SOLID STATE

Solids are generally characterised by their high density and low compressibility as compared to liquids and gases. The magnitude of these properties for solids is an indication that the constituent species (ions or atoms or molecules) are closely packed together. These solids can be easily distinguishable from liquids and gases by their definite shape, considerable mechanical strength and rigidity. These characteristics are due to the existence of very strong forces of attraction among the constituent species of the solid. Due to these strong forces, the structural units of the solid do not possess any translatory motion but can have only vibrational motion about their mean positions.

Solids can be divided into two categories: crystalline and amorphous. Crystalline solids (such as NaCl, CaO, ZnO etc.) are the one which are rigid and possess long range order i.e. its atoms, molecules or ions occupy specific positions. The arrangement of such particles in a crystalline solid is such that the net attractive intermolecular forces are at their maximum. The forces responsible for the stability of a crystal can be ionic forces, covalent bonds, van der Waals forces, hydrogen bonds or a combination of these forces.

Amorphous solids (such as glass) lack a regular three−dimensional arrangement of atoms.

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled suddenly), its atoms or molecules do not have time to allign themselves and may become locked in positions other than those of a regular crystal. Such resulting solids are called amorphous solids.

There are three distinctive features between crystalline and amorphous solids. These are

(i) Crystalline solids have long range order while amorphous solids have short range order. The long range order means the atoms or ions or molecules are arranged in a regular fashion and this symmetrical arrangement extends throughout the crystal length. The regular pattern is such that once we observe such pattern in a small region of the crystal, we will be able to predict accurately the positions of constituent particles in any region of the crystal, however far it may be from the region under investigation.

(ii) Crystalline solids have sharp melting point while amorphous solids have diffused melting point.

(iii) Crystalline solids are anisotropic while amorphous solids are isotropic (like liquids and gases).

Isotropic means the value of any physical property (like refractive index, conductivity etc.) measured in different directions is same since they are homogeneous. Anisotropic means the value of any physical property measured in different directions is not same and this phenomenon is called anisotropy. Anisotropy is a strong evidence for the existence of regular arrangement of the constituent species. Figure 1(a) and 1(b) represents two−dimensional representation of a crystalline solid and an amorphous solid.
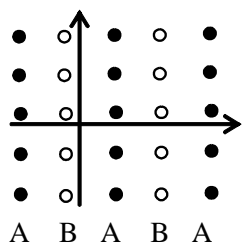

1(a) Crystalline solid
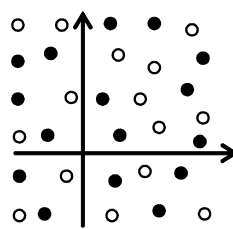
1(b) Amorphous solid

1. Unit Cell

A large lump of solid contains large number of constituent species and thus to study any property of a solid, we need to consider these large number of constituent species. Dealing with large number of atoms would be complicated and thus to avoid complications, we consider a smallest portion of this large lump of solid, which represents the properties of a solid. This smallest repeating structural unit of a crystalline solid is called unit cell. If we extend unit cells in three dimensions, we can prepare a solid of desired number of unit cells. A cubic unit cell and its extension in three dimension is shown in figure 2(a) and 2(b) as
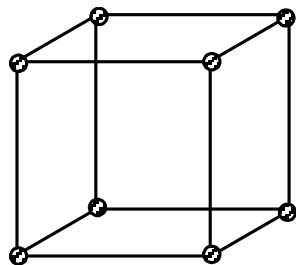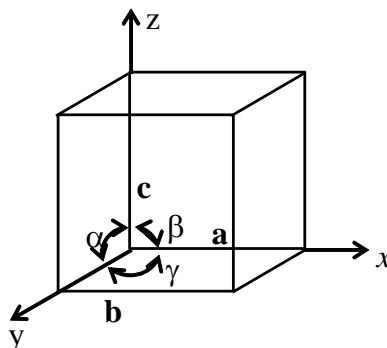
Figure 2(a)
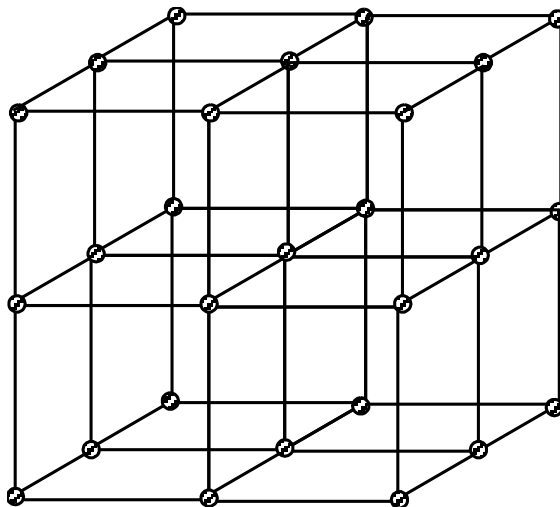
Figure 2(b)

Lattice points or lattice sites are the sites at which constituent species are located. In a cubic arrangement, the lattice sites can be either corners or face centres or body centre. It is not essential that the lattice site should be occupied by the constituent particle. In many crystals, the lattice site does not actually contain a constituent particle and such crystals are called defective crystals. In the foregoing discussion, we will assume that each lattice site is occupied by constituent species. Such crystals are called ideal crystals.

