Q1. Classify the following solids in different categories based on the nature of intermolecular forces operating in them – tin, benzene, urea, ammonia, water, graphite, rubidium, argon, silicon carbide.

Q2. How many atoms can be assigned to its unit cell if an element forms (a) a body centred cubic cell, and (b) a face centred cubic cell?

Q3. Find out the number of atoms per unit cell in a face centred cubic structure having only single atoms at its lattice points.

Q4. Give the significance of 'lattice point'.

Q5. Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

Q6. Why is glass considered as a supercooled liquid?

Q7. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show the cleavage property?

Q8. How many lattice points are there in one unit cell of each of the following lattices?
(a) Face centred cubic   (b) Face centred tetragonal   (c) Body centred cubic.

Q9. Assign reasons for the following:
(a) Phosphorus doped silicon is a semiconductor.
(b) Schottky defect lowers the density of a solid.
(c) Some of the very old glass objects appear slightly milky instead of being transparent.

Q10. A cube solid is made of two elements P and Q. Atoms Q are at the corners of the cube and P at the body centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Q11. A compound formed by elements A and B crystallises in the cubic arrangement in which A atoms are at the corners of a cube and B atoms are at the face centres. What is the formula of the compound?

Q12. If three elements P, Q and R crystallise in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centres and R atoms at the centre of the edges, then write the formula of the compound.

Q13. In a solid 'AB', 'A' atoms have ccp arrangement and B atoms occupy all the octahedral sites. If all the face centred atoms along one of the axis are removed, then what will be the resultant stoichiometry of the compound?

Q14. A compound formed atom P, Q and oxygen P atom at the corner Q atom at alternate face and O atom at the remaining faces what is formula of compound.

Q15. A compound formed by X and Y has a cubic structure in which X atoms are at the corner of cube and Y atoms are at the face centres, one atom of X is missing from a corner. What is formula of compound?

Q16. A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. Determine the formula of this compound.

Q17. What is the simplest formula of a solid whose cubic cell has the atom *A* at each corner, the atom *B* at each face centre and a *C* atom at the body centre?

Q18. A solid has a structure in which *W* atoms are present at the corners of the cubic unit cell, O atoms are located at cube edges and Na atoms are present at cube centres. What is the formula of the compound?

Q19. Sodium crystallizes in a bcc unit cell. Calculate the approximate number of unit cells in 9.2 g of sodium (Atomic mass of Na = 23 u)

Q20. Distinguish between face centred and end centred unit cell.

Q21. The ionic radius of $Na^{\oplus}$ and $Cl^{\ominus}$ ions are 90 pm and 180 pm respectively. Calculate the edge length of unit cell.

Q22. If the radius of an atom is 75 pm and the lattice is bcc the edge length of the unit cell is

Q23. A binary solid *AB* has NaCl type structure. If edge length is 400 pm and radius of cation is 75 pm. Calculate the radius of anion.

Q24. What is relation between radius of sphere (*r*) and edge length (*a*) of BCC unit cell?

Q25. What is relation between radius of sphere (*r*) and edge length (*a*) of FCC unit cell?

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S1. (a) **Molecular:** Benzene, Urea, Water, Argon, Ammonia.

(b) **Ionic:** Tin, Rubidium.

(c) **Covalent or network solids:** Graphite, Silicon carbide.

S2. (a) Body centred cubic cell $= 1 + \frac{1}{8} \times 8 = 2$.

(b) Face centred cubic cell $= 1 + 6 \times \frac{1}{2} = 4$.

S3. Number of atoms present at Lattice points is eight atom of corner and atoms at the faces.

Effective number of atoms in FCC is (Z) $= \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

S4. **A lattice point:**

(a) represents one constituent particle which may be an atom, a molecule (group of atom) or an ion.

(b) lattice points when joined by straight lines bring out the geometry of the lattice.

(c) It is convenient method to draw the structure of a crystal and understand to it.

S5. (a) **Amorpheous solids:** Polyurethane, teflon, cellophane, polyvinyl chloride, fibre glass.

(b) **Crystalline solids:** Napthalene, benzoic acid, potassium nitrate, copper.

S6. Glass is an amorphous solid. Like liquids, glass has a tendency to flow, though very slowly. Therefore, it is called pseudo-solid or supercooled liquid. Glass panes fixed in the windows of old buildings are invariably found to be slightly thicker at bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

S7. We know, if a solid has same value of refractive index along in all direction, the solid will be *amorphous* and *isotropic* in nature. No,when cut it with knife it would be cut into two pieces with irregular surfaces.

S8. (a) Eight points located, one at each corner of a cube, six more lattice point each one situated at the centre of each face of cube. So total lattice point is 14.

8 (at corners) + 6 (at face centred)

(b) Eight points located, one at each corner of tetragonal, six more lattice points each one located at the centre of each face of tetragonal. So total lattice point is 14.

8 (at corners) + 6 (at face centred)

(c) Eight points are located, one at each corner of a cube and one point at centre of the cube. So total lattice point is 9.

8 (at corners) + 1 (at body centre)

S9. (a) It is because its conductance is intermediate between conductor and insulator.

(b) In Schottky defect, both cations and anions are missing which leads to lowering in density of a solid.

(c) Glass is supercooled liquid, therefore very old glass objects become slightly milky because of heating during the day and cooling at nights *i.e.*, anealing over a number of years glass acquires some crystalline structure.

S10. The atom at corner makes $\frac{1}{8}$ contribution while atom at body centre makes 1 contribution to the unit cell.

No. of atoms of Q per unit cell = 8 (at corners) $\times \frac{1}{8}$ = 1

No. of atoms of P per unit cell = 1 (at body centre) $\times$ 1 = 1

$\therefore$ Formula of the compound is PQ

The atom at the body centre would be in contact with all the atoms at the corners. Hence, the coordination number of P would 8. Similarly, coordination number of Q is also 8.

S11. In a cube, A atoms are at the 8 corners, each shared by 8 cubes. Therefore,

The number of A atoms in the unit cell is 8/8 = 1.

B atoms are at the centres of 6 faces and each face is shared by two cubes. Therefore,

The number of B atom = 6/2 = 3

The formula of the compound = AB_3.

S12. As P atoms are present at the 8 corners of the cube. Therefore,

No. of P atoms in the unit cell = $8 \times \frac{1}{8} = 1$

Q atoms are present at the cube centres.
No. of Q atoms in the unit cell = 1
R atoms are present at the edge. Since there are 12 edges and atom at each edge is shared by four atoms.
No. of R atoms in the unit cell = 3
Therefore, the formula of the compound = PQR_3.

S13. In ccp type structure, there are 8A at the corners of the cube and 6A atoms on the face centres. If all the face centred atoms along one of the axis are removed, it means removal of 2A atoms. Therefore, only 4 atoms will be left on faces.

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

No. of B atoms in ccp structure are 12 at edge centred and 1 at body centre. Therefore,

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

$\therefore$ Stoichiometry of compound = A_3B_4.

S14.
$$\text{Number of } P \text{ atom} = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } Q \text{ atom} = \frac{1}{2} \times 2 = 1 \quad \text{(alternate face are two)}$$

$$\text{Number of } O \text{ atom} = \frac{1}{2} \times 4 = 2$$

Hence, formula, PQO_2

S15.
$$\text{No. of } X \text{ atoms} = \frac{1}{8} \times 7 = \frac{7}{8}$$

$$\text{No. of } Y \text{ atoms} = \frac{1}{2} \times 6 = 3$$

Hence, $\quad y_{\frac{7}{8}} y_3 \quad$ (OR) $\quad \left(y_{\frac{7}{8}} y_3 \right) \times 8 = x_7 y_{24}$

S16. One-eighth of each corner atom (Au) and one-half of each face-centred atom (Cu) are contained within the unit cell of the compound.

Thus, number of Au atoms per unit cell = $8 \times \frac{1}{8} = 1$ and number of Cu atoms per unit cell = $6 \times \frac{1}{2} = 3$. The formula of the compound is $AuCu_3$.

S17. An atom at the corner of a cube is shared among 8 unit cells. As there are 8 corners in a cube.

Number of corner atom (A) per unit cell = $8 \times \frac{1}{8} = 1$

A face-centred atom in a cube is shared by two unit cells. As there are 6 faces in a cubes.

Number of face-centred atoms (B) per unit cell = $6 \times \frac{1}{2} = 3$.

An atom in the body of the cube is not shared by other cells.

$\therefore$ Number of atoms (C) at the body centre per unit cell = 1.

Hence, the formula of the solid is AB_3C.

