Chapter-15 : The Solid State

1. (c) In fluorite structure each F^- ion is surrounded by four Ca^{2+} ions whereas each Ca^{2+} is surrounded by eight F^- ions, giving a body centred cubic arrangement. Thus the co-ordination number of Ca^{2+} and F^- are 8 and 4 respectively.

2. (b) The radius ratio $\frac{r_+}{r_-} = \frac{146}{216} = 0.675$
It lies between 0.414 – 0.732. Hence, it exhibits rock salt type structure.

3. (c) In a *fcc* lattice, the distance between the cation and anion is equal to the sum of their radii, which is equal to half of the edge length of unit cell,
i.e. $r^+ + r^- = \frac{a}{2}$ (where a = edge length)
$r^+ = 95$ pm, $r^- = 181$ pm
Edge length $= 2r^+ + 2r^- = (2 \times 95 + 2 \times 181)$ pm
$= (190 + 362)$ pm $= 552$ pm.

4. (b) For orthorhombic system $\alpha = \beta = \gamma = 90°$

5. (b) The face centred cubic unit cell contains 4 atom
$\therefore$ Total volume of atoms $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

6. (c) Piezoelectric crystals are used in record player.

7. (b) More is the Schottky defect in crystal more is the decrease in density.

8. (a) *p*-type of semiconductors are produced
(i) due to metal deficiency defects
(ii) by adding impurity containing less electrons (i.e., atoms of group 13)
Ge belongs to Group 14 and In to Group 13. Hence on doping, *p*-type semicondutor is obtained.

9. (b) $\rho = \frac{Z\,M}{N_A V}$
$Z = \frac{\rho N_A V}{M} = \frac{8.92 \times 6.02 \times 10^{23} \times (362)^3 \times 10^{-30}}{63.55}$
$= 4$
$\therefore$ It has *fcc* unit cell.

10. (d) Since in NaCl type structure 4 formula units form a cell.
58.5 g of NaCl $= 6.023 \times 10^{23}$ atoms
1 g of NaCl $= \frac{6.023 \times 10^{23}}{58.5}$ atoms
4 atoms constitute 1 unit cell
$\therefore \frac{6.023 \times 10^{23}}{58.5}$ atoms constitute
$= \frac{6.023 \times 10^{23}}{58.5 \times 4} = 2.57 \times 10^{21}$ unit cells.

11. (d) In KCl, co-ordination number of cation and anion is 6 and 6 respectively. KCl is highly ionic so Schottky defect is common.
Note : Schottky defect is common in compounds having high coordination nummber while Frenkel defect is common in compounds with low coordination number.

12. (a) There are two atoms in a *bcc* unit cell.
So, number of atoms in 12.08×10^{23} unit cells
$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}$ atoms.

13. (b) Liquid crystals on heating first become turbid and then clear.

14. (d) Body diagonal (d) of a cubic crystal of edge length (a) is given by,
$d = a\sqrt{3}$
putting $a = 400$ pm, we get
$d = \sqrt{3} \times 400$ pm $= 692.8$ pm ≈ 693 pm.

15. (c) 40 g $= N_A$ atoms $\Rightarrow$ 4g $= 0.1 \times N_A$ atoms
2 atoms form 1 unit cell in *bcc* crystal
$\therefore 0.1 \times N_A$ atoms $= \frac{0.1 \times N_A}{2}$ unit cells

16. (d) The *bcc* cell consists of 8 atoms at the corners and one atom at centre. Contribution of each atom at each corner is equal to $\frac{1}{8}$.
$\therefore n = \left(8 \times \frac{1}{8}\right) + 1 = 2$
The *fcc* cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.
$\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$

17. (c) Let the number of Z atoms in the *ccp* arrangement = 100
Thus the number of tetrahedral sites = 200
Since all the tetrahedral sites are occupied by X atoms, the number of X atoms = 200
Hence ratio of X : Z = 2 : 1
Thus the formula is X_2Z.

18. (a) In NaCl type, Cl^- ions form *ccp* structures while Na^+ ions are present in all octahedral voids.

