

All the halides MCl have negative enthalpies of formation, which indicates that thermodynamically (that is in terms of energy) it is feasible to form the compounds MCl from the elements.

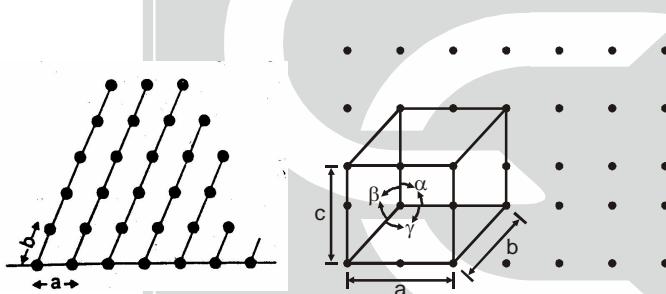
- The most negative enthalpies of formation occur with the fluorides. For any given metal, the values decrease in the sequence fluoride > chloride > bromide > iodide. Thus the fluorides are the most stable, and the iodides the least stable.
- The enthalpies of formation for the chlorides, bromides and iodides become more negative on descending the group. This trend is observed with most salts, but the opposite trend is found in the fluorides. Ionic compounds may also be formed in solution, when a similar cycle of energy changes must be considered, but the hydration energies of the positive and negative ions must be substituted for the lattice energy.

THE SPACE LATTICE AND UNIT CELL

The regular arrangement of an infinite set of points (atoms, ions or molecule) in space is called a **lattice** or **space lattice**. The space lattice may be one dimensional, two dimensional and three dimensional depending upon the number of parameters required to define it

Table Lattices and the Parameters Required for Defining Space Lattice

Type of lattice	Repeat distances	Interfacial angles	No. of parameters required for defining the lattice
1-Dimensional	a	—	Only one repeat distance
2-Dimensional	a, b	γ	Two repeat distances and an interfacial angle
3-Dimensional	a, b, c	α, β, γ	Three repeat distances and three interfacial angles



A space lattice : The regular arrangement of constituent particles (i.e., atoms, ions or molecules) of a crystal in a three dimensional space is called crystal lattice or space lattices.

Unit cell: The smallest three dimensional portion of a complete space lattice when repeated over and again in different directions produces the complete space lattice is called the unit cell.

For describing a unit cell, we must know:

- (a) the distances a , b and c i.e; the lengths of the edges of unit cell.
- (b) the angles α , β and γ between the three imaginary axes,

Classification of Unit Cell : On the basis of the location of the lattice points within a unit cell, we can classify unit cells into the following 2 types :

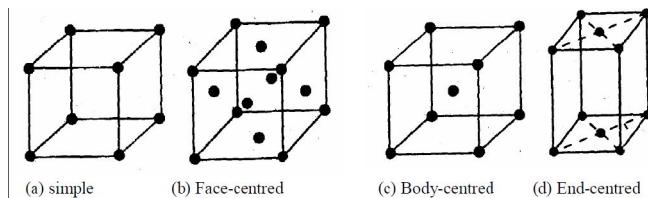
- Primitive unit cell
- Non-primitive unit cell

(1) Simple or primitive: In this type, points (i.e, atoms, ions or molecules) are present only at the corners of the unit cell. E.g. SCC (Simple Cubic Cell).

(2) Non-primitive : In this type of unit cell, the lattice points are present not only at corners but also at some other specific positions.

(i) Face-centred: In this type, points are present at the corners as well as the centre of each of the six faces.

(ii) Body-centred: In this type, points are present at the corners and an additional point is present at the centre of the unit cell.



(iii) End face centred : In this type, points are present at the corners and at the centre of the two endfaces.

(iv) Edge centred unit cell : Lattice points at all corners + at each edge centre.

SOLVED EXAMPLES

1. The crystal lattice structure of sodium, vanadium and molybdenum is BCC (Body centered cubic). Which of the following metallic mixtures are most likely to form a solid solution? [TIFR 2010]
- (a) V and Mo (b) V and Na (c) Mo and Na (d) Na, V, Mo

Soln. Atomic radii : Na = 180, V = 135, Mo = 145.

Metallic mixtures of element having comparable size form solid solution.

Correct option is (a)

2. Which of the parallelogram in the figure below are viable unit cells?

[TIFR 2010]

- (a) i (b) ii (c) iii (d) all of the above

Soln. **Correct option is (d)**

Bravais lattice: Bravais showed that the unit cells can be arranged in a regular three dimensional order in, the seven types of crystal systems in 14 different ways. These arrangements are called *space lattices or Bravais lattices*.

The 14 Bravais lattices may belong to either of the above mentioned four types of unit cells.

Second Classification of Unit Cell : On the basis of axial length and inter-facial angle, the unit cells can be classified into the following 7 types which are known as 7-crystal systems.

Crystal Systems:

At first sight there seems to be infinite number of shapes of crystals. However, careful examination of several thousand crystals of various substances has revealed that only seven possible crystal symmetries are possible. The seven different combinations of symmetry elements are called **crystals systems**. These crystal systems differ in the length of the unit cell edges (a , b and c) and the angle between the unit cell edges.

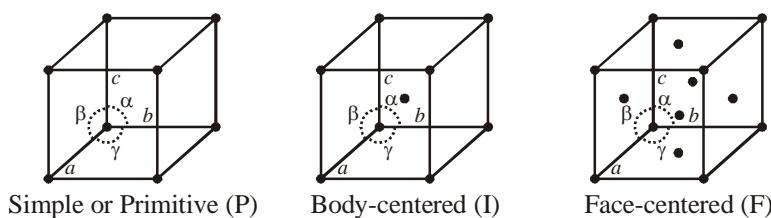


Figure-(a) : Cubic Space Lattices

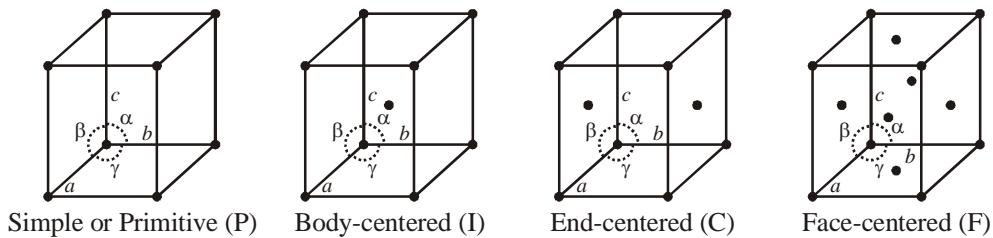


Figure-(b) : Orthorhombic Space Lattices

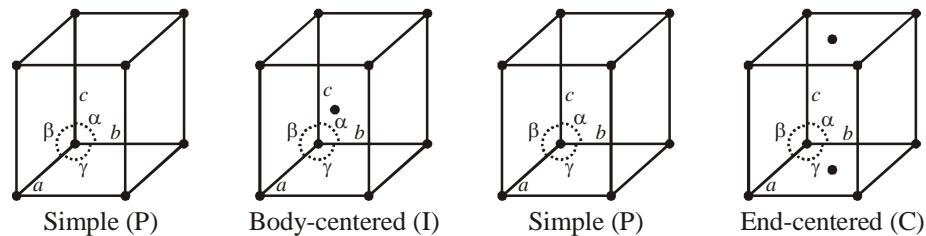


Figure-(c) : Tetragonal and Monoclinic Space Lattices

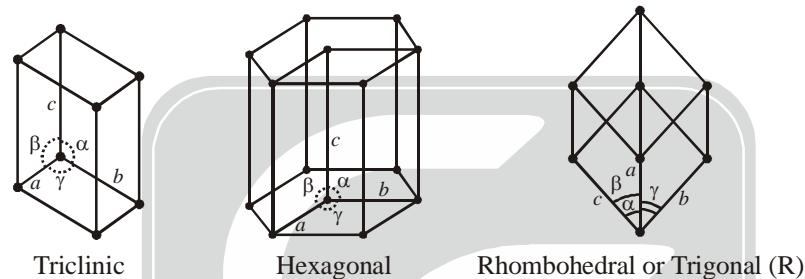


Figure-(d) : Triclinic, Hexagonal and Rhombohedral Space Lattices

Space Groups : The collection of total number of symmetry operations of all the symmetry elements in a crystal is called its *space group*.