In a 3–dimensional space lattice, we need to specify the values of three vectors which gives three repeat distances along the three axes and three angles are shown in figure 3 as

Figure 3

According to Bravais "three vectors and their angles study shows morphologically that the unit cells can be classified into seven crystal systems based on the presence of certain rotation axes." These seven crystal systems are classified according to geometrical and symmetrical considerations as

(i) Cubic   (ii) Orthorhombic   (iii) Rhombohedral   (iv) Monoclinic
(v) Triclinic   (vi) Tetragonal   (vii) Hexagonal

Bravais further showed that there would be only four possible ways in which constituent species of a unit cell can be arranged. They are

(a) Primitive or simple
(b) Body centred
(c) Face centred and
(d) End centred

So, the total number of possible unit cells are $7 \times 4 = 28$. Bravais, then went on to predict that out of these 28 possible unit cells, only 14 of them exist in nature. These predictions of Bravais were based on certain

symmetry operations carried out by him on the unit cells. These predictions given by him in 19th century were found to be correct in the mid of 20th century. So, in honour of Bravais, the 14 unit cells which exist in nature are called Bravais lattices.

The seven crystal systems and their unit cell parameters are shown as

| Crystal systems		Bravais lattices	Unit cell parameters	
			Intercepts	Crystal angles
1.	Cubic	Primitive, Face centered, Body centered	$a = b = c$	$\alpha = \beta = \gamma = 90°$
2.	Orthorhombic	Primitive, Face centered, Body centered, End centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
3.	Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
4.	Monoclinic	Primitive, End centered	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$
5.	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
6.	Tetragonal	Primitive, Body centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
7.	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
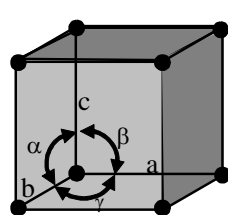
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$
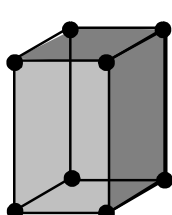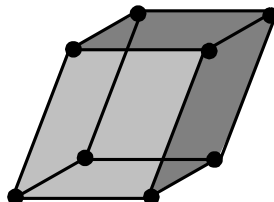
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
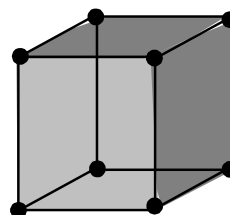
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
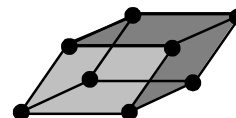
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
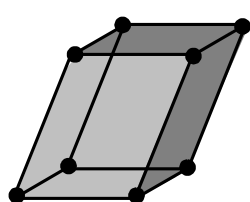
Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$

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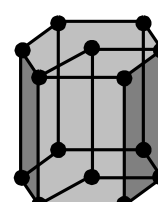
Hexagonal Primitive
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

Figure 4

In in chapter we have to study only
(i) Primitive or simple cubic
(ii) Body centered cubic
(iii) Face centered cubic
(iv) Hexagonal primitive

Before proceeding further, let us first understand the term rank of a unit cell and coordination number. Rank of a unit cell means the number of effective atoms (or ions or ion−pairs) in a unit cell and the coordination number is the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice.

SOLID STATE

1.1 Primitive or Simple Cubic (PC/SC) Unit Cell

In a primitive cubic unit cell, all the eight corners of the cube are occupied by atoms and they are not present anywhere else in the cube. If all the eight atoms are of same type, the unit cell is called ideal primitive and if they are not same, it is referred as pseudo primitive or primitive–like.

Figure 5(a) shows an ideal primitive cubic unit cell.

In the above figure, we are unable to see that an atom is in contact with how many other atoms. So, in order to view this, we should look at the landscape view of the primitive arrangement in figure 5(b).

Figure 5(a)

In this layer, each atom is in contact with its immediate neighbours. If the centres of these four atoms are joined, a face of the unit cell can be generated. Now, place a layer of four other atoms over this layer in such a way that the atoms of the second layer eclipse the atoms of the first layer and join the centre of all the eight atoms to get a primitive cubic arrangement.
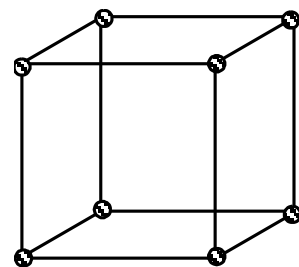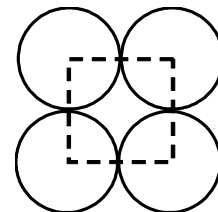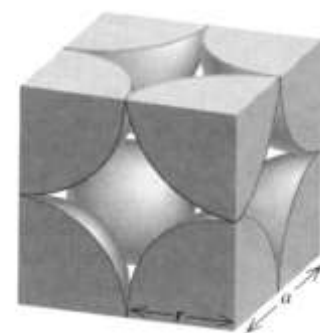

Figure 5(b)

In such an arrangement, each atom is in contact with six immediate neighbouring atoms, so the coordination number of each atom is 6. If 'a' represents edge length of the unit cell, then a = 2r where 'r' is the radius of an atom. This is shown in figure 5(d).

