BRUSH UP YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.com. The queries will be entertained by the author.*

In continuation with previous article.

SOLID STATE (CRYSTALLOGRAPHY)

- Radius ratio $\left(\frac{r^+}{r^-} \text{ or } \frac{r}{R}\right)$, Coordination number (C.N.) and Geometry

S. No.	*r/R* ratio	C.N.	Geometry	Examples
1.	0.225 to 0.414	4	Tetrahedral	ZnS, HgS, Cu*X*, etc.
2.	0.414 to 0.732	6	Octahedral, square planar	NaCl, $[PtCl_4]^{2-}$, MgO, etc.
3.	0.732 to 1.0	8	*bcc*	CsBr, CsCl, etc.
4.	1.0	12	*ccp* or *fcc*	Mg, Zn, etc.

- **Structures of Ionic Crystals**

I. *AB*-Type

(i) Rock salt or NaCl type : *fcc* of A^+ and B^- penetrate into each other with C.N. of 6, 6, $\frac{r^+}{r^-}$ ratio 0.414 to 0.732. Per unit cell of *AB* type, one ion has 14 locations and other 13 locations. *Z*-value is 4 *i.e.*, 4*AB* units per cell.

Next neighbours of Na^+ in NaCl, w.r.t. body centre location.

1st	2nd	3rd
8 Cl^- at faces	12 Na^+ at edge centres	8 Cl^- at corners

(ii) CsCl type : A^+ is located at body centre and B^- at corners.

C.N. of 8, 8, $\frac{r^+}{r^-}$ ratio 0.732 to 1.0. *Z* value is 1, *i.e.*, one *AB* unit per unit cell.

Next neighbouring of Cs^+ in CsCl.

1st	2nd
8 Cl^- at corners	6 Cs^+ at centres of six cubes joined on faces.

(iii) Zinc Blende or Sphalerite or ZnS type : S^{2-} forms *fcc* and Zn^{2+} are located at centres of alternate tetrahedra, dividing a cube into 8 sub-cubes.

C.N. of 4, 4, $\frac{r^+}{r^-}$ ratio 0.225 to 0.414. *Z*-value is 4, *i.e.*, 4 *AB* units per unit cell.

II. Fluoride CaF_2 – AB_2 type

Cations form *ccp* and anions occupy all tetrahedral voids. C.N. $A^{2+} : B^- = 8 : 4$. One unit cell has 4 AB_2 formula units (*Z*-value)

III. Antifluorite Na_2O or Li_2O – A_2B-type

Anions forms *ccp* and cations occupy all tetrahedral voids. C.N. $A^+ : B^- = 4 : 8$. One unit cell has 4 formula units (*Z*-value).

- Rock salt system (NaCl-system), C.N. = 6 : 6 changes to CsCl system, C.N. = 8: 8 under pressure and reverse is observed on heating.
- In CaF_2 packing, two F^- ions (at tetrahedral locations) are separated by a distance of $\frac{a}{2}, \frac{\sqrt{2}a}{2}$ and $\frac{\sqrt{3}a}{2}$.
- In Na_2O packing, two Na^+ ions (at tetrahedral locations) are separated by a distance of $\frac{a}{2}, \frac{\sqrt{2}a}{2}$ and $\frac{\sqrt{3}a}{2}$.
- Diamond has ZnS-packing where, all positions of Zn^{2+} and S^{2-} are occupied by C-atoms. Thus 8C-atoms are present in one cubic cell. The packing efficiency is 34%.

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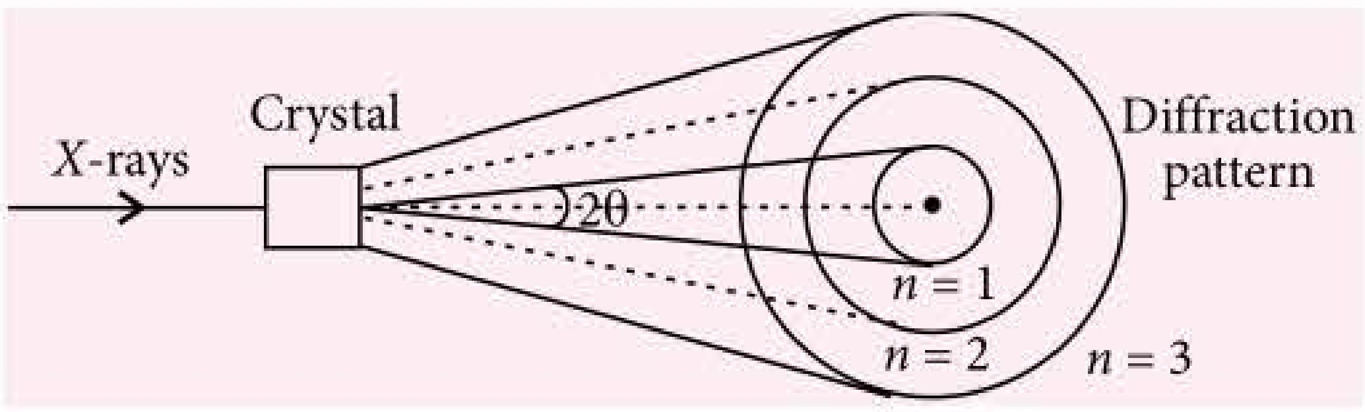
*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