Characteristics of Seven types of Crystal Systems

System	No. of Bravais Lattices (14)	Maximum symmetry elements	Axes and Angles	Examples	Space Group
1. Cubic	3	9 Planes 13 axes	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, CaF ₂ , ZnS, Cu ₂ O, Diamond Alums, Pb, Ag, Au, Hg	36
2. Tetragonal	2	5 Planes 5 axes	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	SnO ₂ , ZnO ₂ , TiO ₂ , NiSO ₄ , ZrSiO ₄ , White Sn	68
3. Hexagonal	1	7 Planes 7 axes	$a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	ZnO, PbI ₂ , CdS, HgS, Graphite, Ice Mg Zn Cd	27
4. Trigonal or Rhombohedral	1	7 Planes 7 axes	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	NaNO ₃ , CaSO ₄ , Calcite, ICl, Quartz, As, Sb, Bi	25
5. Orthorhombic (Rhombic)	4	3 Planes 3 axes	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	KNO ₃ , K ₂ SO ₄ , PbCO ₃ , BaSO ₄ , Rhombic Sulphur, MgSO ₄ · 7H ₂ O	59
6. Monoclinic	2	1 Planes 1 axes	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Na ₂ SO ₄ · 10H ₂ O, Na ₂ B ₄ O ₇ · 10H ₂ O, CaSO ₄ · 2H ₂ O, Monoclinic Sulphur	13
7. Triclinic	1	No Planes No axes	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	CuSO ₄ · 5H ₂ O, K ₂ Cr ₂ O ₇ , H ₃ BO ₃	2

SOLVED EXAMPLES

Soln. Correct option is (b)

2. Which of the following is true for an orthorhombic lattice? [BHU 2017]

 - (a) $a = b = c, \alpha = \beta = \gamma = 90^\circ$
 - (b) $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
 - (c) $a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
 - (d) $a = b \neq c, \alpha = \beta = \gamma$

Soln. Correct option is (b)

3. What is the unit cell having dimension $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$? [CUCET 2017]
(a) orthorhombic (b) monoclinic (c) triclinic (d) rhombohedral

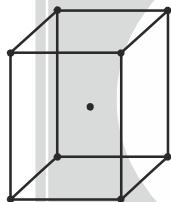
Soln. Correct option is (c)

4. In a tetragonal crystal [DU 2016]

 - (a) $a = b = c, \alpha = \beta = 90^\circ \neq \gamma$
 - (b) $a = b \neq c, \alpha = \beta = 90^\circ$
 - (c) $a \neq b \neq c, \alpha = \beta = 90^\circ$
 - (d) $a = b \neq c, \alpha = \beta = 120^\circ, \gamma = 90^\circ$

Soln. Correct option is (b)

5. Assign the Bravais lattice type for the following unit-cell structure [DU 2017]



- (a) Tetragonal I (b) Cubic I (c) Orthorhombic I (d) Monoclinic

Soln. $\alpha = \beta = \gamma = 90^\circ$

$$a = b \neq c$$

Therefore, tetragonal crystal system.

Correct option is (a)

Soln. Monoclinic crystal system, $\alpha = \gamma = 90^\circ$

$$\beta \neq 90$$

Therefore, either greater or less than 90° .

Correct option is (a, b)

Interplanar Distance:

The perpendicular separation between 2 adjacent planes of a crystal lattice is called inter planar spacing, or the length of the perpendicular from the origin on the unit plane represented by a set of miller indices is also known as *interplanar spacing*.

For an orthorhombic system, $a \neq b \neq c$

$$\text{So, } \frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}; \quad \frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

where h, k, l are Miller indices of the plane and a, b, c are the dimensions of the cell.

For a cubic system, $a = b = c$

$$\text{So, } d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For a tetragonal system, $a = b \neq c$

$$\text{So, } \frac{1}{(d_{hkl})^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

SOLVED EXAMPLES

1. How do the spacings of the three planes 100, 110 and 111 of cubic lattice vary ?

Soln. $d_{\text{hkl}} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} ; d_{100} = \frac{a}{\sqrt{(1^2 + 0^2 + 0^2)}} = a$

$$d_{110} = \frac{a}{\sqrt{(1^2 + 1^2 + 0^2)}} = \frac{a}{\sqrt{2}}; \quad d_{111} = \frac{a}{\sqrt{(1^2 + 1^2 + 1^2)}} = \frac{a}{\sqrt{3}}$$

Thus, $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$.

2. Potassium chloride crystallises with a body centred cubic lattice. Calculate the distance between the 200, 110 and 222 planes. The length of the side of the unit cell is 5.34 Å

Soln. Since we know that for cubic system, $d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$

$$\text{For } 200 \text{ plane; } d_{200} = \frac{5.34}{\sqrt{(2^2 + 0^2 + 0^2)}} = \frac{5.34}{\sqrt{4}} = 2.67 \text{ \AA}$$

$$\text{For } 110 \text{ plane; } d_{110} = \frac{5.34}{\sqrt{(1^2 + 1^2 + 0^2)}} = \frac{5.34}{\sqrt{2}} = 3.77 \text{ \AA}$$

$$\text{For } 110 \text{ plane; } d_{110} = \frac{5.34}{\sqrt{(1^2 + 1^2 + 0^2)}} = \frac{5.34}{\sqrt{2}} = 3.77 \text{ \AA}$$

$$\text{For } 222 \text{ plane, } d_{222} = \frac{5.34}{\sqrt{(2^2 + 2^2 + 2^2)}} = \frac{5.34}{\sqrt{12}} = 1.54 \text{ \AA}$$

3. Consider a crystal with a simple cubic lattice. If on heating, the unit cell volume increases by 5% isotropically (equally in all directions), the percentage increase in the (110) interplanar distance is [HCU 2012]

$$\text{Soln. } a'^3 = a^3 + \frac{5}{100} \times a^3$$

$$a'^3 = \left(\frac{105}{100} \right) a^3$$

$$a' = 1.0164a$$

$$d' = \frac{1.0164a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{1.0164a}{\sqrt{2}} \quad d = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}.$$

$$\% \text{ increase} = \left(\frac{1.0164a}{\sqrt{2}} - \frac{a}{\sqrt{2}} \right) \Bigg/ \frac{a}{\sqrt{2}} \times 100$$

$$= 0.0164 \times 100 = 1.64\%.$$

Correct option is (a)

4. For a simple cubic system the spacing of (100), (110) and (111) planes are in the ratio of

- (a) $1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}$ (b) $\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}:1$ (c) 1:1:1 (d) $\sqrt{3}:\sqrt{2}:1$ [BHU-2012]

Soln.	(100)	(110)	(111)
	$d_1 = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}}$	$d_2 = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}}$	$d_3 = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}}$

$$\text{Ratio} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}.$$

Correct option is (a)

LATTICE POINT

The points representing the atoms, molecules or ions in a unit cell are known as **lattice points**. In the various unit cells, there are three kinds of lattice points.