In a lattice of this type, each corner atom is shared by eight unit cells, four in one layer and four in the layer above it, as shown in figure 5(c).

Thus, the contribution of each atom placed at the corner of single cubic unit cell is 1/8. Since, there are eight corners of a cube, the effective number of atoms associated with a single primitive unit cell is $\frac{1}{8} \times 8 = 1$. Thus, the rank of a primitive cubic unit cell is 1.

Simple or Primitive Cubic
a = 2r

Figure 5(c)

The volume of a cubic unit cell is not completely occupied by atoms. The ratio of volume occupied by the effective atoms to the volume of the unit cell is called packing fraction (PF). The fraction of volume of a unit cell, that is empty is called void fraction (VF). Thus,

$$\text{Packing fraction} = \frac{\text{Volume occupied by the effective atoms in a unit cell}}{\text{Volume of the unit cell } (a^3)}$$

and void fraction = (1 − Packing fraction)

$$\therefore \quad PF = \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.523$$

Thus, the structure is relatively open since only 52.3% of the total volume is occupied by the atoms. The remainder 47.7% of the total volume is empty space or void volume. In general, the packing fraction is independent of the radius of atom and edge length of the unit cell and depends only on the nature of packing. This type of structure is exhibited by polonium, Po.

SOLID STATE

1.2   Body Centered Cubic (Bcc) Unit Cell

In body centered cubic unit cell, the lattice points are corners and body centre. This implies that the atoms are present at all the corners and at the body centered position and are not present anywhere else in the cube. If all the nine atoms are of same size, the unit cell is referred as ideal BCC while it is called BCC–like or pseudo BCC, if the atoms present at the corners and the body centre are different. Figure 6(a) represents an ideal BCC lattice.
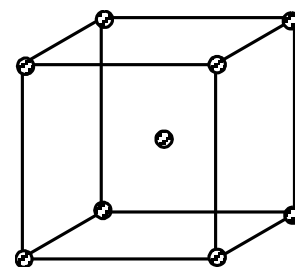

Figure 6(a)

The landscape view of the BCC arrangement is shown in the figure 6(b). Here, packing consists of a base of 4 atoms. This constitutes first layer. It is followed by a second layer in which each atom rests in the groove formed by the atoms of first layer and the atom of second layer would also be in contact with all the four atoms of first layer. Then a third layer of four atoms is kept over the second layer in such a way that atoms of third layer eclipse the atoms of first layer. It must be noted here that atoms of third layer and first layer are not in contact with each other while the atom of second layer is in contact with 8 atoms (4 of first layer and 4 of third layer). So, the coordination number of each atom is 8.

In a BCC lattice, each corner atom is shared by 8 unit cells while the body centered atom is not shared by any other unit cell. So, the number of effective atoms associated with a BCC unit cell is $\left(\dfrac{1}{8} \times 8\right) + 1 = 2$. Thus, the rank of a BCC unit cell is 2.

Figure 6(b)

Since, the body centered atom touches all 8 corner atoms, so the body diagonal ($\sqrt{3}$ a) would be equal to 4r, where 'a' represents the edge length and 'r' is the radius of atom. This is shown in figure 6(c). The fraction of volume occupied by the atoms is given by

$$PF = \frac{2 \times \dfrac{4}{3}\pi r^3}{\left(\dfrac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\,\pi}{8} = 0.6802u$$

Thus, 68.02% of the volume of the unit cell is occupied by atoms and the remaining 31.98% is the void volume. This type of structure is exhibited by K, Fe, Li, V, Cr, Mo etc.
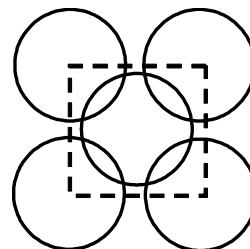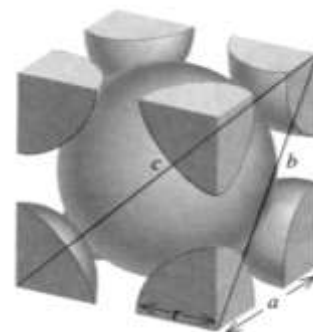
BCC
$b^2 = a^2 + a^2$
$c^2 = a^2 + b^2 = 3a^2$
$c = \sqrt{3}\,a = 4r$
$a = \dfrac{4r}{\sqrt{3}}$

Figure 6(c)

Illustration 1

Lithium forms body centered cubic crystals and its edge length is 351 pm. Calculate the atomic radius of lithium.