S18.
$$\text{No. of } W \text{ atoms} = \frac{1}{8} \times 8 = 1$$

$$\text{No. of } O \text{ atoms} = \frac{1}{4} \times 12 = 3$$

$$\text{No. of Na atom} = 1$$

Formula is $NaWO_3$

S19.

$$1 \text{ mol of sodium} = 23 \text{ g}$$
$$= 6.022 \times 10^{23} \text{ atoms}$$

No. of atoms present in 9.2 g of sodium $= \dfrac{6.022 \times 10^{23}}{23} \times 9.2$
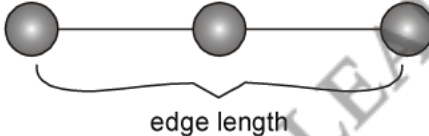
$$= 2.4088 \times 10^{23}$$

A bcc unit cell contains 2 atoms,

$\therefore$ No. of unit cells present $= \dfrac{2.4088 \times 10^{23}}{2} = \mathbf{1.2044 \times 10^{23}}$

S20. Face centred and end centred unit cell:

Face centred	*End centred*
1 Position of particles in **face centred** is, such that, one constituent particle is present at the centre of its each face beside the ones that are at its corners.	Position of particles in End centred is, such that, one constituent particle is present at the centre any two opposite faces besides the ones that are at its corners.
2 Number of atoms per unit cell : $= \dfrac{1}{8} \times 8 + \dfrac{1}{2} \times 6 = 4$	Number of atoms per unit cell : $= \dfrac{1}{8} \times 8 + \dfrac{1}{2} \times 2 = 2$

S21.

edge length

$a = 2\,(r_{Na^+} + r_{Cl^{\ominus}})$
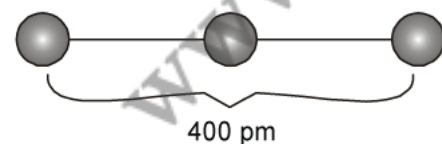$\quad = 2\,(90 + 180)\text{ pm}$
$\quad = 540 \text{ pm.}$

S22. For bcc

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

$$= \frac{4 \times r}{\sqrt{3}} = \frac{4 \times 75}{\sqrt{3}} = \frac{4 \times 75}{1.732} = 173.2 \text{ pm}$$

S23. Distance between cation and anion in NaCl type $= \dfrac{400}{2} = 200 \text{ pm}$

400 pm

$r_+ + r_- = 200$

$r_- = 200 - 75 = 125 \text{ pm}$

S24. Body Centred Cubic Cell (BCC)

Two diametre of three atoms ($r + 2r + r$) form diagonal of the body.

AC diagonal of face:

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

$$(AC)^2 = a^2 + a^2$$

$$(AC)^2 = 2a^2$$
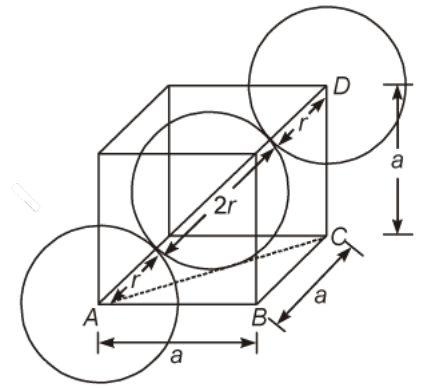
$$AC = a\sqrt{2}$$

AD diagonal of body:

$$(AD)^2 = (AC)^2 + (DC)^2$$

$$(4r)^2 = (a\sqrt{2})^2 + (a)^2$$

$$16r^2 = 3a^2$$

$$r^2 = \frac{3a^2}{16} \ , \qquad r = \frac{\sqrt{3}\,a}{4} \qquad\qquad i.e., \quad r_{BCC}$$

S25. Face Centred Cubic Cell (FCC)

Two diametre of three atom $(r + 2r + r)$ form diagonal of face

According to Pythagoras theorem

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

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

OR $\qquad\qquad 16r^2 = 2a^2$
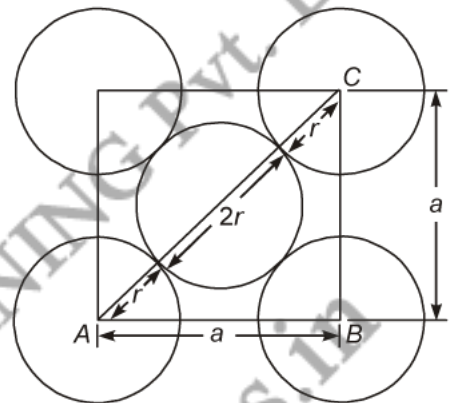
OR $\qquad\qquad 8r^2 = a^2$

OR $\qquad\qquad r^2 = \dfrac{a^2}{8}$

$$a = 2\sqrt{2}\,r \qquad\qquad i.e., \quad r\,(FCC)$$

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Q1. If the length of body diagonal for CsCl, which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of unit cell, is 7 Å and the radius of Cs^+ ion is 1.69 Å. What is the radius of Cl^- ion?

Q2. In a crystalline solid, anions C are arranged in cubic close-packing. Cations A occupy 50% of the tetrahedral voids and cations B occupy 50% of the octahedral voids. What is the formula of the solid?

Q3. Silver crystallises in face-centred cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom.
(Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms.)

Q4. Gold (atomic radius = 0.144 nm) crystallises in a face crentred unit cell. What is the length of a side of the cell?

Q5. What is the two-dimensional coordination number of a molecule in square closed packed layer?

Q6. In the figure given below the site marked as P is a ?

Q7. Which of the following lattices has the highest packing efficiency (a) simply cubic (b) body centred cubic and (c) hexagonal closed packed lattice?

Q8. A compound is formed by two elements M and N. The element N forms ccp and M atoms occupy 1/3 of tetrahedral voids. What is the formula of the compound?

Q9. A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Q10. Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive formula of the ferric oxide.

Q11. In a crystalline solid, oxide ions are arranged in cubic close-packing. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the solid?

Q12. For a cubic crystal, the face diagonal is 3.50 Å. Calculate the face length.

Q13. A solid AB has CsCl-type structure. The edge length of the unit cell is 404 pm. Calculate the distance of closest approach between $A^\oplus$ and $B^\ominus$ ions.

Q14. Two ions $A^\oplus$ and $B^\ominus$ have radii 88 and 200 pm, respectively. In the close-packed crystal of compound AB, predict co-ordination number of $A^\oplus$.

Q15. In a close packing of A spheres, how many
(a) tetrahedral and   (b) Octahedral sites are present?

Q16. What is the coordination number of each of ions in a rock-salt type crystal structure?

Q17. How will you distinguish between the following pair of terms:
Tetrahedral void and octahedral void.

Q18. Sodium metal crystallises in body centred cubic lattice with the cell edge = 4.29 Å. What is the radius of sodium atom?

Q19. Calculate the efficiency of packing in case of a metal crystal for Body Centred Cubic (with the assumption that atoms are touching each other).

Q20. Calculate the efficiency of packing in case of a metal crystal for Face Centred Cubic (with the assumption that atoms are touching each other).

Q21. Calculate the efficiency of packing in case of a metal crystal for Simple Cubic Cell (with the assumption that atoms are touching each other).

Q22. In a face centred cubic (FCC) crystal lattice, edge length is 400 pm. Find the diameter of the largest sphere which can be fitted into the interstitial void without distortion of the lattice.

Q23. A compound *AB* crystallises in bcc lattice with unit cell edge length of 380 pm. Calculate (a) the distance between oppositely charged ions in the lattice, (b) radius of A^+ if radius of B^- is 175 pm. (assuming that cation fits exactly in the cubic void).

Q24. The radius of anion in an ionic solid is 100 pm. Find the radius of cation which just fits in its (a) cubic (b) octahedral void (c) tetrahedral void.

Q25. If the radius of Mg^{2+}, $Cs^{\oplus}$, O^{2-}, S^{2-} and $Cl^{\ominus}$ ions are 0.65, 1.69, 1.40, 1.84 and 1.81 Å, respectively, calculate the co-ordination number of the cations in the crystals of MgS, MgO and CsCl.

Q26. If the close-packed cations in an *AB*-type solid have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids?

Q27. Xenon crystallizes in the face-centered cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Q28. The radius of an atom of an element is 500 pm. If it crystallizes as a face-centred cubic lattice, what is the length of the side of the unit cell?

Q29. If the radius of the octahedral void is *r* and radius of the atoms in close packing is *R*, derive relation between *r* and *R*.

Q30. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(a) What is the length of the side of the unit cell?
(b) How many unit cells are there in 1.00 cm³ of aluminium?

Q31. Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

Q32. Calculate the efficiency of packing in case of a metal crystal for Hexagonal Close Packing (HCP) (with the assumption that atoms are touching each other).

Q33. CsCl has bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Q34 A spinel is an important class of oxides consisting of two types of metal ions with the oxide loss arranged in ccp layers. The normal spinel has 1/8th of the tetrahedral void occupied by one type of metal and one half of the octahedral voids occupied by another type of metal ions. Such a spinel is formed by Zn^{2+}, Ai^{3+} and O^{2-} with Zn^{2+} in tetrahedral void. Give the simplest formula of the spinel.

S1. For CsCl structure, body diagonal

$$= 2r^+ + 2r^-$$

$$7\,\text{Å} = 2 \times 1.69\,\text{Å} + 2r^-$$

$$3.5\,\text{Å} = 1.69\,\text{Å} + r^-$$

$$r^- = 3.5\,\text{Å} - 1.69\,\text{Å} = \mathbf{1.81\,\text{Å}}.$$

S2. No. of atoms of $C = \dfrac{1}{8} \times 8 + \dfrac{1}{2} \times 6 = 4\ (z)$

No. of tetrahedral void $= z \times 2 = 8$

No. of octahedral void $= z \times 1 = 4$

No. of A cation = 4

No. of B cation = 2

Hence formula is $A_4B_2C_4$ (OR) A_2BC_2

S3.