- (a)** Points located at the corners of a unit cell. Since such point lies at the corner of a unit cell, it is shared between eight such unit cells. Thus only $(1/8)^{\text{th}}$ part of each such point contributes to any one unit cell.

(b) Points located at the centre of a face of a unit cell. Since such point is shared between two such unit cells, only $1/2$ of each such point contributes to any unit cell.

Points located at the centre of the unit cell. This point, being present entirely within a unit cell, wholly belongs to this unit cell.

Contribution of a lattice point at a particular location (per unit cell):

Location	Contribution
1. Body centre	1
2. Face centre	1/2
3. Edge centre	1/4
4. Corner	1/8

The number of atoms belonging to unit cell is also termed as lattice sites and is denoted by Z .

$Z \equiv T \cdot L \cdot P$ (Total Lattice Points) \times Contribution

Thus the total number of lattice points (or number of atoms) per unit cell in the four types of unit cells may be calculated as below.

(a) Simple or primitive: $Z = 8 \times \frac{1}{8} = 1$

(b) Face-centred: $Z = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

(c) Body-centred: $Z = 8 \times \frac{1}{8} + 1 = 2$

(d) End-centred : In addition to 8 points present on the corners, such unit cell also has points only on the end

(two) faces. Since each point of the latter type is shared between two, unit cells, it contributes to $\frac{1}{2}$ to each unit cell. Such points are present only in end face-centred unit cells. Thus the number of atoms per unit cell = $8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2$.

$$\text{(e) Edge-centred : } Z = 8 \times \frac{1}{8} + 12 \times \frac{1}{4} = 4$$

The number of particles immediately adjacent to each particle in the crystal lattice is known as the **coordination number** for that lattice. In other words, coordination number is the nearest neighbours surrounding a particular lattice point. It is characteristic of a given lattice. In a simple cubic lattice, each particle is adjoined by 6 other particles and so the coordination number of a simple cubic lattice is 6. Similarly, the coordination number for body centred and face centred cubic lattices are 8 and 12 respectively.

	Lattice	Z	C.N.
1.	SCC	1	6
2.	BCC	2	8
3.	FCC	4	12
4.	End CC	2	4
5.	HCP	6	12

SOLVED EXAMPLES

1. A compound having BCC lattice structure is formed by elements X and Y. Atoms X' are present at the corners and atom Y at the centre of the cube. Derive the formula of the compound ?

Soln. Since corner atoms are shared between eight corners, therefore, the number of atoms, "X" at eight corners = 1 atom

The atom "Y" present at the centre of cube is not being shared i.e. one atom; unit cube Hence the formula of the compound is **XY**.

2. A compound, formed by elements X and Y, crystallises in the cubic structure, where Y atoms are at the corner of a cube and X atoms are at alternate faces. What is the formula of the compound?

Soln. Number of atoms Y at eight corners of a cubic unit cell = $\left(8 \times \frac{1}{8}\right) = 1$

Number of atoms X present on alternate face of unit cell = $\left(2 \times \frac{1}{2}\right) = 1$

Formula of compound = **XY**

3. In a crystalline solid anions A, are arranged in ccp manner. 50% of the octahedral voids are occupied by B and 50% of the tetrahedral voids are occupied by atoms C. What is the formula of the solid ?

Soln. We know that the number of octahedral voids are equal in number to the atoms forming ccp, while the number of tetrahedral voids are double in number.

∴ Ratio of the number of octahedral voids and tetrahedral voids is 1 : 2

Now 50% of the octahedral voids are occupied, therefore the ratio of A and B is

$$2A : B$$

The 50% of the tetrahedral voids are occupied by C so, the ratio of A and C is 1 : 1 i.e. A : C or 2A : 2C, Hence the ratio of A, B and C is

$$2A : B : 2C$$

So, the formula of the compound is **A₂BC₂**.

4. Calculate the number of atoms present in the unit cell of a monoatomic substance (element) of (a) simple cubic lattice-(b) body-centred cubic (c) face-centred cubic.

Soln. (a) Number of atoms in a unit cell of Simple Cubic Lattice. A simple cubic lattice has only eight atoms on the corners. As contribution by each therefore number of atoms present in the unit cell $\times 8 = 1$

(b) Number of atoms in a unit cell of Body Centred Cubic (BCC). This lattice has 8 atoms on the corners and one atom within the body.

Therefore, Contribution by 8 atoms present on the corners $\times 8 = 1$

Contribution by the atom present within the body = 1

Therefore, Number of atoms present in the unit cell = $1 + 1 = 2$.

(c) Number of atoms in a unit cell of the Face Centred Cubic (FCC). This lattice has 8 atoms on the corners and 6 atoms on the faces (one on each face).

Contribution by atoms on the corners $\times 8 = 1$

Contribution by atoms on the faces $\times 6 = 3$

Therefore, Number of atoms present in the unit cell = $1 + 3 = 4$.

5. Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.

Soln. There are four body diagonals. Thus there are 8 atoms within the body of the unit cell which are not shared by any other unit cell. Contribution by atoms unit cell at the corners $= 8 \times \frac{1}{8}$. Hence total atom/unit cell = $8 + 1 = 9$.

6. If three elements P, Q and R crystallize in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centre and R atoms at the centre of the faces of the cube, then write the formula of the compound.

Soln. Atoms P per unit cell $= 8 \times \frac{1}{8} = 1$.

Atoms Q per unit cell = 1

Atoms R per unit cell $= 6 \times \frac{1}{2} = 3$

Hence the formula is PQR_3 .

7. In a face centred arrangement of A and B atoms. Where A atoms are at the corners of the unit cell and B atoms are at the face centres. For each unit cell, one A atom is missing from a corner position and one B atoms is missing from one face position. The simplest formula of the resulting compound will be

(a) $A_{14}B_{40}$ (b) A_7B_{20} (c) $A_{1-x}B_{3-x}$ (d) AB_2 [TIFR 2016]

Soln. One A atom is missing from corner position $= 7 \times \frac{1}{8} = \frac{7}{8}$.

One B atom is missing from one face position $= 5 \times \frac{1}{2} = \frac{5}{2}$.

$A_{7/8} B_{5/2}$

Multiply by 8 : $A_7 B_{20}$.

Correct option is (b)

8. A compound alloy of metals P and Q has a unit cell containing P atoms at the corners, while atom Q are present at the face centres. The formula of the compound should be

[BHU-2011]

(a) PQ (b) PQ_2 (c) PQ_3 (d) P_3Q

Soln. $P = \text{Corners} = 8 \times \frac{1}{8} = 1$ $Q = \text{Face centres} = 6 \times \frac{1}{2} = 3$

Formula = PQ_3 .

Correct option is (c)

Soln. For FCC lattice, $Z = 4$.

Correct option is (d)

Soln. For BCC lattice, $Z = 2$.