Solution:

In BCC lattice, atoms touch one another along the cross–diagonal of the cube. Thus,

$$\sqrt{3}\,a = 4r_{Li}$$

or $r_{Li} = \dfrac{\sqrt{3}\,a}{4} = \dfrac{\sqrt{3} \times 351}{4}$

$\therefore\ r_{Li} = \textbf{151.9 pm}$

1.3 Face Centered Cubic (FCC) Unit Cell

In FCC unit cell, the lattice sites are corners and face centres. Thus, in face centered cubic unit cell, the atoms are present at the corners and at the face centres and are not present anywhere else in the cube. When all the 14 atoms are of same size, the unit cell is called ideal FCC while if the atoms present at the corners and face centres are different, the unit cell is referred as pseudo FCC or FCC–like. Figure 7(a) represents an ideal FCC lattice.
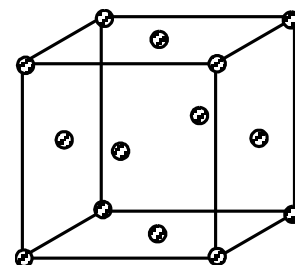
Figure 7(a)

In this structure, two adjacent corner atoms are not in contact with each other and each face centered atom is in contact with four corner atoms of its face. If 'a' represents the edge length of a FCC unit cell and 'r' is the radius of atom, then face diagonal $(\sqrt{2}a)$ would be equal to 4r.

In a FCC unit cell, each corner atom is shared by 8 unit cells and each face centered atom is shared by 2 unit cells, so the number of effective atoms in a FCC unit cell would be $\left(\dfrac{1}{8} \times 8\right) + \left(\dfrac{1}{2} \times 6\right) = 4$. Thus, the rank of a FCC unit cell is 4. This is shown in figure 7(b).

The fraction of volume occupied by the atoms is given by

$$PF = \frac{4 \times \dfrac{4}{3} \pi r^3}{\left(\dfrac{4r}{\sqrt{2}}\right)^3} = \frac{\sqrt{2}\,\pi}{6} = 0.7405$$

$b = 4r$
$b^2 = a^2 + a^2$
$16r^2 = 2a^2$
$a = \sqrt{8}\ r = 2\sqrt{2}\,r$

Figure 7(b)

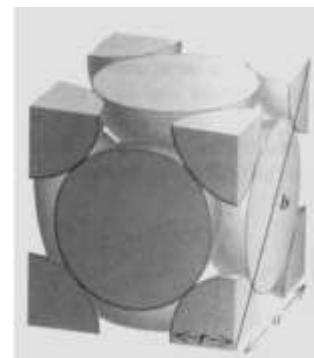Thus, 74.05% of the volume of the unit cell is occupied by atoms and the remaining 25.95% is the empty space. Al, Ni, Ag, Fe, Pd, Cu, Au, Pb, all solid noble gases etc exhibit this type of structure.

2. Density of Cubic Crystals

The density of cubic crystal structures can be calculated from the mass contained in a unit cell and its volume. In order to calculate the density of crystal lattice, we calculate the density of a unit cell. Thus,

Density of cubic lattice = Density of unit cell (ρ)

$\therefore \qquad \rho = \dfrac{\text{Mass of the unit cell}}{\text{Volume of unit cell}}$

$= \dfrac{\text{Mass of effective number of atoms in the unit cell}}{\text{Volume of unit cell}}$

$= \dfrac{\text{Number of effective atoms in the unit cell} \times \text{mass of each atom of the unit cell}}{\text{Volume of unit cell}}$

$= \dfrac{\text{Number of effective atoms in the unit cell} \times \text{atomic mass}}{\text{Volume of unit cell} \times \text{Avogadro's number}}$

(since atomic mass represents mass of Avogadro's number of atoms, so the mass of each atom would be given by $\dfrac{\text{Atomic mass}}{\text{Avogadro's number}}$).

$$\therefore \quad \rho = \frac{n \times M}{N_{AV} \times a^3}$$

In order to get the density of unit cell (or cubic crystal) in g/cm^3, 'M' should be kept in g/mole and 'a' should be in cm.

Illustration 2

The unit cell of aluminium is a cube with edge length 405 pm. The density of aluminium is 2.70 g/cm^3. What is the structure of aluminium crystals?

Solution:

Density of a cubic unit cell is given by

$$\rho = \frac{n \times M}{N_{AV} \times a^3}$$

$$\therefore \quad n = \frac{\rho \times N_{AV} \times a^3}{M} = \frac{2.70 \times 6.023 \times 10^{23} \times (4.05 \times 10^{-8})^3}{27}$$

$$n \simeq 4$$

Thus, the unit cell of aluminium is face centered cubic.

Illustration 3

Iron occurs as body centered as well as face centered cubic unit cell. If the effective radius of an atom of iron is 124 pm, compute the density of iron in both these structures.