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

$$4r = \sqrt{2} \times 400\ \text{pm}$$

$$r = \frac{\sqrt{2} \times 400}{4}\ \text{pm}$$

$$r = 1.414 \times 100\ \text{pm} = 141.4\ \text{pm}.$$

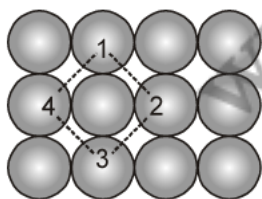**S4.** Radius of gold atom, $r = 0.144$ nm

In face centred unit cell, face diagonal $= 4r = \sqrt{2}\,a$

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

$$= 2 \times 1.414 \times 0.144\ \text{nm} = 0.407\ \text{nm}$$

Edge length of unit cell, $a = 0.407$ nm.

S5. 4

Square close packing

S6. Octahedral void.

S7. (a) Simple cubic = 52.4%

   (b) Body centred cubic = 68%

   (c) Hexagonal closed packed = 74%

So hexagonal closed packing has the highest efficiency.

S8. Since N forms ccp arrangement, it will have 4 atoms in a unit cell.

Hence, Tetrahedral void $(Z \times 2)$ = $4 \times 2 = 8$

And, M atoms = $\dfrac{1}{3} \times 8 = \dfrac{8}{3}$

and formula $M_{8/3} N_4$ (OR) $M_2 N_3$

S9. An atom in hcp structure has three voids, one octahedral and two tetrahedral

No. of atoms in 0.5 mole = $0.5 \times 6.022 \times 10^{23}$

$= 3.011 \times 10^{23}$

Total number of voids = $3 \times 3.011 \times 10^{23}$

$= 9.033 \times 10^{23}$

Number of tetrahedral voids = $2 \times 3.011 \times 10^{23}$

$= 6.022 \times 10^{23}$

S10. Suppose number O^{2-} ion in packing = N.

Number of octahedral void = N.

$2/3^{rd}$ of the octahedral voids are occupied by Fe^{3+} ions.

Number of Fe^{3+} ions = $\dfrac{2}{3} \times N = \dfrac{2N}{3}$

Ratio of $Fe^{3+} : O^{2-}$

$\dfrac{2N}{3} = N$

2 : 3.   So formula of ferric oxide is **Fe_2O_3**.

S11. In a cubic close packing of oxide ions there would be 4 oxide ions per unit cell. Each oxide ion is associated with 2 tetrahedral voids and one octahedral void. Thus, there would be 4 octahedral voids and 8 tetrahedral voids. Since all the octahedral voids are occupied by A, there would be 4 cations A in the octahedral voids and an equal number of cations A are in tetrahedral voids. Thus, for 4 oxide ions there are 8 cations A. Therefore, formula of the solid is **A_8O_4** or **A_2O**.

S12.   Face diagonal = $\sqrt{a^2 + a^2} = \sqrt{2}a$

Face length (a) = $\dfrac{\text{Face diagonal}}{\sqrt{2}} = \dfrac{3.50\,\text{Å}}{\sqrt{2}} = \dfrac{3.50\,\text{Å}}{1.414} = 2.47\,\text{Å}$.

S13. The distance of closest approach is equal to the distance between the nearest neighbours (d). As CsCl has bcc lattice,

$$d = \frac{\sqrt{3}}{2}\, a = \frac{1.732}{2} \times 404 \text{ pm .}$$

S14.

$$\frac{r_{\oplus}}{r_{\ominus}} = \frac{r(A^{\oplus})}{r(B^{\ominus})} = \frac{88}{200} = 0.44$$

It lies in the range 0.414 to 0.732.

Hence, the co-ordination number of $A^{\oplus}$ = 6.

S15. (a) tetrahedral = $2A$ (b) Octahedral = A.

**S16.** 6 : 6.

S17. Tetrahedral void and octahedral void:

Tetrahedral void	Octahedral void
1. It is the open space between four touching spheres of two layers of atom.	It is the open space between six touching spheres of two layers of atoms.
2. The radius of the tetrahedral void relative to radius of sphere is 0.225.	The radius of octahedral void relative to radius of sphere is 0.414.

S18. For body centred cubic unit cell, the body diagonal is four times the radius of atom.

Body diagonal = $\sqrt{3} \times$ edge length (a)

$$= \sqrt{3} \times 4.29 \text{ Å}$$

Radius of atom = $\frac{1}{4} \cdot \sqrt{3} \times 4.29 \text{ Å} = 1.86 \text{ Å}$
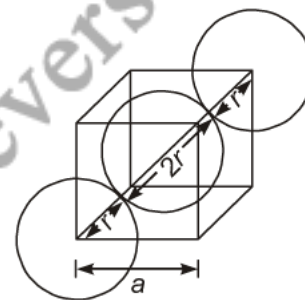
S19. If r is radius of atom and a is edge length.

Packing efficiency of BCC.

No. of atoms in BCC (Z) = 2

Hence,

$$PF = \frac{2 \times \frac{4}{3} \times \pi r^3}{a^3} \times 100$$

and for BCC relation between r and a is

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

i.e.,

$$= \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} \times 100$$

$$= \frac{2 \times \frac{4}{3} \times \frac{22}{7} \times \frac{3\sqrt{3}}{64}a^3}{a^3} \times 100$$

After calculation PF for BCC is 68%

Means occupied space in BCC is 68%

and, empty space in BCC = 100 – 68 = **32%**

S20. If *r* is radius of atom and *a* is edge length.

Packing efficiency of FCC (CCP)

No. of atoms in FCC (*Z*) = 4

Hence,

$$PF = \frac{4 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

and for FCC relation between *r* and *a* is

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

Hence,

$$PF = \frac{4 \times \frac{4}{3}\pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} \times 100$$

$$= \frac{\frac{16}{3} \times \frac{22}{7} \times \frac{a^3}{22.6}}{a^3} \times 100$$

After calculation PF for FCC is 74%

Means occupied space of FCC is 74%

and, empty space in FCC is 100 – 74 = **26%**

S21. If *r* is radius of atom and *a* is edge length.

Packing efficiency of Simple Cubic Cell:

No. of atom in SCC (Z) = 1

Hence,
$$PF = \frac{1 \times \frac{4}{3}\pi r^3}{a^3} \times 100$$

and, For SCC relation between r and a is

$$a = 2r \qquad \text{and} \qquad r = \frac{a}{2}$$

i.e.,
$$= \frac{\frac{4}{3} \times \pi \left(\frac{a}{2}\right)^3}{a^3} \times 100$$

After calculation PF for SCC is 52.4%

Means occupied space in SCC 52.4%

and empty space in SSC = 100 − 52.4 = **47.6%**

S22. For FCC, the face diagonal $= \sqrt{2} \times$ edge length

$\qquad\qquad\qquad = 4 \times$ radius of atom (R)

$\therefore \qquad 4R = \sqrt{2} \times$ edge length

$$R = \frac{\sqrt{2} \times 400}{4} \text{ pm} = 141.4 \text{ pm}$$

In close packing there are two types of voids, tetrahedral and octahedral. Octahedral void is larger than the tetrahedral void. Hence, the largest sphere can be fitted into octahedral void.

For octahedral void, $\dfrac{r_{void}}{r_{atom}} = 0.414$

$\qquad r_{void} = 0.414 \times r_{atom} = 0.414 \times 141.4$ pm

$\qquad\qquad = 58.54$ pm

The diameter of the largest sphere that can be fitted into this void

$\qquad\qquad = (2 \times 58.54)$ pm

$\qquad\qquad = 117.08$ pm

S23. In bcc structure, body diagonal $= 2 (r_+ + r_-)$

If 'a' is the edge length of unit cell, then,

$\qquad$ Body diagonal $= a\sqrt{3} = 2 (r_+ + r_-)$

(a) The distance between oppositely charged ions,

$$(r_+ + r_-) = \frac{a \cdot \sqrt{3}}{2} = \frac{380 \times 1.732}{2} = 329.1 \text{pm}$$

(b) For exact fitting the radius ratio for cubic void,

$$\frac{r_+}{r_-} = 0.732$$

$$\therefore \quad r_+ = 0.732 \times 175 \text{ pm}$$

$$= 128.1 \text{ pm}$$

S24. (a) For a cubic void, $\quad \dfrac{r_+}{r_-} = 0.732$

$\therefore$ Radius of cation, $r_+ \quad = 0.732 \times r_-$

$$= 0.732 \times \text{radius of anion,}$$

$$= 0.732 \times 100 = 73.2 \text{ pm}$$

(b) For octahedral void, $\quad \dfrac{r_+}{r_-} = 0.414$

$\therefore \quad r_+ = 0.414 \times r_- = 0.414 \times 100$

$$= 41.4 \text{ pm.}$$

(c) For tetrahedral void, $\quad \dfrac{r_+}{r_-} = 0.225$

$\therefore \quad r_+ = 0.225 \times r_-$

$$= 0.225 \times 100$$

$$= 22.5 \text{ pm.}$$

S25. CN of MgS

(a)

$$\frac{Mg^{2+}}{S^{2-}} = \frac{0.65}{1.84} = 0.35$$

(Range lies between 0.225 and 0.414)

$$\therefore \quad CN = 4.$$

(b) In MgO:

$$\frac{Mg^{2+}}{O^{2-}} = \frac{0.65}{1.40} = 0.48$$

(Range lies between 0.414 and 0.732)

$$\therefore \quad CN = 6.$$

(C) In CsCl:

$$\frac{Cs^{\oplus}}{Cl^{\ominus}} = \frac{1.69}{1.81} = 0.93$$

(Range lies between 0.732 and 1)

$$\therefore \quad CN = 8.$$

S26. For close-packed AB-type solid,

$$\frac{r_{\oplus}}{r_{\ominus}} = 0.414 - 0.732$$

$\therefore$ Minimum value of $r_{\ominus} = \dfrac{r_{\oplus}}{0.732} = \dfrac{75}{0.732}$ pm $= 102.5$ pm