Correct option is (b)

NUMBER AND LOCATION OF VOIDS IN A CRYSTAL

In a close-packed structure (*ccp* or *hcp*), if there are N spheres (atoms or ions) in the packing, then

Number of octahedral voids = N'

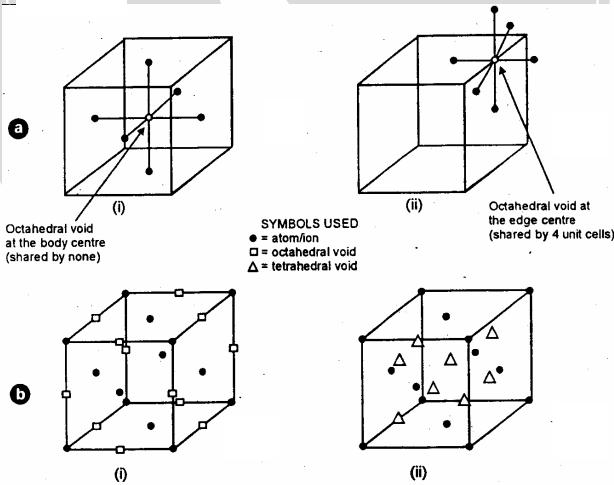
Number of tetrahedral voids = 2 N

For example, in the cubic close packing (*ccp*) i.e. face-centred cubic (*fcc*) unit cell there are 4 atoms or ions, therefore, there are 4 octahedral voids.

(a) Octahedral voids: One octahedral void is present at the body centre of the cube and 12 octahedral voids are present on the centres of the 12 edges of the cube. But each void on the edge centre is shared by 4 unit

cells. Hence its contribution in the unit cell = $\frac{1}{4}$. Hence the effective number of octahedral voids in the CCP

(b) Tetrahedral voids: The 8 tetrahedral voids present in the ccp arise from the fact that there are 8 spheres at the corners of the unit cell and each sphere touches three spheres present on the face-centres of the three adjoining faces, each giving rise to one tetrahedral void.



Note:

(i) Number of octahedral voids = Number of atoms present in the close packed arrangement and
(ii) Number of tetrahedral voids = $2 \times$ Number of octahedral voids = $2 \times$ Number of atoms.

SOLVED EXAMPLES

Soln. ccp arrangement ($Z = 4$)

Tetrahedral voids = 8

Octahedral voids = 4

$$\text{Ratio} = \frac{8}{4} = 2:1.$$

Correct option is (b)

2. In a crystalline solid, anions B are arranged in a 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?

Soln. Suppose the number of anions B = 100 Then

Number of octahedral voids = 100

Number of tetrahedral voids = 200

As octahedral and tetrahedral voids are equally occupied by cations A and all the octahedral voids are occupied (*given*), therefore 100 cations A are present in octahedral voids and 100 cation A are present in tetrahedral voids. In other words, corresponding to 100 anions B, there are 200 cations A *i.e.* cation A and anions B are in the ratio 2 : 1. Hence the formula of the solid will be A_2B .

3. In corundum, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-third of the octahedral voids. What is the formula of corundum.

Soln. Suppose oxide ions = 90. Then octahedral voids = 90. Hence Al³⁺ ions $\frac{2}{3} \times 90 = 60$.

Therefore, ratio $\text{Al}^{3+} : \text{O}^{2-} = 60 : 90 = 2 : 3$ i.e. formula is Al_2O_3 .

4. In a solid, oxide ions are arranged in ccp. One-sixth of the tetrahedral voids are occupied by the cations A while one-third of the octahedral voids are occupied by the cation B. What is the formula of the compound?

Soln. Suppose O^{2-} ions = 90. Then octahedral voids = 90 and tetrahedral voids = 180. Cations A = $\frac{1}{6} \times 180 = 30$

and cation B = $\frac{1}{3} \times 90 = 30$.

Therefore, ratio A : B : O²⁻ = 30 : 30 : 90 = 1 : 1 : 3 i.e. formula is ABO₃.

5. A solid is made up of two elements P and Q. Atoms Q are in ccp arrangement while atoms P occupy all the tetrahedral sites. What is the formula of the compound?

Sol. Suppose number of atoms $Q = n$

Then number of tetrahedral sites = $2n$

∴ Number of atoms $P = 2n$

∴ Ratio $P : Q = 2n : n = 2 : 1$ i.e. formula is P_2Q .

STRUCTURES OF IONIC COMPOUNDS

It has already been discussed that ionic compounds consist of positive and negative ions arranged in a manner so as to acquire minimum potential energy (maximum stability). To achieve the maximum stability, ions in a crystal should be arranged in such a way that forces of attraction are maximum and forces of repulsion are minimum. Hence, for maximum stability the oppositely charged ions should be as close as possible to one another and similarly charged ions as far away as possible from one another.



Among the two ions constituting the binary compounds, the larger ions (usually anions) form a close-packed arrangement (*hcp* or *ccp*) and the smaller ions (usually cations) occupy the interstitial voids. Thus in every ionic compound, positive ions are surrounded by negative ions and vice versa. Normally each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number**. The coordination number of positive and negative ions of a compound are same when the two types of ions are equal in number (e.g., NaCl, ZnS, etc.). On the other hand, when an ionic compound contains different number of positive and negative ions (as in CaCl₂, Na₂S etc.), the coordination numbers of positive and negative ions are different. For example, in CaCl₂ since Cl⁻ ions are twice the number of Ca²⁺ ions, the coordination number of calcium ion is twice the coordination number of chloride ion.

Simple ionic compounds are of two types, i.e., AB and AB₂ type. From the knowledge of close packed structures and the voids developed therein, we can have an idea about the structure of simple ionic compounds.

- (a) If the anions (B⁻) constitute the crystal lattice and all octahedral voids are occupied by cations (A⁺), then the formula of the ionic solid is A⁺B⁻.
- (b) Similarly, if half of the tetrahedral voids are occupied by cations, then the formula of the solid crystal becomes A⁺B⁻.
- (c) When the anions (B²⁻) are constituting space lattice and all the tetrahedral voids are occupied by the cations (A⁺), then the formula of the solid crystal will be A₂B.
- (d) When the anions (B²⁻) are present at the lattice points and all the octahedral voids are occupied by the cations (A⁺), then the formula of crystalline solid will become A₂B.

AB type ionic solids – NaCl, CsCl, ZnS

AB₂ type ionic solids – CaF₂, SrF₂

Ionic Compounds of AB Type:

1. Structure of sodium chloride (NaCl) or Rock Salt crystal : It has *fcc* arrangement also called cubic close packed (*ccp*).

Salient features of NaCl crystal structure are summarised below:

- (i) The anions (Cl⁻) are present at the lattice points of a face centred cubic close structure.
- (ii) Na⁺ ions are occupying all the octahedral voids, so each Na⁺ ion is surrounded by six Cl⁻ ions.
- (iii) Since there will be six octahedral voids (holes) around each chloride ion, so each chloride ion is surrounded by six sodium ions.
- (iv) The co-ordination number of Cl⁻ as well as of Na⁺ ion is **six**. Therefore, it is termed as 6:6 co-ordination crystal.
- (v) On applying pressure, NaCl structure (6 : 6 coordination changes to CsCl structure (8 : 8 coordination).
- (vi) The ionic radius of Na⁺ ion ($r = 95$ pm) and the radius of Cl⁻ ion ($R = 181$ pm) gives radius ratio $r/R = 0.525$. This value of radius ratio suggest an octahedral arrangement of ions.
- (vii) The total number of Na⁺ cation and Cl⁻ anion present in one unit cell are calculated as below.

Number of sodium ions : In NaCl, the Na⁺ ions have been shown by dark spheres),

$$= (12 \text{ ions at the edge centre} \times \frac{1}{4}) + (1 \text{ ion at body centre} \times 1) = 3 + 1 = 4$$

Number of chloride ions :

$$= (8 \text{ ions at the corner} \times \frac{1}{8}) + (6 \text{ ions at the face centres} \times \frac{1}{2}) = 1 + 3 = 4$$

Therefore, the unit cell of NaCl has contribution of 4 Na⁺ ions and 4 Cl⁻ ions i.e. 4 NaCl formula unit per unit cell. The sodium chloride structure is also called as **rock-salt structure**.

