Density of a crystal

$$d \quad \frac{M \quad Z}{N_A \quad a^3} \qquad M \quad \frac{d \quad N_A \quad a^3}{Z}$$

Given, $d \quad 9 \quad 10^3$ kg m ^{3}

M Molar mass of the solid

Z 4 (for fcc crystal)

N_A Avogadro's constant $\quad 6 \quad 10^{23}$ mol ^{1}

a Edge length of the unit cell

$200\sqrt{2}$ pm $\quad 200\sqrt{2} \quad 10^{\;12}$ m

On substituting all the given values, we get

$$\frac{(9 \quad 10^3)\ \text{kg m}^{\;3} \quad (6 \quad 10^{23})\ \text{mol}^{\;1} \quad (200\sqrt{2} \quad 10^{\;12})^3\text{m}^3}{4}$$

$$0.0305\ \text{kg mol}^{\;1}$$

8. Total effective number of atoms in hcp unit lattice Number of octahedral voids in hcp 6

Number of tetrahedral voids (TV) in hcp

2 Number of atoms in hcp lattice

2 6 12

As, formula of the lattice is A_2B_3.

Suppose,	A	B
	$\frac{1}{3}$ TV	(hcp)
	$\frac{1}{3}$ 12	6
	$\frac{2}{3}$	1
	2	3

So, $A \quad \dfrac{1}{3}$ tetrahedral voids, B hcp lattice

9. Triclinic primitive unit cell has dimensions as, $a \quad b \quad c$ and $\quad 90$.

Among the seven basic or primitive crystalline systems, the triclinic system is most unsymmetrical. In other cases, edge length and axial angles are given as follows :

Hexagonal : $a \quad b \quad c$ and $\quad 90 , \quad 120$

Monoclinic : $a \quad b \quad c$ and $\quad 90 , \quad 90$

Tetragonal : $a \quad b \quad c$ and $\quad 90$

10. For fcc, rank of the unit cell (Z) 4

Mass of one Cu-atom, M 63.55 u

Avogadro's number, N_A 6.023 10^{23} atom

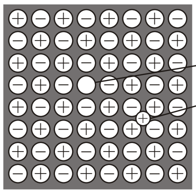
Edge length, $a \quad x$ Å $\quad x \quad 10^{\;8}$ cm

density (d) $\dfrac{Z \quad M}{N_A \quad a^3}$

$$\frac{4 \quad 63.55}{6.023 \quad 10^{23} \quad (x \quad 10^{\ 8})^3} \quad \frac{422.048}{x^3} \text{ g cm}^{\ 3}$$

11. Piezoelectric materials are those materials that produce an electric current when they are placed under mechanical stress. Crystalline solids can be used as piezoelectric material hence, quartz is a correct answer.

12. It is the ''Frenkel defect'' in which cations leave their original site and occupy interstitial site as shown below.



13. For fcc arrangement, $4r \quad \sqrt{2}a$

where, r radius and a edge length

Closest distance $2r \quad \frac{\sqrt{2}\,a}{2} \quad \frac{a}{\sqrt{2}}$

14. For bcc unit cell, $\sqrt{3}\,a \quad 4a$

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

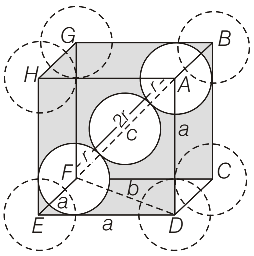
$$\frac{\sqrt{3}}{4} \quad 4.29\text{Å} \quad 1.85\text{Å}$$

$$r \quad 1.85\text{Å} \quad 1.86\text{Å}$$

15. In CsCl, Cl lies at corners of simple cube and Cs at the body centre. Hence, along the body diagonal, Cs and Cl touch each other so $r_{\text{Cs}} \quad r_{\text{Cl}} \quad 2r$

Calculation of *r*

In EDF,



Body centred cubic unit cell

$$FD \quad b \quad \sqrt{a^2 \quad a^2} \quad \sqrt{2}\,a$$

In AFD,

$$c^2 \quad a^2 \quad b^2 \quad a^2 \quad (\sqrt{2}\,a)^2 \quad a^2 \quad 2a^2$$

$$c^2 \quad 3a^2 \qquad c \quad \sqrt{3}\,a$$

As AFD is an equilateral triangle.

$$\sqrt{3}\,a \quad 4r \qquad [\because C \quad 3r \quad r \quad r]$$

$$r \quad \frac{\sqrt{3}\,a}{4}$$

Hence, $r_{\text{Cs}} \quad r_{\text{Cl}} \quad 2r \quad 2 \quad \frac{\sqrt{3}}{4}a \quad \frac{\sqrt{3}}{2}a$