Maximum value of $r_{\ominus} = \dfrac{r_{\oplus}}{0.414} = \dfrac{75}{0.414}$ pm $= 181.2$ pm

S27. Here, $a = 620$ pm, $d = ?$, $r = ?$

For the face-centered cubic lattice,

$$d = \dfrac{a}{\sqrt{2}} = \dfrac{620 \text{ pm}}{1.414} = 438.5 \text{ pm}$$

$$r = d/2 = 438.5/2 = 219.25 \text{ pm}.$$

S28. For fcc, $\qquad\qquad r = \dfrac{a}{2\sqrt{2}}$

or $\qquad\qquad a = 2\sqrt{2} = 2 \times 1.414 \times 500$ pm

$\qquad\qquad\qquad\qquad = 1414$ pm

S29. Suppose the length of the each arm of the square is $2R$ (R is radius of atom). Let r be the radius of void.

In right triangle ABC

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

$$= \sqrt{8}\,R \quad \text{or} \quad 2\sqrt{2}\,R$$

Octahedral void

Also, $\qquad\qquad AC = R + R + 2r$

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

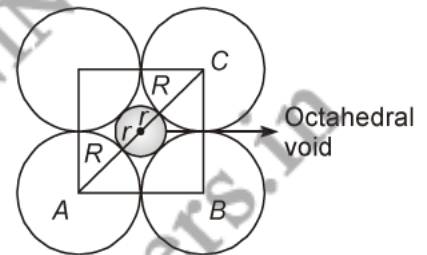$$2\sqrt{2}\,R = 2(r + R)$$

or $\qquad\qquad 2r = 2\sqrt{2}\,R - 2R$

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

$$r = (1.414 - 1)\,R$$

$$r = \mathbf{0.414 \times R.}$$

S30. According to question,

radius of atom $(r) = 125$ pm

(a) For ccp structure, $\qquad r = \dfrac{a}{2\sqrt{2}} \quad$ or $\quad a = 2\sqrt{2}\,r$

Edge length $(a) = 125 \times 2\sqrt{2}$

$$= 125 \times 2 \times 1.414 = \mathbf{353.5 \text{ pm}.}$$

(b)   Volume of one unit cell $(a^3) = (353.5 \times 10^{-10}\text{ cm})^3 = \mathbf{442 \times 10^{-25}\text{ cm}^3}$.

Number of unit cell of aluminium in 1 cm^3 = $\dfrac{1}{442 \times 10^{-25}}$ = $\mathbf{2.26 \times 10^{22}}$ **unit cell**.

S31. According to question

In $\mathbf{Ni_{0.98}\,O_{1.00}}$

Let $Ni = 98$ $O = 100$

                             $Ni^{2+} = a$ $O^{2-} = 100$

                             $Ni^{3+} = 98 - a$

Average oxidation number of Ni

             $2 \times Ni^{2+} + 3 \times Ni^{3+} = 100 \times O^{2-}$

             $2 \times a + 3 \times (98 - a) = 100 \times 2$

$\therefore$ $a = 94$

So, $Ni^{2+} = 94$

Fraction of Ni^{2+} = $\dfrac{94}{98} \times 100 = \mathbf{96\%}$.

Fraction of Ni^{3+} = $\dfrac{4}{98} \times 100 = \mathbf{4\%}$.

S32. Packing efficiency of Hexagonal Close Packing (HCP)

             radius of sphere = r

Then,   Volume of unit cell = Base area $\times$ Height (h)

Base of area of regular hexagon = $6 \times \dfrac{\sqrt{3}}{4}(2r)^2 = 6 \times \sqrt{3}\,r^3$

Height of unit cell = $4r.\sqrt{\dfrac{2}{3}}$

Volume of unit cell = $6\sqrt{3}\,r^2 \times 4r.\sqrt{\dfrac{2}{3}} = 24\sqrt{2}\,r^3$

No. of atoms in HCP unit cell = $12 \times \dfrac{1}{6}\,(\text{corners}) + 2 \times \dfrac{1}{2}\,(\text{face centres}) + 3\,(\text{in body}) = 6$

Volume of 6 spheres = $6 \times \dfrac{4}{3}\pi r^3 = 8\pi r^3$

Packing efficiency = $\dfrac{\text{Volume occupied by spheres in unit cell}}{\text{Volume of hcp unit cell}} \times 100$

$$= \frac{8\pi r^3}{24\sqrt{2}\,r^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = \frac{3.142}{3 \times 1.414} \times 100$$

$$= 74\%$$

After calculation PF for HCP is 74%

Means occupied space in HCP is 74%

and, empty space in HCP = 100 – 74 = **26%**

S33. The bcc arrangement of CsCl is shown in the figure below. The aim is to find half of the body diagonal *AE*. If the edge of the unit cell is *a*, then

$$CE = \sqrt{a^2 + a^2} = \sqrt{2}a$$

∴
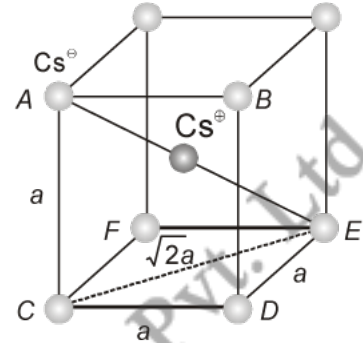$$AE = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

$$= \sqrt{3} \times 400$$

∴ Interionic distance $= \frac{1}{2} \times \sqrt{3} \times 400$

$$= \sqrt{3} \times 200 = 346.4 \text{ pm.}$$

S34. Let the no. of tetrahedral voids = *n*

No. of octahedral voids $= \dfrac{n}{2}$

$\dfrac{1}{8}$ th tetrahedral voids is occupied by Zn^{2+}

∴ No of $Zn^{2+} = \dfrac{n}{8}$

$\dfrac{1}{2}$ of octahedral voids occupied by Al^{3+}

∴ No. of $Al^{3+} = \dfrac{n}{2 \times 2} = \dfrac{n}{4}$

Ratio of $Zn^{2+} : Al^{3+}$

    1 : 2

For 1 mole Zn^{2+} and 2 mol Al^{3+}

Total +ve charge = 2 + 3 × 2 = 8

∴ No. of O^{2-} = 4

∴ The simplest formula will be $ZnAl_2O_4$

Q1. An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If it's density is 2.7×10^3 kg m^{-3}, what is the nature of the cubic unit cell?

Q2. (a) Determine the type of cubic lattice to which a given crystal belongs, if it has edge length of 290 pm and density 7.80 g cm^{-3}. (Molecular mass = 56 g mol^{-1})

(b) Why does zinc oxide exhibit enhanced electrical conductivity on heating?

Q3. If the radius of copper atom is 128 pm and copper crystallises into FCC lattice. Calculate density of unit cell (copper atomic weight 63.5).

Q4. A compound formed by elements X and Y, Crystallizes in the cubic structure, where X is at the corners of the cube and Y is at the six face centres. What is the formula of the compound? If side length is 5 Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Q5. The compound CuCl has ZnS structure and the edge length of its unit cell is 500 pm. Calculate its density (Atomic masses : Cu = 63, Cl = 35.5, Avogadro's constant = 6.02×10^{23} mol^{-1}).

Q6. A metal crystallizes in two cubic phases, face centred cubic (fcc) and body centred cubic (bcc) whose unit cell length are 3.5 and 3.0 Å respectively. Calculate the ratio of density of fcc and bcc.

Q7. Silver crytallises in *fcc* lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

Q8. Copper has FCC crystal structure. Assuming an atomic radius of 130 pm for copper atom (Atomic wt. of Cu = 63.54 g/mole):

(a) What is the length of unit cell of Cu?   (b) What is the volume of the unit cell?

(c) How many atoms belong to one unit cell?   (d) Find the density of Cu.

Q9. Silver metal crystallises with a face centred cubic lattice. The length of the unit cell is found to be 4.077×10^{-8} cm. Calculate atomic radius and density of silver. (Atomic mass of Ag = 108u, N$_A$ = 6.02×10^{23} mol^{-1})

Q10. An element crystallizes as face centred cubic lattice with density 5.20 g/cm^3 and edge length of unit cell as 300 pm. Calculate the mass of the element which contains 3.01×10^{24} atoms.

Q11. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes 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.

Q12. The unit cell of an element of atomic mass 108 and density 10.5 g cm^{-3} is a cube with edge length 409 pm. Find the structure of the crystal lattice (simple cubic, *fcc* or *bcc*). Avogadro's constant = 6.023×10^{23} mol^{-1}.