19. (d) For an *fcc* crystal
$r_{cation} + r_{anion} = \frac{\text{edge length}}{2}$
$110 + r_{anion} = \frac{508}{2}$
$r_{anion} = 254 - 110 = 144$ pm

20. (b)

Unit cell	No. of atoms
Simple cubic	$\frac{1}{8} \times 8 = 1$
BCC	$\frac{1}{8} \times 8 + 1 \times 1 = 2$
FCC	$\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

21. (b) For body centred cubic lattice Z = 2
Atomic mass of unit cell = 133 + 80 = 213 a.m.u
Volume of cell $= (436.6 \times 10^{-10})^3$ cm^3

Density, $\rho = \frac{ZM}{a^3 N_A} = \frac{2 \times 213}{(436.6 \times 10^{-10})^3 \times 6.02 \times 10^{23}}$

$= 8.50\ g/cm^3$

22. (a) Let the units of ferrous oxide in a unit cell = n,
Molecular weight of ferrous oxide (FeO) $= 56 + 16$
$= 72\ g\ mol^{-1}$

Weight of n units $= \frac{72n}{6.023 \times 10^{23}}$

Volume of one unit = (length of corner)^3
$= (5Å)^3 = 125 \times 10^{-24}\ cm^3$

$$\text{Density} = \frac{\text{wt. of cell}}{\text{volume}}$$

$$4.09 = \frac{72 \times n}{6.023 \times 10^{23} \times 125 \times 10^{-24}}$$

$$n = \frac{3079.2 \times 10^{-1}}{72} = 42.7 \times 10^{-1} = 4.27 \approx 4$$

23. (d) Effective number of 'A' atoms $= \left(8 \times \frac{1}{8}\right) + \left(4 \times \frac{1}{2}\right) = 3$

Effective number of 'B' atoms $= \left(12 \times \frac{1}{4}\right) + 1 = 4$

$\therefore$ Formula of the solid $= A_3B_4$.

24. (a) ZnS has cubic close packed (*ccp*) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, S^{2-} ion is surrounded by four Zn^{2+} ions.

25. (c) Among the three options KCl, NaCl and $MgCl_2$, the size of anion is same. So larger the cation, larger will be the cation/anion ratio i.e., KCl will have larger cation/anion ratio among the three. So, we left with two options KCl and CaF_2. Among these two CaF_2 will have maximum value of cation/anion ratio because decrease in ionic radii of anion from Cl^- to F^- does not overcome the effect of decrease in ionic radii of cation from K^+ to Ca^{2+}.

26. (a) In crystalline solid there is perfect arrangement of the constituent particles only at 0 K. As the temperature increases, the chance that a lattice site may be unoccupied by an ion, increases. As the number of defects increases with temperature solid changes into liquid.

27. (d) Packing efficiency

$$= \frac{\text{Area occupied by circles within the square}}{\text{Area of square}}$$

$$= \frac{2\pi r^2}{L^2} \times 100 = \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100 = \frac{\pi}{4} \times 100 = 78.54\%$$

28. (c) When coordination number is eight, the radius ratio $\left(\frac{r^+}{r^-}\right)$ lies between 0.732 to 1.000.

29. (d) Number of atoms per unit cell = 1

Atoms touch each other along edges. Hence $r = \frac{a}{2}$

(r = radius of atom and a = edge length)

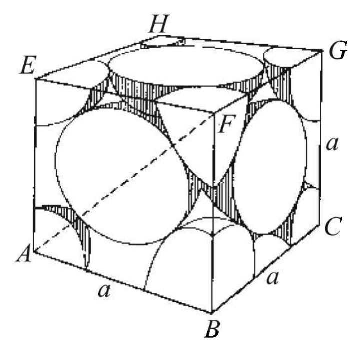
Therefore % fraction $= \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$

30. (d) For a *fcc* unit cell

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

$\therefore$ closest distance (2r) $= \frac{\sqrt{2}\,a}{4} = \frac{a}{\sqrt{2}}$

31. (c)



An isolated *fcc* cell is shown here. Each face of the cell is common to two adjacent cells. Therefore, each face centre atom contributes only half of its volume and mass to one cell. Arranging six cells each sharing the remaining half of the face centred atoms, constitutes *fcc* cubic lattice. e.g., Cu and Al.

32. (d) No. of atoms of P $= 8 \times \frac{1}{8} = 1$

No. of atoms of Q $= 1 \times 1 = 1$

The formula of the compound is PQ.

Coordination no. of P and Q = 8 : 8

33. (d) For *n*-type, impurity added to silicon should have more than 4 valence electrons.

34. (c) $Z = \frac{V \times N_A \times \rho}{M}$

$$= \frac{4.2 \times 8.6 \times 8.3 \times 10^{-24} \times 6.023 \times 10^{23} \times 3.3}{155} = 3.84 \approx 4$$

35. (c) C_6H_6 is diamagnetic

CrO_2 is ferromagnetic

MnO is antiferromagnetic

Fe_3O_4 is ferrimagnetic

Fe^{3+} is paramagnetic with 5 unpaired electrons

36. (b) Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the total volume of the unit cell.

P.F. for *cpp* and *bcc* are 0.74 and 0.68 respectively.
So, the free space in *ccp* and bcc are 26% & 32% respectively.