❍ Bragg Equation

For n^{th} order of diffraction of a crystalline substance, using X-rays of wavelength λ, when diffraction angle is 2θ. The interplanar distance d is calculated by using the formula, $n\lambda = 2d\sin\theta$



❍ Imperfections in Crystalline Solids

I. Stoichiometric Defects

(i) In non-ionic solids

(a) Vacancy defect : Here, lattice sites are vacant. This decreases density.

(b) Interstitial defect : Here, extra atoms or molecules occupy interstitial sites. This increases density.

(ii) In ionic solids

(a) Frenkel defect : This defect occurs in ionic crystals having low radius ratio, *i.e.*, smaller size of cation and low C.N. Here, shift of some cations to interstitial sites takes place. Electrical conductivity increases. Density remains the same.
Examples : ZnS, CaF_2, AgBr, etc.

(b) Schottky defect : This defect occurs in ionic crystals having high C.N. like NaCl, CsCl, AgBr, etc. Here, some cations and anions leave the crystals. Electrical conductivity increases but density decreases.
1 cm^3 NaCl, on an average, has 10^6 and 10^{22} ionic pairs *i.e.*, one Schottky defect per 10^{16} ionic pairs.

II. Non-Stoichiometric Defects

(i) Metal excess defect (Anion vacancy) : These are present in those ionic compounds where Schottky defect occurs.

(a) *F*-centre defect : When alkali metal halide is heated in vapours of metal, some halide ions shift to surface and electrons from metal (vapour) occupy their sites. These sites are called *F*-centres and the defect as *F*-centre defect, from German word *Farbenzenter* meaning colour. KCl acquires violet colour due to absorption of yellow part of visible spectrum by electrons.

(b) In some ionic compounds, simple heating causes the removal of some anions from the crystal leaving the extra electrons. These entrapped electrons and the excess metal ions shift to nearby interstitial sites. The substance gains some colour because of absorption of some part of visible region. ZnO gains yellow colour on heating.

(ii) Metal deficiency defect (Cation vacancy)

This defect occurs when a metal cation of higher charge enters and replaces metal ions of lower charge but maintains electrical neutrality. In Fe_3O_4, ions Fe^{2+} and Fe^{3+} are present in the ratio 1 : 2 but the charge of all O^{2-} ions is balanced.

(iii) Impurity defect or Doping defect

NaCl is doped by $SrCl_2$ and creates one cation vacancy per Sr^{2+} ion.

❍ Semiconductors

These are network covalent crystalline substances whose conductivity increases by increase in temperature. *e.g.* Ge, Si, etc. Doping by elements of group 13th creates holes in Si and Ge to give *p*-type semiconductors. '*p*' stands for hole density.

Doping by elements of group 15th creates *n*-type semiconductor where every new atom is giving one extra electron for conductivity.

Compounds of 12th group and 13th group with 16th group and 15th group respectively also work as semiconductors. *e.g.*, CdSe, GaAs, etc.

❍ Conductivity of Solids

27 orders of magnitude of conductivity 10^{-20} to 10^7 S m^{-1} have been proposed.

(a) Metallic conductors have overlapping of occupied orbital bands and empty bands where electrons can easily shift. Their conductivities are between 10^4 to 10^7 S m^{-1}.

(b) In semiconductors there is small energy gap between occupied and empty bands where electrons may jump. Their conductivity ranges between 10^{-6} to 10^4 S m^{-1}.

(c) In insulator, the conductivity range is between 10^{-20} to 10^{-10} S m^{-1}.

❍ Magnetic Properties

(a) Diamagnetic substances like NaCl, Zn, etc, do not have unpaired electrons. These feel weak repulsion in magnetic field and weigh less.

(b) Paramagnetic substances like O_2, Cu^{2+}, etc., have unpaired electrons. These feel attraction by magnetic field and weigh more.

(c) Ferromagnetic substances like CrO_2, Co, Fe, etc., can be magnetised permanently where their magnetic domains (groups of ions or kernels) align in one direction.

(d) Ferrimagnetic substances like Fe_3O_4, $MgFe_2O_4$, etc., show a small magnetic moment due to higher alignment of magnetic domains in one direction and less in opposite direction. These substance become paramagnetic on heating above a temperature called Curie point.