(viii) The edge length of the unit cell of NaCl type of crystal 2 ($r + R$).

$$\text{Edge length (a) of unit cell of the NaCl type} = 2 \left[\frac{\text{Ionic radius of the cation}}{2} + \frac{\text{Ionic radius of the anion}}{2} \right]$$

Or

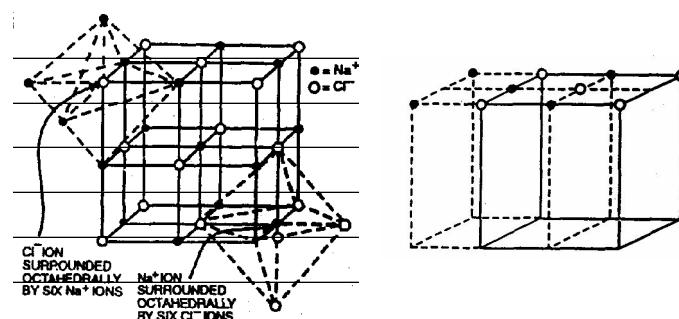
$$a = 2(r_{Na^+} + r_{Cl^-})$$

Thus the distance between Na^+ and Cl^- ions $= \frac{1}{2} \times a$

Examples having rock-salt structure i.e. NaCl type of structure are

Alkali halides : NaCl, LiCl, KBr, RbI, AgCl, AgBr, AgI, NH_4Cl , NH_4Br , NH_4I

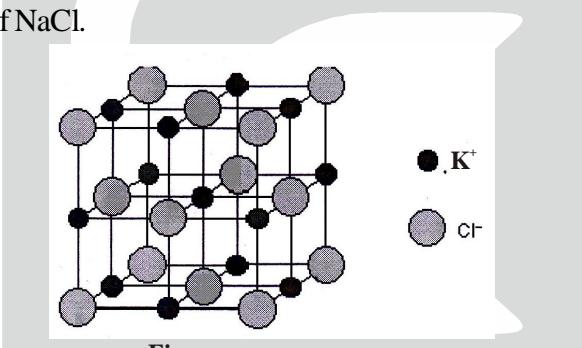
Oxides of alkaline earth metals : MgO, CaO, TiO, FeO, NiO



2.

Potassium Chloride (KCl):

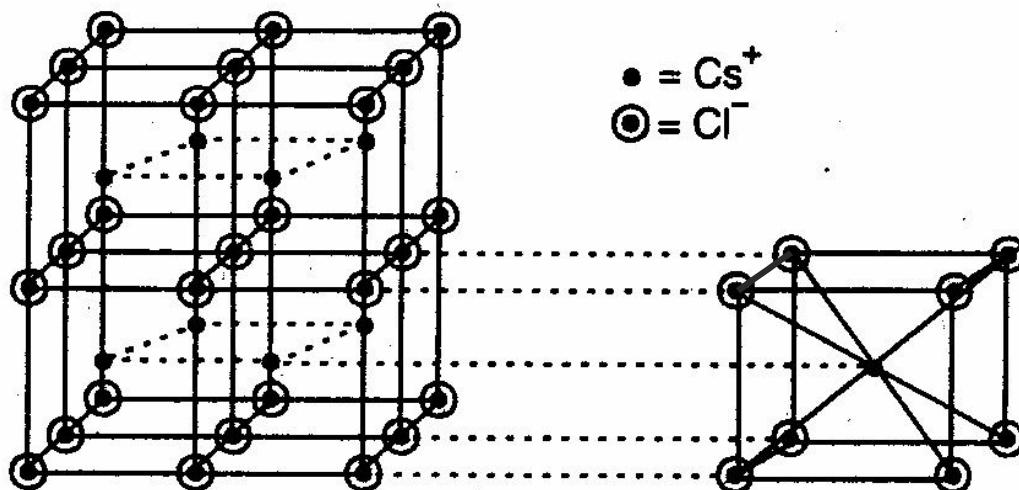
- * KCl is a metal halide salt.
- * In its pure state, it is odorless and has a white or colourless crystal appearance with a crystal structure that cleaves easily in three direction.
- * It is a face centred cubic crystal.
- * Structure similar to that of NaCl.



Figure

3.

Cesium chloride (CsCl) type structure : In this type of ionic crystal, the size of Cs^+ ion is quite big as compared to Cl^- ion. Therefore, it acquires the body centred cubic lattice structure



- (i) The Cl^- ions are present at the corners of the cubic unit cell and the Cs^+ ions are at the body centre of the unit cell.
- (ii) Each Cs^+ ion in this mode of packing is touching 8 chloride ions and each Cl^- ion is touching eight Cs^+ ions. Therefore, this structure will have 8 : 8 co-ordination.
- (iii) At high temperature, CsCl structure (8 : 8 co-ordination) changes to NaCl structure (6 : 6 coordination).
- (iv) The ionic radii of Cs^+ and Cl^- ions are 169 pm and 181 pm respectively. This gives radius ratio as 0.93.

$$\frac{r}{R} = \frac{169 \text{ pm}}{181 \text{ pm}} = 0.93$$

(v) This value of radius ratio corresponds to BCC type of unit cell.

(vi) Each unit cell will have the contribution of one Cs^+ and one Cl^- ion as shown below Number of Cs^+ ion = 1 (ion at the body centre) $\times 1 = 1$

Number of Cl^- ion = 8 (ions at the corner) $\times 1/8 = 1$

Therefore, the unit cell has contribution of one Cs^+ ion and one Cl^- ion per unit cell

(vii) Relation between radius of cation, anion and edge length of the cube

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

The undermentioned ionic crystals are the examples of CsCl type of crystal lattice.

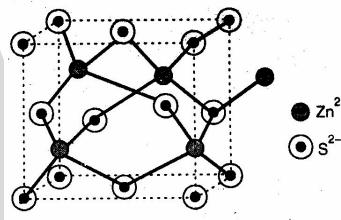
CsCl , CsBr , CsI , TlCl , TlBr , CaS .

4.

Zinc sulphide structure :

Zinc sulphide exists in two forms: (i) ZnS Blende (ii) ZnS Wurtzite

(i) **zinc blende or Sphalerite:** Structure of zinc blende is cubic close packing (ccp).



- (i) The sulphide ions (S^{2-}) occupy face centred cubic lattice points. and the zinc ions (Zn^{2+}) occupy half of the total number of tetrahedral voids
- (ii) Each sulphide ion is surrounded by 4 Zn^{2+} ions and each Zn^{2+} ion is surrounded by 4 S^{2-} ions. Therefore, ZnS has 4 : 4 coordination.
- (iii) The ionic radii of zinc ion (Zn^{2+}) and sulphide ions (S^{2-}) are 74 pm and 184 pm respectively. Therefore, the radius ratio $r/R = 0.40$ It suggests the tetrahedral arrangement of ions in the-crystal lattice.
- (iv) The contribution of Zn^{2+} and S^{2-} ions per unit cell is calculated as discussed below.

$$\text{Number of sulphide ions} = (8 \text{ ions at the corners} \times \frac{1}{8}) + (6 \text{ ions present at the faces} \times \frac{1}{2}) = 1 + 3 = 4$$

$$\text{Number of zinc ions} = 4 \text{ (ions within the body of unit cell)} \times 1 = 4$$

Thus the number of ZnS units per unit cell is 4.

The following ionic solids are observed to form ZnS type of crystal structure.