Q13. CsCl has cubic structure, Its density is 3.99 g cm^{-3}. What is the distance between Cs$^\oplus$ and Cl$^\ominus$ ions? (Atomic mass of Cs = 133)

Q14. A unit cell of sodium chloride has four formula units. The length of the unit cell is 0.564 nm. What is the density of sodium chloride?

Q15. A face-centered cubic element (atomic mass 60) has a cell of 400 pm. What is its density?

Q16. Sodium has a bcc structure with nearest neighbour distance of 365.9 pm. Calculate its density. (Atomic mass of sodium = 23)

Q17. Calcium crystallizes in fcc unit cell with 0.556 nm. Calculate the density if
   (a)   It contains 0.2% Frenkel defects   (b)   It contains 0.1% Schottky defects

Q18. Silver has atomic mass 108 a.m.u. and density 10.5 g cm^{-3}. If the edge length of its unit cell is 409 pm, identify the type of unit cell. Also calculate the radius of an atom of silver.

Q19. Calculate the distance between Na$^+$ and Cl$^-$ ions in NaCl crystal if its density is 2.165 g cm^{-3}. [Molar mass of NaCl = 56.5 g mol^{-1}; N_A = 6.02 $\times 10^{23}$ mol^{-1}]

Q20. Calculate the value of Avogadro constant from the following data:
Density of NaCl = 2.165 g cm^{-3}, Distance between Na$^+$ and Cl$^-$ in NaCl = 281 pm (Molar mass of NaCl = 58.5 g mol^{-1}).

Q21. KF has NaCl type structure. What is the distance between K$^\oplus$ and F$^\ominus$ in KF if density is 2.48 g cm^{-3}?

S1. According to question,

$d = 2.7 \times 10^3 \, kg \, m^{-3}; \quad M = 2.7 \times 10^{-2} \, kg \, mol^{-1}, \quad a = 405 \, pm \quad or \quad 405 \times 10^{-12} \, m$

We know that

Density. $\qquad d = \dfrac{z \times M}{a^3 \times N_A}$

or $\qquad z = \dfrac{d \times a^3 \times N_A}{M}$

$\qquad = \dfrac{2.7 \times 10^3 \times (405 \times 10^{-12})^3 \times 6.022 \times 10^{23}}{2.7 \times 10^{-2}} = \mathbf{4}.$

Thus value of $z = 4$ suggests that the lattice is **ccp** (cubic close packed) Or (FCC).

S2. (a) $\qquad d = \dfrac{Z \times M}{a^3 \times N_A}$

$\qquad 7.80 = \dfrac{Z \times 56}{(290)^3 \times 10^{-30} \, cm^3 \times 6.02 \times 10^{23}}$

$\qquad Z = \dfrac{7.80 \times (290)^3 \times 10^{-30} \times 6.02 \times 10^{23}}{56}$

$\qquad = \dfrac{114.52}{56} = 2.04 \simeq 2.00, \, bcc$

(b) It is because electrons are trapped in place of O^{2-} which increases electrical conductivity. O^{2-} changes to O_2 which is lost to atmosphere.

S3. In face centred cubic arrangement face diagonal is four times the radius of atom.

$\qquad$ Face diagonal $= 4 \times 128 = 512 \, pm$

$\qquad$ Face diagonal $= \sqrt{2} \times$ edge length (a)

$\qquad$ Edge length (a) $= \dfrac{512}{\sqrt{2}} = 362 \, pm = 362 \times 10^{-10} \, cm$

$\qquad$ Volume of the unit cell $(a^3) = (362 \times 10^{-10})^3 \, cm^3$

$\qquad = 47.4 \times 10^{-24} \, cm^3$

In a face centred cubic unit cell $(Z) = 4$

$\qquad \rho = \dfrac{Z \times M}{a^3 \times N_A}$

$$= \frac{4 \times 63.5}{47.4 \times 10^{-24} \times 6.0 \times 10^{23}}$$

$$= 9.62 \text{ g/cm}^3$$

S4. From eight corner atoms, one atom (X) contributes to one unit cell.

From six face centres, three atoms (Y) contribute to one unit cell.

So, the formula of the compound is XY_3.

Molecular Weight XY_3 = 330

Effective Moleculars in unit cell (z) = 1

Edge Length (a) = 5A° = 5×10^{-8} cm

Hence,

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

$$\rho = \frac{1 \times 330}{6.023 \times 10^{23} \times (5 \times 10^{-8})^3} \text{ gm/cm}^3$$

$$= 4.38 \text{ gm/cm}^3$$

S5. ZnS has FCC structure,

Therefore, $n = 4$

$M_m = 63 + 35.5$

$= 98.5 \text{ g mol}^{-1}$

$a = 500 \text{ pm}$

$= 500 \times 10^{-10} \text{ cm}$

$$\text{Density} = \frac{n \times M_m}{N_A \times a^3}$$

$$= \frac{4 \times 98.5}{(500 \times 10^{-10})^3 \times 6.02 \times 10^{23}} = 5.24 \text{ g cm}^{-3}$$

S6.

$$\rho = \frac{n \times M_m}{N_A \times a^3}$$

For face centred cubic cell

$n = 4, \ a = 3.5 \text{ Å}$

$$\therefore \qquad r_{(fcc)} = \frac{4 \times M_m}{N_A \times (3.5)^3} \qquad \qquad \dots \text{(i)}$$

For (bcc) lattice

$n = 2, \ a = 3.0 \text{ Å}$

$$\rho_{(bcc)} = \frac{2 \times M_m}{N_A \times (3.0)^3} \qquad \text{... (ii)}$$

From equation (i) and (ii)

$$\therefore \qquad \frac{\rho_{(fcc)}}{\rho_{(bcc)}} = \frac{4}{2} \times \frac{3^3}{(3.5)^3} = 1.259$$

S7. Given,

Edge length, $a = 4.07 \times 10^{-8}$ cm,

For FCC (Z) = 4

$\therefore$ Volume of unit cell, $(a^3) = (4.07 \times 10^{-8})^3 = 67.41 \times 10^{-24}$ cm^3

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

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

$$= \frac{10.5 \times 6.023 \times 10^{23} \times 67.41 \times 10^{-24}}{4}$$

$$= 106.57 \text{ g mol}^{-1}.$$

S8. (a) For FCC structure $\quad 4r = \sqrt{2}\, a$

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

$$= 2\sqrt{2} \times 130 \text{ pm} = \textbf{367.64 pm}$$

(b) Volume of unit cell = a^3

$$= (3.67 \times 10^{-8})^3 = \textbf{4.94} \times \textbf{10}^{-23} \textbf{ cm}^3$$

(c) $\qquad n = 4$

(d) $\qquad \rho = \frac{n \times M}{N_o \times a^3} = \frac{4 \times 63.54}{6.023 \times 10^{23} \times (3.67 \times 10^{-8})^3} = \textbf{8.54 gm/cm}^3$

S9. Edge length of unit cell, $a = 4.077 \times 10^{-8}$ cm.

For FCC lattice, radius of an atom is related to edge length, a as :

$$r = \frac{a}{2\sqrt{2}} = \frac{4.077 \times 10^{-8}}{2 \times 1.414} = 1.441 \times 10^{-8} \text{ cm}$$

Density, $\qquad \rho = \frac{Z \times M}{a^3 \times N_A}$

$$= \frac{4 \times 108}{(4.077 \times 10^{-8})^3 \times (6.02 \times 10^{23})} \qquad (\because \ Z = 4 \text{ for } fcc)$$

$$= 10.58 \text{ g cm}^{-3}$$

S10.

$$z = 4, \quad d = 5.2 \text{ g/cm}^3, \quad M = ?$$

$$a = 300 \text{ pm} = 3 \times 10^{-10} \text{ m} = 3 \times 10^{-8} \text{ cm}$$

$$a^3 = 27 \times 10^{-24} \text{ cm}^3$$

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

$$\rho = \frac{Z \times M}{a^3 \times No}$$

$$M = \frac{\rho N_o a^3}{z} = \frac{5.2 \times 6.023 \times 10^{23} \times 27 \times 10^{-24}}{4}$$

$$= 21.113 \text{ g/mol}$$

$$6.023 \times 10^{23} \text{ atoms have} = 21.13 \text{ g}$$

$$\therefore \quad 3.01 \times 10^{24} \text{ atoms have} = \frac{21.13 \times 3.01 \times 10^{24}}{6.023 \times 10^{23}} = 105.65 \text{ g}$$

S11.

$$\rho = \frac{ZA}{NV}$$

$$\rho = \frac{ZA}{N_o V} \Rightarrow Z = \frac{\rho N_o V}{a}$$

$$= \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} = 2$$

$\Rightarrow$ Unit cell is BCC.

$\Rightarrow$

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

$$= 500 \times \frac{\sqrt{3}}{4} \text{ pm} = \textbf{216 pm}$$

S12. Given

Atomic Weight $M = 108$;

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

$$a = 409 \text{ pm} \quad \text{or} \quad 409 \times 10^{-10} \text{ cm}$$

We know,

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

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

$$= \frac{10.5 \times (409)^3 \times 10^{-30} \times 6.022 \times 10^{23}}{108} = 4.$$

Since there are 4 atoms per unit cell, the crystal lattice must be face centred cubic (*fcc*).