37. (b) Number of tetrahedral voids (V_T) in a crystal is twice the number of atoms (n) in a crystal i.e.,

$V_T = 2n$

So, number of tetrahedral voids per atom is given by

$V_T / n = 2$

38. (d) Permitted co-ordination number for *ccp* is 8 but two A atoms are missing

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

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

So, composition is $A_{6/8}\,B_3$ or A_6B_{24}.

39. (c) In FCC, tetrahedral voids are located on the body diagonal at a distance of $\frac{\sqrt{3}a}{4}$ from the corner.

Together they form a smaller cube of edge length $\frac{a}{2}$.

Therefore, distance between centres of two nearest tetrahedral voids in the lattice is also $\frac{a}{2}$.

40. (b) Since each Sr^{2+} ion provides one cation vacancy,

$\therefore$ Concentration of cation vacancies

= mole % of $SrCl_2$ added

$= 10^{-4}$ mole %

$$= \frac{10^{-4}}{100} \times 6.023 \times 10^{23} = 6.023 \times 10^{17}\ \text{mol}^{-1}$$

41. (a) For cubic, $a = b = c,\ \alpha = \beta = \gamma = 90°$

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

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

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

42. (a) Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length (a) of the cell and r the radius of the sphere.

For simple cubic : $a = 2r$ or $r = \frac{a}{2}$

For body centred cubic :

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

For face centred cubic :

$$a = 2\sqrt{2} r \text{ or } r = \frac{1}{2\sqrt{2}} a$$

Thus the ratio of radii of spheres for these will be

$$scc : bcc : fcc = \frac{a}{2} : \frac{\sqrt{3}}{4} a : \frac{1}{2\sqrt{2}} a$$

43. (c) F - centres impart yellow colour to the crystals of NaCl when heated in an atmosphere of sodium vapour. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

44. (b) No. of lattice points = No. of Oh voids

$= \frac{1}{2} \times$ No. of *Td* voids in *ccp* structure

$\therefore$ No. of atoms of $B = 4$

No. of atoms of $A = \frac{1}{2} \times$ No. of Oh voids

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

No. of atoms of O = No. of all Td voids

$= 2 \times$ No. of lattice points

$= 2 \times 4 = 8$

Hence, A : B : O = 1 : 2 : 4

Therefore, the formula of the compound is AB_2O_4

45. (a) γ–form *fcc* Z = 4 a = 386 pm

β–form *bcc* Z = 2 a = 290 pm

$$\frac{\rho_\gamma}{\rho_\beta} = \frac{4M/N_A(386)^3}{2M/N_A(290)^3} = \frac{2(290)^3}{(386)^3} = 0.8481$$

46. (c) Let the fraction of metal which exists as M^{3+} be x.
Then the fraction of metal as $M^{2+} = (0.98 - x)$

$\therefore\quad 3x + 2(0.98 - x) = 2$

$x + 1.96 = 2$

$x = 0.04$

$$\therefore\ \%\text{ of } M^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\%$$

47. (c) No. of *hcp* particles in 0.5 mole $= 0.5 \times 6.023 \times 10^{23}$ $= 3.011 \times 10^{23}$

No. of Octahedral void (n) $= 3.011 \times 10^{23}$

No. of Tetrahedral void ($2n$) $= 2 \times 3.011 \times 10^{23}$ $= 6.022 \times 10^{23}$

$\therefore$ Total no. of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$ $= 9.033 \times 10^{23}$

48. (a) $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55$ and $\frac{r_{K^+}}{r_{Cl^-}} = 0.74$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 0.55 + 1 \text{ and } \frac{r_{K^+}}{r_{Cl^-}} + 1 = 0.74 + 1$$

$$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.55 \text{ and } \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.74$$

Now edge length ratio of KCl and NaCl is

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.123.$$

49. (a) $\rho = \frac{ZM}{N_A a^3}$

Molar mass of KF = 58.08 g mol^{-1}

$Z = 4$ for KF

$$a^3 = \frac{ZM}{\rho.N_A} = \frac{4 \times 58.08}{2.48 \times 6.023 \times 10^{23}}$$

$= 15.56061621 \times 10^{-23}$

$a = 5.37 \times 10^{-10} \text{cm} = 537 \text{pm}$

$a = 2\,(r_c + r_a)$

$$r_c + r_a = \frac{a}{2} = \frac{537}{2} = 268.5 \text{ pm}$$

50. **(d)** We know that, density $= \dfrac{ZM}{N_A \times a^3}$

Given that: $Z = 4$ (*fcc*)

$M = 63.5$ g

$N_A = 6 \times 10^{23}$

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

After putting the values, we get

$$d = \frac{4 \times 63.5}{6 \times 10^{23} \times x^3 \times 10^{-24}}$$

$$= \frac{422 \text{ g cm}^{-3}}{x^3}$$