ZnS , CuCl , CuBr , CuI , US , AgI , BeS

(ii) **Wurtzite Structure.** The unit cell for wurtzite structure is shown in following figure in which each Zn^{2+} ion is represented by a hollow circle and each S^{2-} ion is represented by a solid circle. The wurtzite structure may be described as follows:

1. The sulphide ions are arranged in a **hexagonal close packed** (hcp) arrangement.
2. The zinc ions occupy half of the tetrahedral sites.

3. There are two tetrahedral sites for each S^{2-} ion in the lattice. Since only half of them are occupied by Zn^{2+} ions, the stoichiometry of the compound is 1 : 1.
4. Each S^{2-} ion is surrounded by four Zn^{2+} ions which are disposed towards the corners of a regular tetrahedron. Similarly, each Zn^{2+} ion is surrounded by four S^{2-} ions. The arrangement around one Zn^{2+} ion and one S^{2-} ion is shown in following Figure. Therefore, the coordination numbers of Zn^{2+} and S^{2-} ions in wurtzite structure are 4 : 4.
5. The radius ratio r_+/r_- in this structure is 0.40 which also suggests that the coordination number is 4 and that the crystal has a tetrahedral structure. Thus, the radius ratio rule supports the above structure. The compounds such as AgI , ZnO , NH_4F and AlN have wurtzite structure.

It will be noted that the basic difference between **zinc blende** and **wurtzite** structure is that whereas in the former case the sulphide ions are arranged in ccp type of packing, in the latter case they are arranged in hcp type of packing.

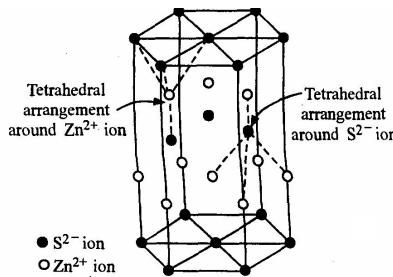


Fig. Unit cell representation of wurtzite structure. S^{2-} ions (solid circles) adopt hcp arrangement and Zn^{2+} ions (hollow circles) occupy half of the tetrahedral sites.

5. Diamond Cubic Structures:

The diamond lattice can be considered to be formed by interpenetrating two fcc lattices along the body diagonal by $(1/4)^{th}$ cube edge. One sublattice has its origin at the point $(0, 0, 0)$ and the other at a point quarter of the way along the body diagonal (at the point $a/4, a/4, a/4$). The basic diamond lattice and the atomic positions in the cubic cell of diamond projected on a cube face are shown in figure below. The fractions denote height about the base in units of cube edge. The point at 0 and $1/2$ are on the fcc lattice, those at $1/4$ and $3/4$ are on a similar lattice displaced along the body diagonal by $1/4$ of the cube edge.

The packing factor of this structure is thus calculated as follows:

$$(XY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8} \quad (XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8} + \frac{a^2}{16} = \frac{3a^2}{16}$$

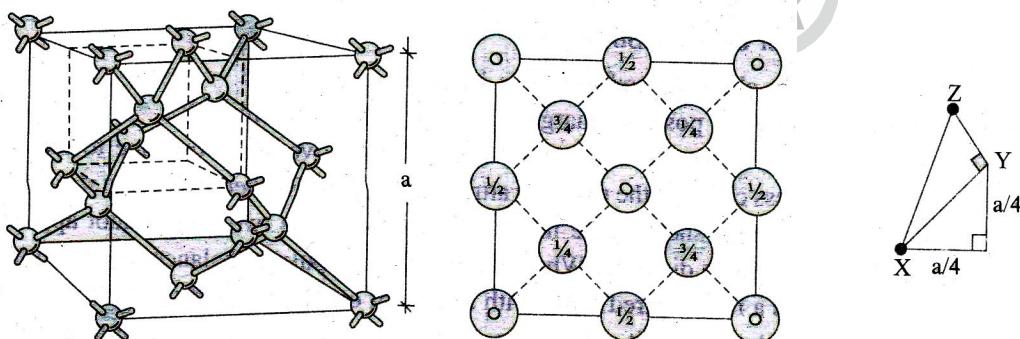


Figure: Diamond Structure

But,

$$XZ = 2r$$

$$\text{Therefore, } (2r)^2 = \frac{3a^2}{16}$$

$$\begin{aligned} Z &= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1 \\ &= 1 + 3 + 4 = 8 \end{aligned}$$

(or) the nearest neighbour distance, $2r = \frac{\sqrt{3}a}{4}$

$$\text{Lattice constant, } a = \frac{8r}{\sqrt{3}}$$

$$\text{Packing factor} = v/V = \frac{\frac{8}{3}\pi r^3}{a^3} = \frac{32}{3} \frac{\pi r^3 3\sqrt{3}}{(8r)^3} = \frac{\pi\sqrt{3}}{16} = 0.34 \text{ or } 34\%$$

β -Cristoballite Structure : SiO_4

$\text{Si}^{4+} = \text{In DCC lattice}$

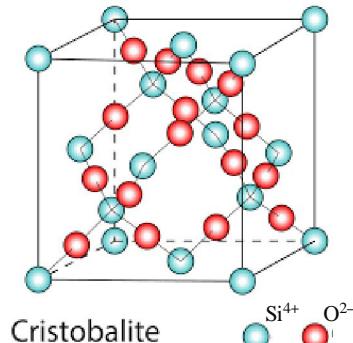
O^{2-} = Each oxide ion in between any Si-Si bond.

$$Z: Si^{4+} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1 = 8.$$

$$\Omega^{2-} = 16 \times 1 = 16$$

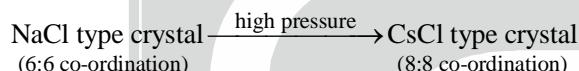
F=8

C.N.: Si⁴⁺ = 4 and O²⁻ = 2.



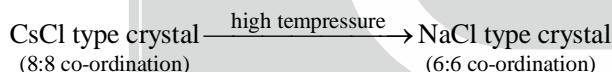
Effect of Pressure on Crystal Structure:

Increase of pressure increases the co-ordination number during crystallization e.g. by applying high pressure, the NaCl crystal structure having 6 : 6 co-ordination number changes to CsCl crystal structure having co-ordination number 8 : 8.



Effect of Temperature on Crystal Structure:

Increase of temperature, however, decreases the co-ordination number e.g., upon heating to 760 K, the CsCl crystal structure having co-ordination of 8 : 8 changes to NaCl crystal structures having co-ordination 6 : 6



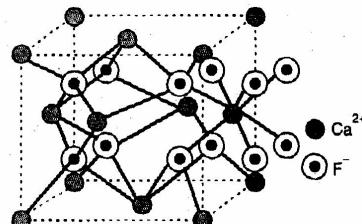
SOLVED EXAMPLES

Soln. CsCl type crystal $\xrightarrow{\text{high temperature}}$ NaCl type crystal
 (8:8 co-ordination) (6:6 co-ordination)

Correct option is (c)

Ionic Compounds of AB, Type:

Fluorite structure (crystal structure of CaF_2) : The calcium fluoride crystal is composed of calcium ions (Ca^{2+}) and fluoride ions (F^-).



It has **Cubic Close packed (ccp)** arrangement.

- (i) The Ca^{2+} ions are present as the face centred cubic lattice and the fluoride ions (F^-) occupy all the tetrahedral voids.
- (ii) The radius ratio, calculated from the ionic radii of Ca^{2+} ion (99 pm) and F^- ion (136 pm), is 0.73. This shows that the coordination number of calcium ion is eight, i.e. each calcium cation is surrounded by eight fluoride anions in a body centred cubic arrangement. Each fluoride ion is in contact with four calcium ions. Thus CaF_2 has 8 : 4 co-ordination.
- (iii) Each unit cell of CaF_2 crystal is observed to have 4 Ca^{2+} ions and 8 F^- ions.