S13. CsCl has simple cubic structure, So Z_{eff} = 1.

$$\rho = \frac{Z_{eff} \times M}{a^3 \times N_A} \qquad \text{or} \qquad a^3 = \frac{Z_{eff} \times M}{\rho \times N_A}$$

$$= \frac{1 \times 168.5}{3.99 \times 6.02 \times 10^{23}}$$

$$= 70.15 \times 10^{-24}$$

$$a = (70.15)^{1/3} \times 10^{-8} \quad = 4.12 \times 10^{-8} \text{ cm} \quad = 4.12 \times 10^{-10} \text{ m}$$

$$= 4.12 \times 10^2 \text{ pm} \quad = 412 \text{ pm}$$

Interionic distance $= \dfrac{\sqrt{3}a}{2}$

$$= \frac{1.732}{2} \times 412 \text{ pm} = 356.8 \text{ pm} .$$

S14.

$$\rho = \frac{Z_{eff} \times Mw}{a^3 \times N_A \times 10^{-30}}$$

where a is in pm (1 nm = 10^3 pm), Z_{eff} for NaCl = 4

$$= \frac{4 \times 58.5}{(0.564 \times 10^3)^3 \times (6.023 \times 10^{23}) \times 10^{-30}} \text{ g cm}^{-3}$$

$$= 2.165 \text{ g cm}^{-3}.$$

S15. For the face-centered cubic, Z_{eff} = 4

$$\rho = \frac{Z_{eff} \times Aw}{a^3 \times N_A \times 10^{-30}} \text{ g cm}^{-3}$$

$$= \frac{4 \times 60}{(400)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} = 6.23 \text{ g cm}^{-3}$$

S16. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as

$$d = \frac{\sqrt{3}}{2} \times a$$

or

$$a = \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

For bcc structure, $\qquad Z_{eff} = 2$

For sodium, $\qquad Aw = 23$

$\therefore \qquad \qquad r = \dfrac{Z_{eff} \times Aw}{a^3 \times N_A}$

$$= \frac{4 \times 23}{(422.5)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} \text{ g cm}^{-3}$$

$$= 1.51 \text{ g cm}^{-3}.$$

S17. (a) Frenkel defects do not change the value of the theoretical density because the atom is occupying and interstitial position instead of a lattice position.

(b) Z_{eff} of Ca = 4 atom/unit cell (since it is fcc type)

So, $$Z_{eff} = \left(4 - \frac{0.1}{100} \times 4 \right) = 3.996$$

$\therefore$ $$\rho = \frac{Z_{eff} \times Aw}{N_A \times a^3}$$ $(\because 1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm})$

$$= \frac{(3.996) \times 40 \text{ g}}{(6 \times 10^{23} \text{ mol}^{-1})(0.556 \times 10^{-7} \text{ cm})^3}$$

$$= 1.547 \text{ g cm}^{-3}.$$

S18. Edge length of unit cell

$$a = 409 \text{ pm}$$
$$= 409 \times 10^{-10} \text{ cm}$$

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

Atomic mass of silver = 108 u

Now, $$\rho = \frac{Z \times M}{a^3 \times N_0}$$

$$10.5 \text{ g cm}^{-3} = \frac{Z \times (108 \text{ g mol}^{-1})}{(409 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

or $$Z = \frac{(10.5 \text{ g cm}^3) \times (409 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})}{108 \text{ g mol}^{-1}}$$

$$Z = 4.0$$

Since the unit cell contains 4 atoms per unit cell, it is face centred cubic (fcc) unit cell.

For fcc, $$r = \frac{a}{2\sqrt{2}} = \frac{409 \text{pm}}{2 \times 1.414} = 144.6 \text{ pm}$$

S19. For NaCl (Z) = 4

Molecular mass of NaCl (M) = 58.5 g mol^{-1}

$$d = 2.165 \text{ g cm}^{-3}$$

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

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

$$a^3 = \frac{4 \times 58.5}{2.165 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{234.0 \times 10}{2.165 \times 6.02 \times 10^{23} \times 10}$$

$$a^3 = \frac{2340 \times 10^{-24}}{2.165 \times 6.02}$$

$$a = \sqrt[3]{\frac{2340 \times 10^{-24}}{2.165 \times 6.02}}$$

$$a = \left(\frac{2340 \times 10^{-24}}{2.165 \times 6.02}\right)^{\frac{1}{3}}$$

Taking log on both side

$$\log a = \log\left(\frac{2340 \times 10^{-24}}{2.165 \times 6.02}\right)^{\frac{1}{3}}$$

$$\log a = \frac{1}{3}\left[\log 2340 + \log 10^{-24} - (\log 2.165 + \log 6.02)\right]$$

$$\log a = \frac{1}{3}\left[3.3692 - 24 - 0.3365 - 0.7796)\right]$$

$$\log a = \frac{1}{3}\left[3.3692 - 24 - 1.1161\right]$$

$$\log a = \frac{1}{3}[2.2531 - 24] = \frac{2.2531 - 24}{3}$$

$$\log a = 0.751 - 8 = -7.249 + 8 - 8 = -8 + 0.751$$

$$\log a = -8.751$$

$$a = \text{Antilog}\,(-8.751)$$

$$a = 5.628 \times 10^{-8}\,\text{cm}$$

$$a = 5.628 \times 10^{-10}\,\text{m}$$

or
$$a = 562.8\,\text{pm}$$

Distance between Na^+ and Cl^- ions $= \dfrac{a}{2} = \dfrac{562.8}{2}$ pm = **281.4 pm**.

S20. According to question,

$$z = 4, \quad d = 2.165 \, \text{g cm}^{-3}, \quad M = 56.5 \, \text{g mol}^{-1}$$
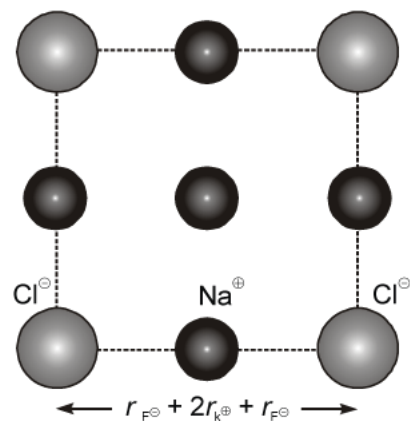
Edge length of unit cell in NaCl

$a = 2 \times$ distance between Na$^+$ and Cl$^-$ ions

$= 2 \times 281 \, \text{pm}$

$= 562 \, \text{pm}$

$= 562 \times 10^{-10} \, \text{cm}^3$

Volume of unit cell $a^3 = (562 \times 10^{-10})^3 \, \text{cm}^3$

We know: $\quad d = \dfrac{z \times M}{a^3 \times N_A}$

or $\quad N_A = \dfrac{z \times M}{a^3 \times d}$

$$N_A = \frac{4 \times 58.5}{(562 \times 10^{-10})^3 \times 2.165}$$

$$= 6.09 \times 10^{23} \, \text{mol}^{-1}.$$

S21. KF has NaCl type structure, therefore, the number of KF molecules per unit cell,

$$Z = 4$$

Molar mass of KF = 58 g mol^{-1}

Let the edge of unit cell = a cm

Density, $\rho = 2.48 \, \text{g cm}^{-3}$

Density, $\rho = \dfrac{Z \times M}{a^3 \times N_0}$

$$2.48 \, \text{g cm}^{-3} = \frac{4 \times 58 \, \text{g mol}^{-1}}{a^3 \times (6.022 \times 10^{23} \, \text{mol}^{-1})}$$

$$a^3 = \frac{4 \times 58 \, \text{g mol}^{-1}}{(2.48 \, \text{g cm}^{-3}) \times (6.022 \times 10^{23} \, \text{mol}^{-1})}$$
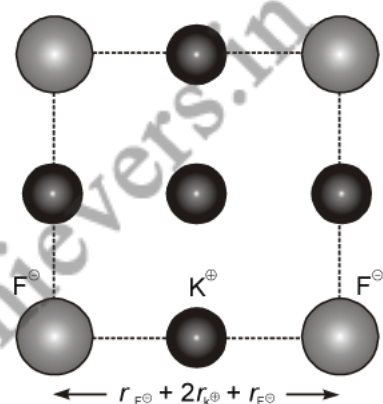
$$= 155.3 \times 10^{-24} \, \text{cm}^3$$

$\therefore \quad a = (155.3 \times 10^{-24})^{1/3} = 5.375 \times 10^{-8} \, \text{cm}$

or $\quad a = 5.375 \times 10^{-10} \, \text{m} \quad$ or $\quad 537.5 \, \text{pm}$

Now, if radius of F$^{\ominus}$ is $r_{F^{\ominus}}$ and radius of K$^{\oplus}$ is, $r_{K^{\oplus}}$ then according to the figure, edge of unit cell,

$$a = r_{F^{\ominus}} + r_{2k^{\oplus}} + r_{F^{\ominus}}$$

$$= 2(r_{K^{\oplus}} + r_{F^{\ominus}})$$

or $\quad r_{K^{\oplus}} + r_{F^{\ominus}} = \dfrac{a}{2}$

Thus, distance between $K^{\oplus}$ and $F^{\ominus}$ ions will be half the edge length in the unit cell.