16. **PLAN** Given arrangement represents octahedral void and for this

$$\frac{r \text{ (cation)}}{r \text{ (anion)}} \quad 0.414$$

$$\frac{r(A \ )}{r(X \ )} \quad 0.414$$

$$r(A \ ) \quad 0.414 \quad r(X \ ) \quad 0.414 \quad 250\text{pm}$$

$$103.5 \text{ pm} \quad 104 \text{ pm}$$

17. From the valency of M^{2} and M^{3}, it is clear that three M^{2} ions will be replaced by M^{3} causing a loss of one M^{3} ion. Total loss of them from one molecule of MO $1 \quad 0.98 \quad 0.02$

Total M^{3} present in one molecule of

MO $2 \quad 0.02 \quad 0.04$

That M^{2} and M^{3} $\quad 0.98$

Thus, % of $M^{3} \quad \frac{0.04 \quad 100}{0.98} \quad 4.08\%$

18. Silicon exists as covalent crystal in solid state. (Network like structure, as seen in diamond).

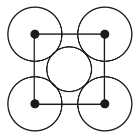
19. Contribution of atom from the edge centre is 1/4. Therefore, number of

$M \quad \frac{1}{4} \quad 4$ (from edge centre) $\quad 1$ (from body centre) $\quad 2$

Number of $X \quad \frac{1}{8} \quad 8$ (from corners) $\quad \frac{1}{2} \quad 6$ (from face centre) $\quad 4$

Empirical formula $M_2X_4 \quad MX_2$

20. Contribution of circle from corner of square $\frac{1}{4}$



Effective number of circle per square

$$\frac{1}{4} \quad 4 \quad 1 \text{(at centre)} \quad 2$$

Area occupied by circle $2 \ r^2, r$ radius.

Also, diagonal of square $4r \quad \sqrt{2}\,L$, where L side of square.

$$\text{Packing fraction} \quad \frac{\text{Area occupied by circles}}{\text{Area of square}}$$

$$\frac{2 \ r^2}{L^2} \quad \frac{2 \ r^2}{8r^2} \quad \frac{}{4} \quad 0.785$$

% packing efficiency $\quad 78.5\%$.

21. In ZnS, S^{2} (sulphide ions) are present at fcc positions giving four sulphide ions per unit cell. To comply with 1 : 1 stoichiometry, four Zn^{2} ions must be present in four alternate tetrahedral voids out of eight tetrahedral voids present.

In NaCl, Na^+ ions are present in octahedral voids while in Na_2O, Na^+ ions are present in all its tetrahedral voids giving the desired 2 : 1 stoichiometry. In CaF_2, Ca^{2+} ions occupies fcc positions and all the tetrahedral voids are occupied by fluoride ions.

22. In cubic system, a corner contribute $\frac{1}{8}$th part of atom to one unit cell and a face centre contribute $\frac{1}{2}$ part of atom to one unit cell.

Therefore,

Number of A per unit cell $\frac{1}{8} \quad 8 \quad 1$

Number of B per unit cell $\frac{1}{2}$ 6 3

Formula AB_3

23. In NaCl, Na^+ occupies body centre and edge centres while Cl occupies corners and face centres, giving four Na and four Cl per unit cell. In the present case A represent Cl and B represents Na^+. Two face centres lies on one axis.

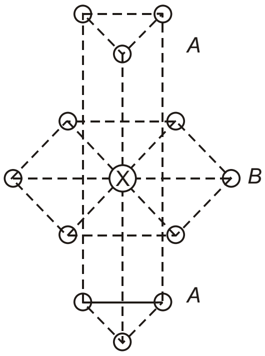
Number of A removed 2 $\frac{1}{2}$ 1

Number of B is removed because it is not present on face centres.

A remaining 4 1 3, B remaining 4,

Formula A_3B_4

24. Three consecutive layers of atoms in hexagonal close packed lattice is shown below:



Atom X is in contact of 12 like atoms, 6 from layer B and 3 from top and bottom layers A each.

25. (a) Nearest neighbour in the topmost layer of ccp structure is 9 thus, incorrect.

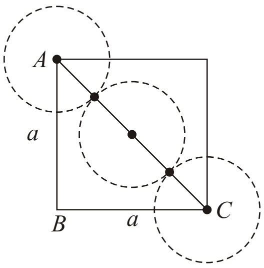
(b) Packing efficiency is 74% thus, correct.