Number of Ca^{2+} ions:

$$= (8 \text{ ions at the corners } \times \frac{1}{8}) + (6 \text{ ions at the face centre } \times \frac{1}{2}) = 1 + 3 = 4$$

Number of F^- ions = (8 ions within the body $\times 1$) = 8

Therefore, each unit cell has 4 CaF_2 molecules.

Solids forming fluorite type of structure are CaF_2 , SrF_2 , BaF_2 , BaCl_2 , CdF_2 , HgF_2 , PbF_2 , CuF_2 , SrCl_2 etc.

Ionic Compounds of A_2B Type

Antifluorite structure (crystal structure of Li_2O):

Antifluorite structure is having arrangement of cations and anions opposite to fluorite structure.

- (i) In the crystal structure of Li_2O , the O^{2-} ions constitute a cubic close packed lattice (FCC structure) and the Li^+ ions occupy all the tetrahedral voids
- (ii) Each oxide ion, O^{2-} ion, is in contact with 8 Li^+ ions and each Li^+ ion is having contact with 4 oxide ions. Therefore, Li_2O has 4 : 8 co-ordination.

Examples forming antifluorite structure include Na_2O , K_2O , K_2S and Na_2S .

Structure of ferrite and related compounds:

Ferrite (Fe_3O_4) and related compounds of general formula $\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ are ferrimagnetic in nature. The M^{2+} can be Fe^{2+} , Mn^{2+} , Zn^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} or some combination of these ions. Ferrite (Fe_3O_4) is the double oxide having composition $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. This shows, that the number of Fe^{3+} ions is twice the number of Fe^{2+} ions. Their respective arrangement in the crystal lattice may be illustrated as below.

- (i) In, Fe_3O_4 , the oxide ions constitute the cubic close packed (FCC) arrangement.
- (ii) All the Fe^{2+} ions and half of the Fe^{3+} ions occupy octahedral voids, while the remaining half of the Fe^{3+} ions occupy tetrahedral voids.

Structure of Titanium Dioxide, TiO_2 (Rutile Structure) : The unit cell of Rutile structure is shown in following figure in which titanium ions are represented by hollow circles and oxide ions are represented by solid circles.

The structure may be described as follows :

Ti^{4+} = In distorted body centered cubic.

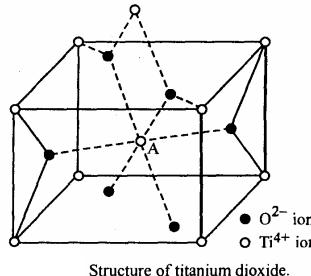
O^{2-} = 2 oxide ions are present at the centres of the triangle generated by any 2 opposite edges at the body centre Ti .

4 oxide ions are present in a plane which is perpendicular to the plane initial 2 oxide ions. These 4 oxide ions are present on 2 opposite faces (two on each face). Each of these 4 oxide ions is present at a $1/4^{\text{th}}$ distance of the face diagonal from a corner along the face diagonal. These 4 oxide ions generate a square planar structure, and all the 6 oxide ions generate an octahedral structure at the body centre Ti .

$$Z = \begin{cases} \text{Ti}^{4+} = 8 \times \frac{1}{8} + 1 \times 1 = 2 \\ \text{O}^{2-} = 2 \times 1 + 4 \times \frac{1}{2} = 4 \end{cases}$$

$$F = 2$$

$$\text{C.N.} = \text{Ti}^{4+} = 6 \text{ and } \text{O}^{2-} = 3.$$

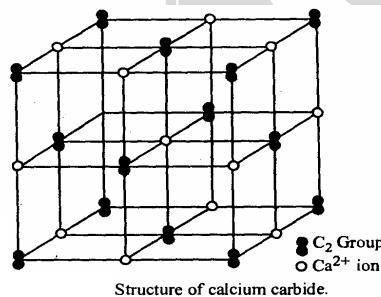


Structure of Calcium Carbide (CaC₂) : The unit cell of calcium carbide is shown in following figure. The structure of calcium carbide is similar to that of sodium chloride. Here sodium ions are replaced by calcium ions and chloride ions by C₂ groups. The carbon atoms are associated in pairs, as shown in following figure, forming the C₂ groups. The C₂ groups are aligned in parallel as shown. The cubic symmetry observed in sodium chloride is, however, distorted considerably in the case of calcium carbide for obvious reasons.

The structure of FeS₂ is similar to that of CaC₂. However, the S₂ units are not aligned in parallel as are the C₂ units in the case of CaC₂.

Ca²⁺ = At body centre + at each edge centre \Rightarrow Oh void.

C₂²⁻ = At corners + at each face centres \Rightarrow FCC



$$Z = \begin{cases} \text{Ca}^{2+} = 1 \times 1 + 12 \times \frac{1}{4} = 4 \\ \text{C}_2^{2-} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \end{cases}$$

$$F = 4$$

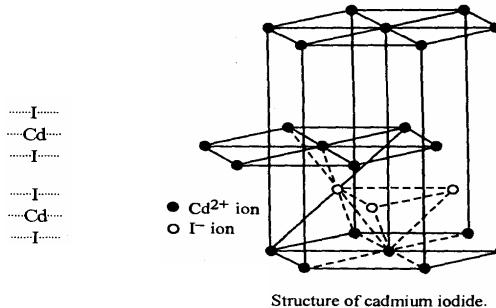
$$\text{C.N.} = \text{Ca}^{2+} = 6 \text{ and } \text{C}_2^{2-} = 6$$

Structure of Cadmium Iodide (CdI₂) : The unit cell of cadmium iodide is shown in following figure in which Cd²⁺ ions are represented by hollow circles and iodide ions are represented by solid circles.

The salient features of this structure are described below:

1. The iodide ions are arranged in a hexagonal close packed (*hcp*) arrangement while cadmium ions lie in octahedral sites between every two layers of iodide ions.
2. Each Cd²⁺ ion is surrounded octahedrally by six I⁻ ions, as shown in following figure. On the other hand, each I⁻ ion has three Cd²⁺ ions as nearest neighbours. The three Cd²⁺ ions surround the I⁻ ion in an arrangement in which Cd²⁺ ions form the base of a trigonal pyramid whose apex is the I⁻ ion.
3. The arrangement of the three layers corresponds to the composition CdI₂.

This arrangement is continued as shown and the structure is referred to as a layer lattice. The forces operating in between the I — Cd — I layers to hold them together are weak. As a result, this compound is flaky and can be easily cleaved.



The Ilmenite Structure:

Ilmenite is the mineral FeTiO_3 . Its structure is closely related to the corundum structure except that the cations are of two kinds. In ilmenite the cations are Fe^{2+} and Ti^{4+} , but many substances with the ilmenite structure have cations with charges of (+1, +5) or (+3, +3).

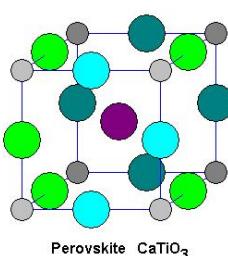
The Perovskite Structure:

Perovskite is the mineral CaTiO_3 . Its structure, shown in following figure, is based on a CCP array of oxide ions together with large cations, similar in size to the oxide ion. The smaller cations lie in octahedral holes formed entirely by oxide ions. Again, the individual cation charges are not important so long as their sum is +6. The structure is adopted by many fluorides with cations of different sizes, such as KZnF_3 .