Thus, the distance between $K^{\oplus}$ and $F^{\ominus}$ ions = $\dfrac{537.5}{2}$ = 268.8 pm.

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Q1. Which point defect lowers the density of a crystal?

Q2. Cation vacancies in some crystals make them good catalysts. Explain.

Q3. Zinc oxide is white, on heating it becomes yellow. Explain.

Q4. Frankel defect is not found in pure alkali metal halides, why?

Q5. Which of the two $CdCl_2$ or NaCl will produce vacancy defect when added to AgCl crystal?

Q6. Fe_3O_4 is ferrimagnetic at room temperature and becomes paramagnetic 850 K. Explain briefly.

Q7. Which type of compounds exhibit Schottky defect?

Q8. Which type of defects are known as thermodynamic defects?

Q9. At which temperature condition Fe_3O_4 become paramagnetic?

Q10. Which point defect is observed in a crystal when the anionic vacancy is filled by an electron.

Q11. What type of stoichiometric defect is shown by
(a)   ZnS   (b)   AgBr.

Q12. What type of defect can arises when a solid is heated? Which physical property is affected by it and in what way?

Q13. How would you account Schottky defects lower the density of related solids?

Q14. Name the non-stoichiometric point defect responsible for colour in alkyl halide.

Q15. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

Q16. Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

Q17. If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

Q18. If NaCl is doped with 10^{-3} mol% $GaCl_3$, what is the concentration of the cation vacancies?

Q19. Assign reasons for the following:
(a)   Name the non-stoichiometric point defect responsible for colour in alkyl halide.
(b)   Phosphorus doped silicon is a semiconductor.
(c)   Schottky defect lowers the density of a solid.
(d)   Some of the very old glass objects appear slightly milky instead of being transparent.

Q20. How would you account for the following?
(a)   Frenkel defects are not found in alkali metal halides.
(b)   Schottky defects lower the density of related solids.
(c)   Impurity doped silicon is a semiconductor.

Q21. Explain the following terms with suitable examples:

    (a)   Schottky defect   (b)   Frenkel defect   (c)   Interstitials   (d)   F-centres.

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S1. Schottky defects.

S2. Cation vacancies are due to the absence of metal ions in its crystal lattice. The charge is balanced by an adjacent ion having higher positive charge which result in increase in chemical adsorption.

S3. Zinc oxide is white but on heating ZnO loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$
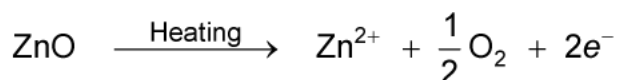
The excess Zn^{2+} ions move to interstitial site and the electrons to neighbouring interstitial sites. These electrons absorb visible light and impart yellow colour to zinc oxide.

S4. In alkali metals cations have bigger atomic size so, it cannot get into the interstitial sites of crystals lattice.

S5. $CdCl_2$. This is because divalent Cd^{2+} ions occupy the Ag^+ sites and thus produces cationic vacancies in crystal.

S6. Due to randomisation of spins at high temperature.

S7. Ionic compounds which have cations and anions of nearly same size.
   For example: NaCl, KCl.

S8. Stoichiometric defects.

S9. 850 K temperature.

S10. *F*-centre, non-stoichiometric point defect with metal.

S11. (a) **ZnS,** shows Frenkel defect due to large difference in size of ions.
   (b) **AgBr,** shows Frenkel defect and Schottky defect.

S12. A vacancy defect may arises when a solid is heated. This results decrease in density of the substance. Because some atoms or ions leave the crystal completely.

S13. It is because large number of cations and anions are missing leading to lowering in density of related solids. There is presence of holes or vacancies which lead to lowering in density.

S14. Due to *F*-centres.

S15. When a cation with higher valence is added as an impurity in the ionic solid, some of the site of the original cations are occupied by the cations of higher valence.

   For example: Sr^{2+} in NaCl. Each Sr^+ replaces two Na^+ ions.

   It occupies the site of one Na^+ ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions.
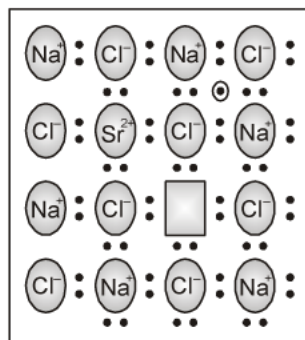
Vacancy Defect

S16. The anionic vacancies due to metal excess defect in ionic solid are occupied by free electrons to maintain the electrical neutrality. These impart colour by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

For example: When NaCl is heated in presence of sodium vapours, Na$^+$ ions are in excess, Cl$^-$ ions leave their normal site and come to the surface.

The vacant site of anion is occupied by electron forming *F*-centre. They absorb light from visible region and radiate complementary colour.

S17. Every Sr^{2+} ion causes one cation vacancy (because two Na$^+$ ions are replaced by one Sr^{2+}).

Therefore, introduction of 10^{-3} moles of SrCl$_2$ per 100 moles of NaCl would introduce 10^{-3} mole cation vacancies in 100 mole of NaCl.

No. of vacancies per mole of NaCl

$$= \frac{10^{-3}}{100} \times 6.02 \times 10^{23} = \textbf{6.02} \times \textbf{10}^{18} \textbf{ vacancies}$$

S18. 100 mol of NaCl are doped with 10^{-3} mol of GaCl$_3$.

∴   1 mol of NaCl is doped with GaCl$_3$ = $\dfrac{10^{-3}}{100}$ = 10^{-5} mol

As one Ga^{3+} ion is introduced, three Na$^\oplus$ have to be removed to maintain the electrical neutrality. So as one vacancy is filled by Ga^{3+}, two cation vacancies are formed.

∴   Concentration of cation vacancy

$$= 2 \times 10^{-5} \text{ mol/mol of NaCl}$$
$$= 2 \times 10^{-5} \times 6.023 \times 10^{23} \text{ mol}^{-1}$$
$$= 12.046 \times 10^{-18} \text{ mol}^{-1}$$
$$= 1.2046 \times 10^{-19} \text{ mol}^{-1}.$$

S19. (a)   Due to *F*-centres.

(b)   Due to presence of free electrons on doping phosphorus.

(c)   Due to the presence of holes or vacancies in the solid.

(d)   Due to crystallization in old glass objects.

S20. (a) It is because cations and anions have similar size and alkali metal ions (cations) are larger and do not fit into voids.

(b) It is because large number of cations and anions are missing leading to lowering in density of related solids. There is presence of holes or vacancies which lead to lowering in density.

(c) Silicon doped with impurity like 'B' leads to formation of hole or void or vacancy which moves like positive charge whereas silicon doped with 'As' leads to movement of electrons and it behaves like semiconductor.

S21. (a) **Schottky defect:** Schottky defect occurs when a pair of ions of opposites charge, *i.e.*, cations and anions, are missing from the ideal lattice. In 1 cm^3 of NaCl there are approximately 10^6 Schottky pairs at room temperature. The presence of a large number of Schottky defect in a crystal lowers its density.

(b) **Frenkel defect:** Frenkel defect occurs when a smaller ion leaves its position in the lattice and occupies an interstitial void leaving a gap in the crystal. The Frenkel defects are found in silver halides because the Ag$^+$ ions are considerably small in size than the halide ions and, thus, can get into the interstitial sites, which does not change its density.

(c) **Interstitials:** The atoms or ions which occupy the normally vacant interstitial sites in a crystal are known as interstitials. The vacant voids filed by small size non-mental like *H*, *B*, *C* and *N*.

(d) ***F*-centres:** When there is an excess of metal ions in non-stoichiometric compounds, the crystal lattice has vacant anion sites. These sites are occupied by electrons. The anion sites occupied by electrons are called ***F*-centre**. The *F*-centres are associated with colour of compounds. Thus, excess of *K* in KCl makes the crystal of KCl violet and excess of Li in LiCl makes it pink. Due to unpaired electron **F-centres** shows paramagnetic character.

Q1. In terms of band theory, what is the difference between
  (a)   a conductor and an insulator?   (b)   a conductor and a semiconductor?

Q2. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a *p*-type semiconductor?

Q3. What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

Q4. What type of substances would make better permanent magnets ferro-magnetic or ferri-magnetic? Justify your answer.

Q5. Ionic solids conduct electricity in molten state but not in solid state. Explain.

Q6. Why does zinc oxide exhibit enhanced electrical conductivity on heating?

Q7. The ions of NaF and MgO have the same number of electrons and internuclear distances are about the same (235 pm and 215). Why are then the melting points of NaF and MgO so different (992 °C and 2642 °C)?

Q8. Why some of the very old glass objects appear slightly milky instead of being transparent?

Q9. Proof Impurity doped silicon is a semiconductor.

Q10. The electrical conductivity of a metal decreases with rise in temperature while that of a semiconductor increases. Explain.

Q11. What is the effect of temperature on the conductivity of metals and semimetals?

Q12. What is doping?

Q13. What is a forbidden zone?

Q14. What is curic temperature?

Q15. Explain the following with suitable examples:
  (a)   Ferromagnetism   (b)   paramagnetism   (c)   ferrimagnetism
  (d)   antiferromagnetism   (e)   12-16 and 13-15 compounds.