(c) Tetrahedral voids 2

Octahedral voids = 1 per atom thus, correct.

(d) Edge length, a $\frac{4}{\sqrt{2}}r$ $2\sqrt{2}r$

thus, correct



Explanation Edge length a

Radius r

AC^2 AB^2 BC^2

$(4r)^2$ a^2 a^2 $2a^2$

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

r $\frac{\sqrt{2}}{4}a$ $\frac{a}{2\sqrt{2}}$ a $2\sqrt{2}\,r$

In ccp structure, number of spheres is 4.

Hence, volume of 4 spheres 4 $\frac{4}{3}$ r^3

Total volume of unit cell a^3 $(2\sqrt{2}r)^3$

% of packing efficiency

$$\frac{\text{Volume of 4 spheres}}{\text{Volume of unit cell}} \quad \frac{4\ \frac{4}{3}\ r^3}{[2(\sqrt{2}r)]^3} \quad 100$$

74.05% ~ 74%

26. Oxide ions are at ccp positions, hence $4O^{2-}$ ions. Also, there are four octahedral voids and eight tetrahedral voids. Since 'm' fraction of octahedral voids contain Al^{3+} and 'n' fraction of tetrahedral voids contain Mg^{2+} ions, to maintain etectroneutrality $2(2Al^{3+} = +6$ charge) and ($Mg^{2+} = +2$ charge), will make unit cell neutral

Hence: m $\frac{2}{4}$ $\frac{1}{2}$, n $\frac{1}{8}$

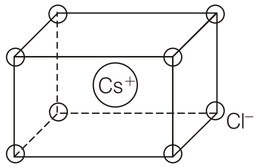
27. (a) Wrong statement. A small difference in sizes of cation and anion favour Schottky defect while Frenkel defect is favoured by large difference in sizes of cation and anion.

(b) Correct statement. In Frenkel defect the smaller atom or ion gets dislocated from its normal lattice positions and occupies the interstitial space.

(c) **Correct Statement** In F-centre defect, some anions leave the lattice and the vacant sites hold the electrons trapped in it maintaining the overall electroneutrality of solid.

(d) Wrong statement : In Schottky defect, some of the atoms or ions remaining absent from their normal lattice points without distorting the original unit cell dimension. This lowers the density of solid.

28. (a) The unit cell of CsCl has bcc arrangement of ions in which each ion has eight oppositely charged ions around it in the nearest neighbours as shown below :



Unit cell of CsCl

(b) In bcc, coordination number of atom is 8.

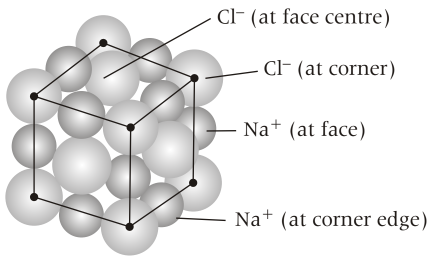
(c) In an unit cell, a corner is shared in eight unit cells and a face centre is shared between two adjacent unit cells.

(d) In NaCl unit cell; $2(r_{Na^+}$ r_{Cl}) a

a 2 (95 181) 552 pm

Hence, a, c, d are correct.

29. The unit cell of initial structure of ionic solid MX looks like



In NaCl type of solids cations (Na) occupy the octahedral voids while anions (Cl) occupy the face centre positions.

However, as per the demand of problem the position of cations and anions are swapped.

We also know that (for 1 unit cell)

(A) Total number of atoms at FCC = 4

(B) Total number of octahedral voids = 4

(as no. of atoms at FCC = No. of octahedral voids)

Now taking the conditions one by one

(i) If we remove all the anions except the central one than number of left anions.

$$4 \quad 3 \quad 1$$

(ii) If we replace all the face centred cations by anions than effective number of cations will be $4 \quad 3 \quad 1$

Likewise effective number of anions will be $1 \quad 3 \quad 4$

(iii) If we remove all the corner cations then effective number of cations will be $1 \quad 1 \quad 0$

(iv) If we replace central anion with cation then effective number of cations will be $0 \quad 1 \quad 1$

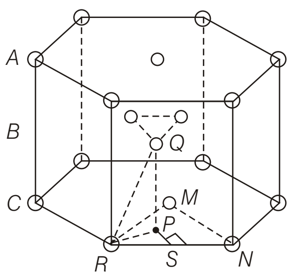
Likewise effective number of anions will be $4 \quad 1 \quad 3$

Thus, as the final outcome, total number of cations present in Z after fulfilling all the four sequential instructions 1

Likewise, total number of anions 3

Hence, the value of $\frac{\text{Number of anions}}{\text{Number of cations}} \quad \frac{3}{1} \quad 3$

30. In ionic solid MX (1 : 1 solid) same number of M^{n} and X^{n} ions are lost in Schottky defect to maintain electroneutrality of solid.