Ca^{2+} = At body centre

Ti^{4+} = At all corners

O^{2-} = At each edge centre



$$Z = \begin{cases} \text{Ca}^{2+} = 1 \\ \text{Ti}^{4+} = 1 \\ \text{O}^{2-} = 3 \end{cases}$$

$$F = 1$$

$$\text{C.N.} = \begin{cases} \text{Ca}^{2+} = 12 \\ \text{Ti}^{4+} = 6 \\ \text{O}^{2-} = 2 \end{cases}$$

From

O^{2-}

O^{2-}

Ti^{4+}

Characteristic properties of various types of ionic solids

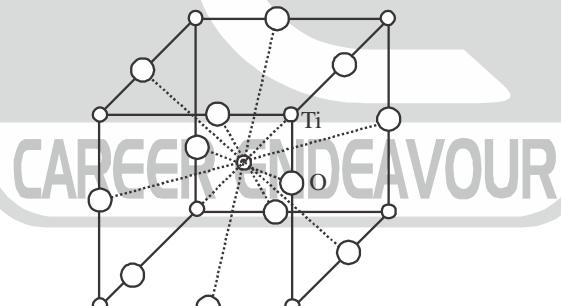
Structure	Ions forming the close packed structure	Ions present in voids	Co-ordination number	Number of formula units per unit cell	Examples
ZnS type	S^{2-} ions form CCP structure	Zn^{2+} ions in alternate tetrahedral void	$\text{Zn}^{2+} = 4$ $\text{S}^{2-} = 4$	4	ZnS , AgI , CuCl , CdS , HgS
NaCl type	Cl^- ions form CCP structure	Na^+ ions in all octahedral holes	$\text{Na}^+ = 6$ $\text{Cl}^- = 6$	4	NaCl , LiCl , KBr , AgBr , MgO , CsI , CaO , FeO
CsCl type	BCC structure Cl^- ions are at cube	Cs^+ ion at the centre of the cube	$\text{Cs}^+ = 8$ $\text{Cl}^- = 8$	1	CsCl , CsCN , CaS , CsI
CaF_2 type (Fluorite)	Ca^{2+} ions form CCP structure	F^- ions in all tetrahedral holes	$\text{Ca}^{2+} = 8$ $\text{F}^- = 4$	4	CaF_2 , Na_2O , BaCl_2 , PbO_2
Li_2O type (Antifluorite structure)	O^{2-} ions form CCP structure	Li^+ ions are in all tetrahedral holes	$\text{Li}^+ = 4$ $\text{O}^{2-} = 8$	4	K_2O , $\text{Li}_2\text{ONa}_2\text{O}$, K_2S

S. No.	Structure	Cation	Anion	Number of ions			F	C.N.	
				Cation	Anion	Total		Cation	Anion
1.	NaCl, KCl	Oh void	FCC	4	4	8	4	6	6
2.	CaC ₂	Oh void	FCC	4	4	8	4	6	6
3.	CaF ₂ , BaF ₂ , SrF ₂	FCC	All Td void	4	8	12	4	8	4
4.	Na ₂ O	All Td void	FCC	8	4	12	4	4	8
5.	CaTiO ₃ , CaTiF ₃	Ca ²⁺ : Body centre Ti ⁴⁺ : Corner	Edge centre	1	3	5	1	12	2
6.	ZnS(B)	Half Td void	FCC	4	4	8	4	4	4
7.	ZnS(W)	Half Td void	HCP old new	6 2	6 2	12 4	6 2	4 4	4
8.	SiO ₂	DCC Si ⁴⁺ — O ²⁻ — Si ⁴⁺		8	16	24	8	4	2
9.	TiO ₂	Distorted BCC		2	4	6	2	6	3
10.	CsCl	Body centre	Corner	1	1	2	1	8	8

SOLVED EXAMPLES

1. What is the empirical formula for the following unit cell:

[TIFR 2010]



(a) CaTi₁₂O₈

(b) CaTi₈O₁₂

(c) CaTiO₃

(d) CaTi₂O₃

Soln. Ca²⁺ = Body centre = 1

Ti⁴⁺ = Corners = $\frac{1}{8} \times 8 = 1$

O²⁻ = Edge centre = $12 \times \frac{1}{4} = 3$



Correct option is (c)

2. NaCl, KCl, NaBr and KBr crystallize in FCC lattices. Their anion and cation touch along the edge of the unit cell. The dimensions of their unit cells are 562.8 pm, 627.7 pm, 596.2 pm and 658.6 pm, respectively. From these data, what can you say about the size of the ionic radii (within an error of about 5%) ?
- Ionic radii of the cations depend on the nature of the anions
 - Ionic radii of the anions depend on the nature of the cations
 - Both (a) and (b)
 - Ionic radii are independent of the ions

Soln. **Correct option is (d)**

3. KCl crystallizes in a cubic unit cell with Cl^- ions at each vertex and face centre. How many K^+ ions and Cl^- ions are there in each unit cell of KCl?
- 1 K^+ ion and 1 Cl^- ion
 - 8 K^+ ions and 8 Cl^- ions
 - 4 K^+ ions and 4 Cl^- ions
 - 2 K^+ ions and 2 Cl^- ions

Soln. Cl^- at each vertex and face centre = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$.

K^+ is present in octahedral voids = 4.

\therefore 4 K^+ ions and 4 Cl^- ions are there in each unit cell of KCl.

Correct option is (c)

4. The Perovskite structure has the formula $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{O}_3$. The A cations form a primitive cubic close packing with the oxide ions occupying the centres of the faces and B cations at the body centre. The total number of ions of A, B and O in the unit cell are, respectively.
- 1, 1 and 3
 - 2, 2 and 6
 - 2, 1 and 3
 - 1, 2 and 3

Soln. Perovskite structure $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{O}_3$.

$$\text{A}^{\text{II}} \text{cation} = \text{only corners as } \text{O}^{2-} \text{ occupy face centred position} = 8 \times \frac{1}{8} = 1.$$

$$\text{O}^{2-} \text{ion} = \text{centre of faces} = 6 \times \frac{1}{2} = 3.$$

$$\text{B}^{\text{IV}} \text{cation} = \text{body centre} = 1.$$

Correct option is (a)

5. Perovskite is the mineral CaTiO_3 . The Perovskite crystal structure is adopted by several oxides as well as some fluorides. Which one, among the given formulae; most likely represents a known fluoride having the perovskite structure ?
- CaTiF_3
 - KZnF_3
 - CaTiF_5
 - CaMgF_4

Soln. **Correct option is (a)**

6. CsF adopts the NaCl crystal structure. If the unit cell edge is of length 4.02 Å, what is the shortest distance between the cation and anion in the crystal ?
- 2.01 Å
 - 2.84 Å
 - 3.48 Å
 - 4.02 Å

Soln. $a = 4.02, d = \frac{a}{2} = \frac{4.02}{2} = 2.01$.

Correct option is (a)

7. Perovskite is the mineral CaTiO_3 . The perovskite crystal structure is adopted by several oxides as well as some fluorides. Which one, among the given formulae, most likely represents a known fluoride having the perovskite structure?
- CaTiF_3
 - KMnF_3
 - NaMnF_4
 - CaFeF_3

Soln. **Correct option is (a)**



Soln. Cu = Face centre = $6 \times \frac{1}{2} = 3$.

$$\text{Au} = \text{Corners} = 8 \times \frac{1}{8} = 1.$$

Therefore, answer is AuCu_3 . i.e., formula unit = 1.

Correct option is (d)

Soln. Correct option is (d)