Solution:

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

(i) For body−centered cubic unit cell (BCC),

$$\text{Mass of unit cell} = \frac{2 \times 56}{6.023 \times 10^{23}}$$

As $\sqrt{3}$ a = 4r for a BCC lattice, the volume of unit cell $= a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \left(\frac{4 \times 124 \times 10^{-10}}{\sqrt{3}}\right)^3$

$$\therefore \quad \text{Density} = \frac{2 \times 56 \times 3\sqrt{3}}{6.023 \times 10^{23}(4 \times 124 \times 10^{-10})^3} = \textbf{7.91 g/cc}$$

(ii) For face−centered cubic unit cell (FCC),

$$\text{Mass of unit cell} = \frac{4 \times 56}{6.023 \times 10^{23}}$$

As, $\sqrt{2}$ a = 4r for a FCC lattice, the volume of unit cell $= a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \left(\frac{4 \times 124 \times 10^{-10}}{\sqrt{2}}\right)^3$

$$\text{Density} = \frac{4 \times 56 \times 2\sqrt{2}}{6.023 \times 10^{23}(4 \times 124 \times 10^{-10})^3} = \textbf{8.62 g/cc}$$

Illustration 4

Methane crystallizes in a cubic unit cell with a = 0.589 nm. If the density of liquid CH_4 is 0.466 g cm^{-3} and assuming that the density of solid is same as that of liquid at the given temperature, predict which type of cubic unit cell methane will crystallize in.

Solution:

The cubic unit cell of methane can be simple cubic, BCC or FCC having effective number of molecules 1, 2 or 4 respectively. Let us first calculate the density of methane when it crystallizes in primitive (simple) cubic structure.

$$\rho_{SC} = \frac{n \times M}{N_{AV} \times a^3} = \frac{1 \times 16}{6.023 \times 10^{23} \times (0.589 \times 10^{-7})^3}$$

$\rho_{SC} = 0.13$ g/cm^3

Since in BCC lattice, the number of effective molecules is double than that in primitive cubic, so the density of methane crystal in BCC would be double of primitive cubic.

$\therefore \ \rho_{BCC} = 2 \times \rho_{SC} = 2 \times 0.13 = 0.26$ g/cm^3.

Similarly, $\rho_{FCC} = 4 \times \rho_{SC} = 4 \times 0.13 = 0.52$ g/cm^3.

The observed value of density (of liquid methane) is more closer to the density of FCC lattice, so methane crystallizes in **FCC structure**.

3.   Closest Packing of Atoms

From the packing fraction data, it is clearly evident that there is more empty space in primitive cubic and body centered cubic unit cells than in the face centered cubic unit cell. This implies that atoms in FCC unit cell are more closely packed than in PC and BCC unit cell. Thus FCC unit cell has the closest packing. The hexagonal primitive (HP) unit cell, also has the closest packing as its packing fraction matches with that of FCC unit cell. Thus, FCC and HP unit cells has the most efficient arrangement of atoms called closest packing. Let us start with the structure shown in figure 8(a), which is called layer A. If we focus on the only enclosed atom, we can notice that each atom is surrounded by six atoms in this layer. There are certain spaces left in between the atoms. These spaces are called voids or grooves. Now, we place an atom (of the same type) into the groove (depression) between the atoms in the first layer, then the adjacent groove gets partially blocked by this atom and we are unable to put the atom in the adjacent groove. So, the atoms of the second layer can only be placed in the alternate grooves between the atoms in the first layer. This constitutes second layer called as layer B shown in figure 8(b). In layer B also, each atom is surrounded by six atoms. Thus, layer A and B are identical, with the only difference in their placement. The layer B has two types of voids, marked as 'a' and 'b' voids. Thus, there are two ways that a third layer atom may cover the second layer to achieve closest packing.

3.1 FCC Unit Cell

The atoms may fit into the voids 'a' such that each third layer atom is directly over a first layer atom. Thus, if we put the atoms on all the 'a' type of voids, they would eclipse all the atoms of the A layer as shown in figure 8(c). This means that there would be no difference between the arrangement of the first and third layer, so we can call the third layer as layer A. Thus, the layering pattern generated is ABABAB….., which is known as hexagonal close packed (HCP) structure, which corresponds to hexagonal primitive (HP) unit cell. Alternatively, the third layer atoms may fit into the 'b' type of voids that lie directly over the voids in the first layer as shown in figure 8(d). The third layer formed in this manner would neither eclipse any atom of A layer nor any atom of B layer. Thus, it would be a unique layer, referred as C layer and the layering pattern generated is ABCABC……, known as cubic close packed (CCP) structure, which corresponds to face centred cubic (FCC) unit cell.
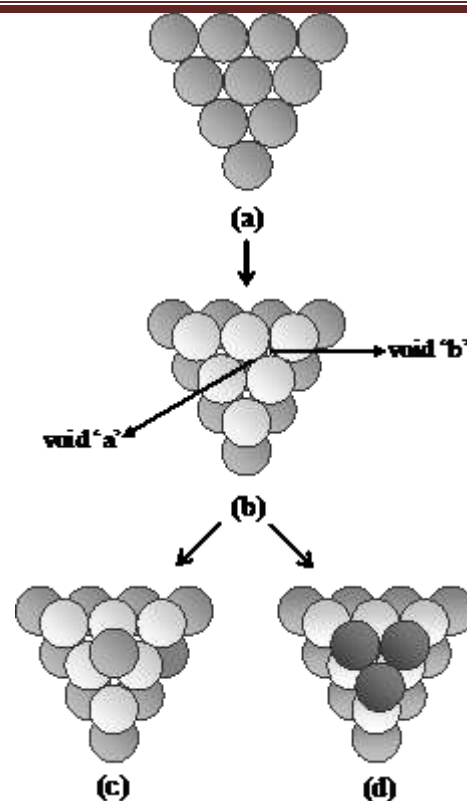
Figure 8

Figure 9 shows the "exploded view" of HCP & CCP and the structures resulting from these two arrangements.