31. 

A hcp unit cell

Contribution of atoms from corner $1/6$

Contribution from face centre $1/2$

Total number of atoms per unit cell $12 \quad \frac{1}{6} \quad 2 \quad \frac{1}{2} \quad 3 \quad 6$

32. In close packed arrangement, side of the base $2r$

$$RS \quad r$$

Also MNR is equilateral triangle, $PRS \quad 30$

In triangle PRS, $\cos 30 \quad \frac{RS}{PR} \quad \frac{\sqrt{3}}{2}$

$$PR \quad \frac{2}{\sqrt{3}} RS \quad \frac{2}{\sqrt{3}} r$$

In right angle triangle $PQR : PQ \quad \sqrt{QR^2 \quad PR^2} \quad 2\sqrt{\frac{2}{3}}\, r$

Height of hexagon $2PQ \quad 4\sqrt{\frac{2}{3}}\, r$

Volume = Area of base height $6\,\frac{\sqrt{3}}{4}\,(2r)^2 \quad 4\sqrt{\frac{2}{3}}\, r$

$$24\sqrt{2}\, r^3$$

33. Packing fraction $\frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$

$$6 \quad \frac{4}{3} \quad r^3 \quad \frac{1}{24\sqrt{2}\, r^3} \quad 0.74$$

Fraction of empty space $1 \quad 0.74 = 0.26 \quad 26\%$

34. A. Simple cubic and face centred cubic both have cell parameters $a \quad b \quad c$ and 90. Also both of them belongs to same, cubic, crystal system.

B. The cubic and rhombohedral crystal system belongs to different crystal system.

C. Cubic and tetragonal are two different types of crystal systems having different cell parameters.

D. Hexagonal and monoclinic are two different crystal system and both have two of their crystallographic angles of 90°.

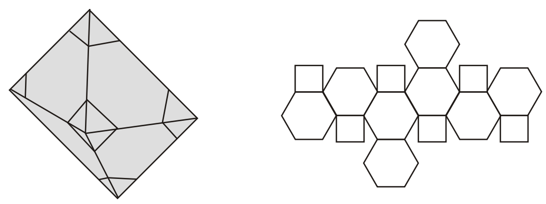
35. Density ( ) $8 \quad \frac{4 \quad M}{N_A(4 \quad 10^{\ 8}\,\text{cm})^3}$

$$M \quad 128 \quad 10^{\ 24} N_A \qquad \text{No of atoms} \quad \frac{256}{M} \quad N_A$$

$$\frac{256}{128 \quad 10^{\ 24} N_A} \quad N_A \quad 2 \quad 10^{24}$$

36. 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 as :



Truncated octahedron

Truncated octahedron unfolded in two-dimension

37. Ag crystallises in fcc unit cell with 4 atoms per unit cell.

$$\frac{4 \quad 108}{6.023 \quad 10^{23} \quad a^3} \quad 10.5\ \text{g cm}^{\ 3}.$$

a^3 (Volume of unit cell) $6.83 \quad 10^{\ 23}\ \text{cm}^3$

$a \quad 4 \quad 10^{\ 8}\ \text{cm} \quad 4 \quad 10^{\ 10}\ \text{m}$

Surface area of unit cell $a^2 \quad 1.6 \quad 10^{\ 19}\ \text{m}^2$

Number of unit cells on $10^{\ 12}\ \text{m}^2$ surface

$$\frac{10^{\ 12}}{1.6 \quad 10^{\ 19}} \quad 6.25 \quad 10^6$$

$\because$ There are two atoms (effectively) on one face of unit cell Number of atoms on $10^{\ 12}\ \text{m}^2$ surface 2 number of unit cell $1.25 \quad 10^7$. $[\because \quad y \quad 10^x]$

$$x \quad 7 \qquad y \quad 1.25$$

38. From the given information, the number of atoms per unit cell and therefore, type of unit cell can be known as

$$\frac{NM}{N_A a^3}$$

$$N \quad \frac{N_A a^3}{M} \quad \frac{2 \quad 6 \quad 10^{23} \quad (5 \quad 10^{\ 8} \text{ cm})^3}{75} \quad 2 \text{ (bcc)}$$