(e) Antiferromagnetic substances like MnO, MnO_2, etc., have zero net magnetic moment due to 50-50 opposite alignments of magnetic domains.

MULTIPLE CHOICE QUESTIONS

1. A solid *PQ* has rock salt structure with radius Q^- as 200 pm. The ideal radius of P^+ is
(a) 73.2 pm (b) 41.4 pm
(c) 82.8 pm (d) 146.4 pm

2. A solid *XY* has rock salt structure. The third nearest neighbours of X^+ are
(a) 6 Y^- at faces (b) 12 X^+ at edges
(c) 8 Y^- at corners
(d) 6 X^+ at centres of cubes sharing the faces.

3. A solid *AB* has radii of cation A^+ and anion B^- as 80 pm and 200 pm. What is the distance between two nearest A^+ cations if '*a*' = 497.73 pm?
(a) 152 pm (b) 252 pm
(c) 352 pm (d) 452 pm

4. A crystalline solid PQ_2 has fluorite type packing. What is the distance between two Q^- ions if '*a*' is edge length?
(a) $a/2$ (b) $a/\sqrt{2}$
(c) $\sqrt{3}a/2$ (d) All of these

5. Diamond has exactly ZnS packing of carbon atoms. How many C-atoms are present in one unit cell?
(a) 4 (b) 6 (c) 8 (d) 12

6. What is the interplanar distance in the packing of a metal if *X*-rays if wavelength 65 pm scatter at an angle of 16° (sin8° = 0.14) for second order diffraction?
(a) 464.28 pm (b) 353.17 pm
(c) 364.82 pm (d) 446.82 pm

7. Which of the following is not correct w.r.t. Frenkel defect?
(a) Radius ratio is low. (b) C.N. is low.
(c) Equal number of cations and anions balancing the charge are missing from their sites.
(d) Electrical conductivity increases.

8. Select the correct statement *w.r.t. F*-centre defect.
(a) The defect appears in silver halides only.
(b) Electrons coming from outside into the crystal are positioned in voids.
(c) The colour appears due to absorption of a part of visible region.
(d) This defect is related with Frenkel defect.

9. The conductivity range of semiconductors is
(a) 10^4 to 10^7 S m^{-1} (b) 10^{-6} to 10^4 S cm^{-1}
(c) 10^{-20} to 10^{-10} S cm^{-1}
(d) 10^{-6} to 10^{-4} S cm^{-1}.

10. In which type of substance all magnetic domains are aligned in one direction to help it for becoming permanent magnet?
(a) Ferrimagnetic substances
(b) Ferromagnetic substances
(c) Antiferromagnetic substances
(d) Diamagnetic substances

11. Solid CO_2 (dry ice or dricold) is an example of
(a) covalent solid (b) metallic solid
(c) ionic solid (d) molecular solid.

12. The number of unit cells in 15 g of ^{60}Co having *ccp* system is
(a) $N_A/2$ (b) $8N_A$ (c) $N_A/8$ (d) $N_A/16$

13. What is the percentage of Fe^{3+} by mass of wustite $Fe_{0.93}O_{1.0}$? (At. wt. of Fe = 56)
(a) 10.53% (b) 11.52% (c) 64.98% (d) 23.04%

14. A crystalline solid *XY* has rock salt structure. The maximum size (radius) of Y^- ion for radius of X^+ being 150 pm, is
(a) 336.2 pm (b) 233.6 pm
(c) 362.3 pm (d) 623.3 pm

15. Density and edge length of a *ccp* crystal respectively are 5 g cm^{-3} and 200 pm. The number of unit cells in its 8 gram is
(a) 2×10^{23} (b) 5×10^{23}
(c) 8×10^{23} (d) 1.6×10^{23}

16. Calculate the ratio of edge lengths of packing of KCl to that of NaCl, if
$r_{Na^+}/r_{Cl^-} = 0.5$ and $r_{Na^+}/r_{K^+} = 0.7$.
(a) 1.18 (b) 1.14 (c) 2.28 (d) 2.36

17. Match the following and select the correct option.

Column-I (Substance)	**Column-II (Magnetic behaviour)**
(p) O_2 molecule	(i) Ferrimagnetic
(q) Zn metal	(ii) Ferromagnetic
(r) CrO_2	(iii) Paramagnetic
(s) Fe_3O_4	(iv) Antiferromagnetic
(t) MnO_2	(v) Diamagnetic

	p	**q**	**r**	**s**	**t**
(a)	(iv)	(v)	(i)	(ii)	(iii)
(b)	(iii)	(i)	(ii)	(v)	(iv)
(c)	(iii)	(v)	(ii)	(i)	(iv)
(d)	(iii)	(v)	(i)	(iv)	(ii)