Exploded view   Hexagonal close−packed structure (a)

Exploded view   Cubic close−packed structure (a)
Figure 9
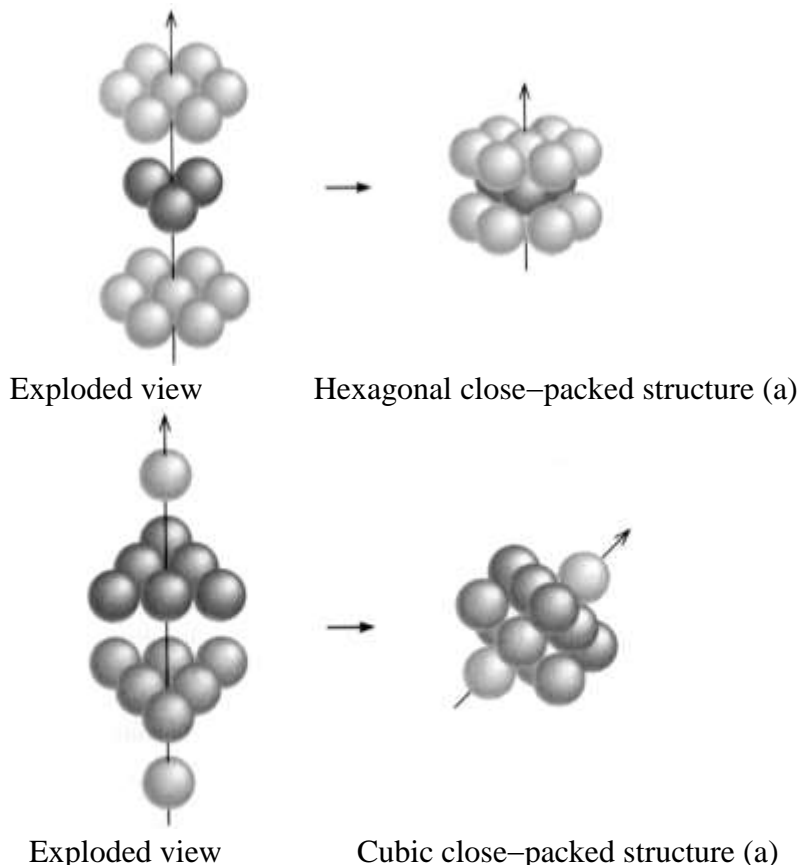
In both the structures, each atom has a coordination number of 12 (each atom is in contact with six atoms in its own layer, three atoms in the layer above and three atoms in the layer below). Both the HCP and CCP structures represent the most efficient way of packing identical atoms in a unit cell, and there is no way to increase the coordination number beyond 12.

3.2   Hexagonal Primitive Unit Cell

A hexagonal primitive unit cell comprises of 3 layers A, B and A and is shown in the figure 10. Each atom has a coordination number of 12. Each corner atom is shared by six unit cells, of which three are in the same layer and three are in the upper layer. Thus, each corner atom makes $1/6^{th}$ contribution to a unit cell. There are 12 such corner atoms, so the effective contribution from corner atoms would be $1/6 \times 12 = 2$. There are two atoms at the centres of top hexagonal face and the bottom hexagonal face. They would contribute half, as they are shared between two unit cells. Three atoms of B layer are completely inside the unit cell. Thus, the total number

of effective atoms in HP unit cell would be $\left(\dfrac{1}{6} \times 12\right) + \left(\dfrac{1}{2} \times 2\right) + 3 = 6$. So, the rank of HP unit cell is 6.

The face centered atom is in contact with six atoms present at the corners of hexagon and two corner spheres are also in contact with each other. If 'a' represents the edge length of the unit cell and 'r' is the radius of atom, then a = 2r.

The coordination number of each atom is 12. The fraction of volume of unit cell occupied by the atoms is given by

Figure 10

$$PF = \dfrac{6 \times \dfrac{4}{3}\pi r^3}{\text{Area of the base} \times \text{height of unit cell (c)}}$$

Height of the unit cell is given by

$$\dfrac{c}{2} = \sqrt{(2r)^2 - \left(\dfrac{2r}{\sqrt{3}}\right)^2} = \sqrt{\dfrac{2}{3} \times 4r^2}$$

$$\therefore \qquad c = 4r\sqrt{\dfrac{2}{3}}$$

Area of the base is calculated by the area of six equilateral triangles.

$$\therefore \qquad \text{Area of the base} = 6 \times \dfrac{\sqrt{3}}{4}a^2 = 6 \times \dfrac{\sqrt{3}}{4}(2r)^2$$

$$\therefore \qquad PF = \dfrac{6 \times \dfrac{4}{3}\pi r^3}{6 \times \dfrac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{\dfrac{2}{3}}} = \dfrac{\sqrt{2}\,\pi}{6} = 0.7405$$