In bcc, $4r \quad \sqrt{3}a$

$$r \quad \frac{\sqrt{3}}{4}a \quad \frac{\sqrt{3}}{4} \quad 5 \quad 10^{\ 10}\text{m}$$

$$2.17 \quad 10^{\ 10} \text{ m} \quad 217 \text{ pm}$$

39. In a cubic crystal system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom creating these voids then

$$\frac{r_1}{r_2}_{\text{octa}} \quad 0.414 \quad \text{and} \quad \frac{r_1}{r_2}_{\text{tetra}} \quad 0.225$$

The above radius ratio values indicate that octahedral void has larger radius, hence for maximum diameter of atom to be present in interstitial space :

$$r_1 \quad 0.414 \ r_2$$

Also in fcc, $4r_2 \quad \sqrt{2}a$

Diameter required $(2r_1) \quad (2r_2) \quad 0.414$

$$\frac{a}{\sqrt{2}} \quad 0.414$$

$$\frac{400 \quad 0.414}{\sqrt{2}} \quad 117 \text{ pm}$$

40. (i) In rock salt like crystal AB, there are four AB units per unit cell. Therefore, density (d) is

$$d \quad \frac{4 \quad 6.023\,y}{6.023 \quad 10^{23} \quad 8y \quad 10^{\ 27}}$$

$$[\because a \quad 2y^{1/3}\text{nm} \quad 2y^{1/3} \quad 10^{\ 9}\text{ m}]$$

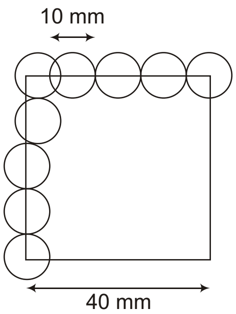
$$5 \quad 10^3 \text{ g/m}^3 \quad 5 \text{ kg/m}^3$$

(ii) Since, observed density is greater than expected, theoretical density, there must be some excess metal occupying interstitial spaces. This type of defect is known as **metal excess defect**.

41. (i) Side of square = 40 mm

Diameter of marble = 10 mm

Number of marble spheres along an edge of square with their centres within the square = 5 (shown in diagram)

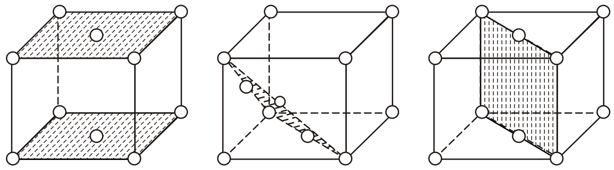


Maximum number of marbles per unit area $\quad 5 \quad 5 \quad 25$

(ii) If x mm is the side of square and d is diameter of marble then maximum number of marbles on square area with centres within square area can be known by the following general formula :

$$N \quad \frac{x}{d} \quad 1^{\ 2}$$

42.



43. Density $\quad \frac{N}{a^3}$

$$\frac{d_1}{d_2} \quad \frac{N_1}{N_2} \quad \frac{a_2}{a_1}^{\ 3} \quad \frac{4}{2} \quad \frac{3}{3.5}^{\ 3} = 1.26$$

44. In bcc unit cell, $4r \quad \sqrt{3}a$

$$r\,(\text{Cr}) \quad \frac{\sqrt{3}a}{4} \quad \frac{\sqrt{3}}{4} \quad 287 \text{ pm} \quad 124.3 \text{ pm}$$

Density of solid $\quad \frac{NM}{N_A \ a^3}$

$N \quad$ Number of atoms per unit cell, $\quad M \quad$ Molar mass

$a^3 \quad$ Volume of cubic unit cell, $\quad N_A \quad$ Avogadro's number

$$\frac{2 \quad 52 \text{ g}}{6.023 \quad 10^{23}} \quad \frac{1}{2.87 \quad 10^{\ 8} \text{ cm}}^{\ 3} \quad 7.3 \text{ g / cm}^3$$

45. The given arrangement : $ABABAB$...... represents hexagonal close-packed unit cell in which there are six atoms per unit cell. Also, volume of unit cell $\quad 24\sqrt{2}r^3$.

$$\text{Packing fraction} \quad \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$6 \quad \frac{4}{3} \quad r^3 \quad \frac{1}{24\sqrt{2}\,r^3} \quad 0.74$$

Percent empty space $\quad 100\ (1 \quad 0.74) \quad 26\%$

46. In bcc arrangement of atoms : $4r \quad \sqrt{3}a$, atoms on body diagonal remain in contact

$$r \quad \frac{\sqrt{3}\,a}{4} \quad \frac{\sqrt{3} \quad 4.29}{4} \quad 1.86 \text{ Å}$$