Q16. Classify each of the following as being either a *p*-type or an *n*-type semiconductor:
  (a)   Ge doped with In. Ge has four valence electrons, whereas In has three valence electrons.
  (b)   B doped with Si. B has three valence electrons, whereas Si has four valence electrons.

Q17. A group 14 element is to be converted into *n*-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Q18. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms.

S1. (a) **Conductor:** In a conductor, there is no energy gap between the valence band and the conduction band (empty band).

Insulator: In an insulator, there is a large energy gap between the valence band and the conduction band (empty band).

(b) **Conductor:** In a conductor there is no energy gap between the valence band and the conduction band (empty band).

Semiconductor: In a energy gap between the valence band and the conduction band is very small. Some electrons by acquiring extra thermal energy jump to the conduction band.

S2. Cu_2O having Cu : O ratio less than 2 : 1 shows, Cu^+ ions have been replaced by Cu^{2+} ions. For electrical neutrality, every two Cu^+ ions will be replaced by Cu^{2+} ion there by creating a holes (metal deficiency). So conduct electricity through positive holes. Hence it is a *p*-type semiconductor.

S3. Glass is an amorphous supercooled liquid, whereas quartz is a crystalline solid. When quartz is heated and the melt is cooled very rapidly, it forms amorphous silica (glass). In glass SiO_4 tetrahedral are randomly joined.

S4. Ferro-magnetic substances would make better permanent magnets because they have high magnetic moment as compared to ferri-magnetic substance.

Schematic alignment of magnetic moments in (a) ferro-magnetic substance and (b) ferri-magnetic substance

S5. Ionic solids do not conduct electricity in solid state because ions in solid state are bound by strong coulombic forces or electrostatic forces and are not free to move. However, in molten state or when dissolved in water, the ions becomes free to move and hence they conduct electricity.

S6. On heating ZnO undergoes decomposition as follows:

$$ZnO \xrightarrow{\Delta} Zn^{2\oplus} + \frac{1}{2}O_2 + 2e^{\ominus}.$$
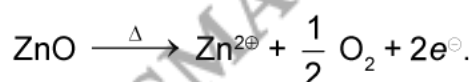
$Zn^{2\oplus}$ ions and electrons are both entrapped in interstitial sites because of which the conductivity increases.

S7. Electrostatic force of attraction is more in $Mg^{2\oplus}O^{2\ominus}$ than in $Na^{\oplus}F^{\ominus}$ because there are +2 and –2 charges in MgO while +1 and –1 charges operate in NaF. Greater the force of attraction, greater the energy required to overcome those forces. Hence, MgO melts at a higher temperature.

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S8. Glass is supercooled liquid, therefore very old glass objects become slightly milky because of heating during the day and cooling at nights i.e., annealing over a number of years glass acquires some crystalline structure.

S9. Silicon doped with impurity like 'B' leads to formation of hole or void or vacancy which moves like positive charge whereas silicon doped with 'As' leads to movement of electrons and it behaves like semiconductor.

S10. In the case of metals, the kernels (atom-outer electrons) start vibrating on increasing the temperature and offer resistance to the flow of electrons. Hence, conductivity of metal decreases with rise of temperature.

In the case of semiconductor, more and more electrons are excited to the conduction band on increase of temperature. Hence, the conductivity increases.

S11. With increase in temperature, the conductivity of metal decreases and that of semimetals increases.

S12. Doping is a process of adding small amount of certain impurities to semiconductor element to enhance electrical conductivity.

S13. The space between valence band and conduction band represent energies forbidden to electrons are called *forbidden zone*.

S14. A temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism.

S15. (a) **Ferromagnetism:** Ferromagnetic substances are those substances which shows permanent magnetism even when the magnetic field is removed.

For examples: Fe, CrO_2.

$$\Uparrow \quad \Uparrow \quad \Uparrow \quad \Uparrow \quad \Uparrow \quad \Uparrow \quad \Uparrow$$

(b) **Paramagnetism:** Paramagnetic substances are those which are attracted by a magnetic field but they lose their magnetism in the absence of a magnetic field due to the presence of atoms, molecules or ions containing unpaired electrons.

For examples: Cu^{2+}, Fe^{3+}, O_2, Cr^{3+} etc.

(c) **Ferrimagnetism:** Ferrimagnetism substances are those substances in which the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in net magnetic moment.

For examples: Fe_2O_4, Ferrites $Mg\,Fe_2O_4$, $ZnFe_2O_4$.

$$\Uparrow \quad \Uparrow \quad \Downarrow \quad \Uparrow \quad \Uparrow \quad \Downarrow \quad \Uparrow$$

(d) **Anti-ferromagnetism:** The substances like MnO showing anti-ferromagnetism have domain structure similar to ferromagnetic substances, but their domains are oppositely oriented and cancel out each other's magnetic moments.

For examples: MnO.

$$\uparrow \quad \downarrow \quad \uparrow \quad \downarrow \quad \uparrow \quad \downarrow$$

(e) **12-16 and 13-15 compounds:** 12-16 compounds are formed by the combination of elements of groups 12 and 16.

**For examples:** ZnS, CdS, $CdSe$, $HgTe$, etc.

13-15 compounds are formed by the combination of elements of groups 13 and 15.

For examples: $InSb$, $GaAs$, AIP, etc.

The bonds in 12-16 and 13-15 compounds are not perfectly covalent. The ionic character of these compounds depends on the electromagnetivities of the two elements.

S16. (a) **Ge** belongs to group 14 and **In** belongs to group 13, therefore an electron deficient hole is created and hence it is *p*-type semiconductor.

(b) **B** belongs to group 13 and **Si** belongs to group 14, therefore, there will be a free electron and hence it is *p*-type semiconductor.

S17. This can be done by doping it with a group **15 element** like **P** or *As*, which contains five valence electrons. Four out of five electrons are used in formation of covalent bonds with the four neighbouring group 14 atoms. The fifth extra electron gets delocalized and increases the conductivity thus producing ***n*-type semi-conductor**.
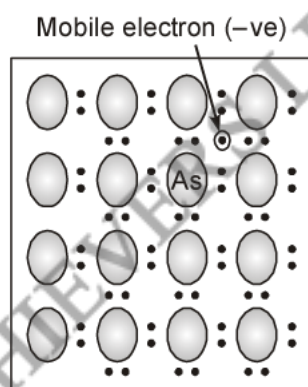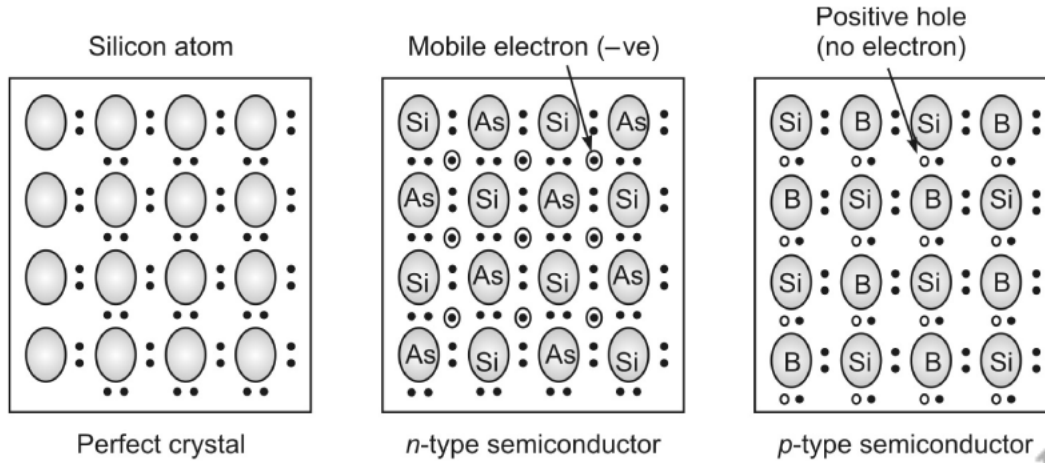

n-type semiconductor

S18. **Semiconductor:** A semiconductor is a solid that has a conductivity intermediate between that of a conductor and an insulator. The conductivity varies from 10^{-6} to 10^4 ohm^{-1} m^{-1}. In other words, due to absence of free electrons, solid substance behave as insulator, but at higher temperature it can conduct electric current, because some covalent bonds break.

Type of Semiconductors

(a) ***n*-type semiconductor:** It is obtained by doping silicon with a group 15 element. Suppose silicon is doped with phosphorus which has 5 valance electrons. Out of 5 valence electrons, only 4 valence electrons are involved in bond formation, fifth electron is not bound anywhere and can be easily promoted to the conduction band. The conduction is, thus mainly caused by the movement of electrons. So due to presence of the negative charge such type of semiconductor is called *n*-type semiconductor.

(b) ***p-type semiconductor:*** It is obtained by doping silicon with a group 13 element. Suppose silicon is doped with gallium which has three valence electrons, three valence electrons form three bonds with neighbouring Si atoms. A vacancy is left which can be filled by the transfer of a valence electron from a neighbouring Si atom. The movement of the one electron into the vacancy leaves behind a hole which carries a positive charge. The movement of positively charged hole is responsible for the conduction of charge. So, such type of semiconductor is called *p*-type semiconductor.

Perfect crystal   *n*-type semiconductor   *p*-type semiconductor