Thus, 74.05% of the volume of the unit cell is occupied by atoms and remaining 25.95% is the empty space. The half of the height of HP unit cell represents the distance between the layers A and B. This distance will be from the centre of an atom of A layer to the plane of the three atoms of B layer that are in contact with it. The distance between two layers in FCC would also be same as in HP. Thus, the distance, $\dfrac{c}{2}$ can also be determined with reference to a FCC unit cell with edge length 'a'. The distance between any two layers is $\dfrac{1}{3}^{rd}$ of the body diagonal.
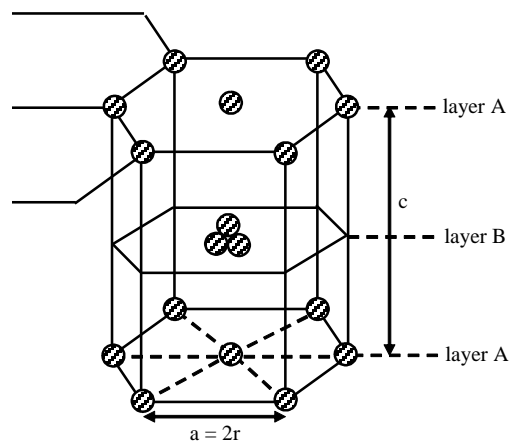
$\therefore$ $\dfrac{c}{2} = \dfrac{\sqrt{3}\,a}{3} = \dfrac{a}{\sqrt{3}}$

In FCC unit cell, $\sqrt{2}\,a = 4r$

$\therefore$ $a = \dfrac{4r}{\sqrt{2}}$

Substituting value of 'a' in the expression of $\dfrac{c}{2}$ gives

$\dfrac{c}{2} = \dfrac{4r}{\sqrt{2 \times 3}}$

$\therefore$ $c = 4r\sqrt{\dfrac{2}{3}}$

This is same as what we have obtained earlier. This type of structure is exhibited by Be, Co, Mg, Zn etc.

4. Types of Voids

In closest packing, we have observed two types of voids 'a' and 'b'. The voids of 'a' type are called tetrahedral voids and voids of 'b' type are called octahedral voids. These tetrahedral and octahedral voids are present only in FCC and HP unit cells.

4.1 Tetrahedral Void

A tetrahedral void is formed when an atom fits into the depression formed by three other closest packed atoms (forming an equilateral triangle). All the four atoms are in contact with each other. If we join the centre of all four atoms, we get a tetrahedron. The centre of tetrahedron represents a tetrahedral void.
Now let us see the location of tetrahedral void in a FCC lattice. Let us consider a FCC unit cell and assume that corner is the origin of FCC unit cell.

Tetrahedral void

Figure 11(a)

We have to find three other atoms with which this corner atom is in contact with. An atom in FCC unit cell touches another atom, if they are present at a distance of $\dfrac{a}{\sqrt{2}}$, where a is the edge length of the unit cell. Thus, this corner atom will touch the face centered atom of those faces which will meet at this corner. When the centre of these four atoms are joined, it gives a tetrahedron and the centre of tetrahedron would be the location of tetrahedral void.

The exact location of tetrahedral void in FCC unit cell can also be traced by cutting the FCC unit cell into eight minicubes by three perpendicular cuts.
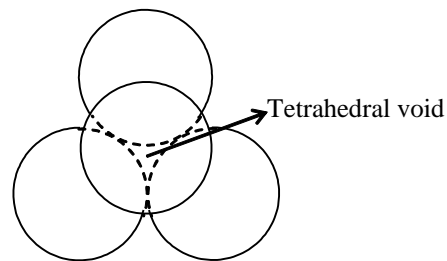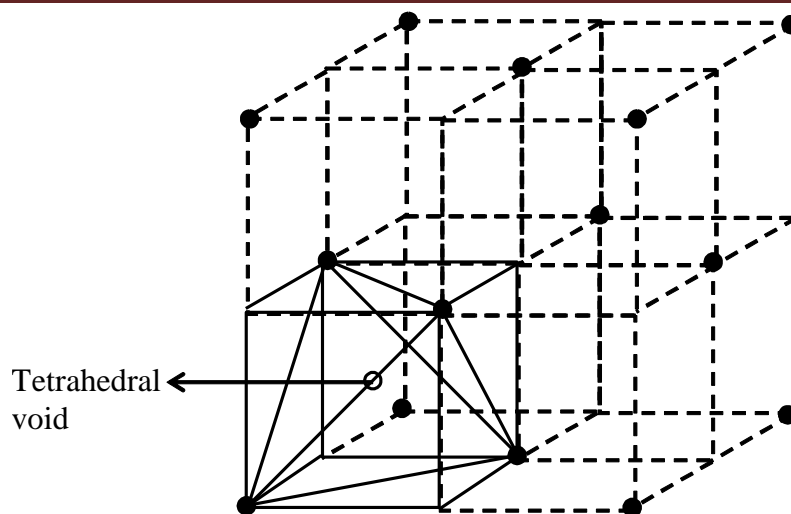
Number of tetrahedral voids per FCC unit cell

Figure 11(b)

The atoms in the minicube are present at the alternate corners of the minicube and these atoms actually touch one another forming a tetrahedron with a hole (void) in the centre. This tetrahedral void would be the exact centre of minicube. Since, there are eight such minicubes, so there are eight tetrahedral voids in FCC unit cell. This is twice the number of effective atoms in FCC unit cell. Thus, in general the number of effective tetrahedral voids in a unit cell is double the number of effective atoms in that unit cell. Let the radius of host atom (forming FCC lattice) be r_h while the radius of foreign atom entering a tetrahedral void in an ideal FCC lattice be r_f, then the sum of radii of host and foreign atom in terms of edge length (a) is given by

$\bullet$ −Centre of tetrahedral void

Figure 11(c)

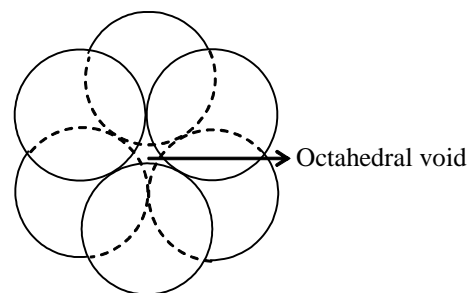$$(r_h + r_f) = \frac{\sqrt{3}\,a}{4}$$
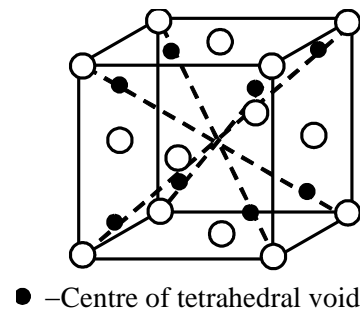
4.2   Octahedral Void

An octahedral void is formed when three closest packed atoms of one layer (forming an equilateral triangle) is placed over three closest packed atoms of the second layer, their positions being inverted with respect to each other. Each atom touches four other atoms, except the atom diagonally opposite to it.

Octahedral void

Figure 12(a)

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If we join centre of all the six atoms, we get an octahedron and the centre of octahedron represents an octahedral void. Now let us see the location of an octahedral void in FCC unit cell. In FCC unit cell, 2 corner atoms do not touch each other, so a foreign atom can be placed between them. If the foreign atom is enlarged such that it starts touching corner atoms, it will also touch four other host atoms (the atoms which forms FCC lattice). These four other host atoms are the face centered atoms of those faces which meet at this edge (bearing two corner atoms).
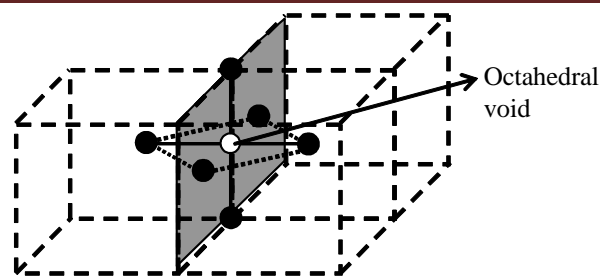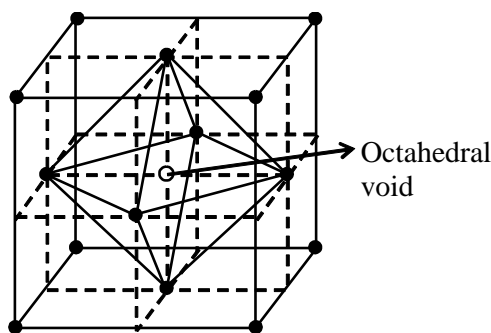

An octahedral void at the centre of an edge in a FCC unit cell.

Figure 12(b)

When the four face centered atoms and two corner atoms are joined, we get an octahedron, the centre of which is occupied by foreign atom. Thus, location of foreign atom is the location of octahedral void. An octahedral void is thus located at the centre of each edge of the FCC unit cell.

Such an octahedral void is also located at the body centred position of FCC unit cell, since this position is also bounded by six face centered atoms, as shown in figure 12(c).

An octahedral void at the body centered position in FCC unit cell.

Figure 12(c)

Now, let us see how many effective octahedral voids are present in a FCC unit cell. We know that there are 12 edges in a cube and each edge is being shared by four unit cells. Thus, an octahedral void at the centre of each edge would make a contribution of 1/4 and octahedral void present at the body centered position would make complete contribution.

Thus, the number of effective octahedral voids in a FCC unit cell would be $\left(\dfrac{1}{4} \times 12\right) + 1 = 4$. We also know that the effective number of atoms in FCC unit cell are also 4, so, in general, the effective number of octahedral voids in a unit cell is equal to the number of effective atoms in that unit cell.

The size of the octahedral void present at the centre of edge and body centered position would be same only for an ideal FCC lattice while for pseudo FCC lattice, their sizes would be different.

Let the radius of host atom (forming FCC lattice) be r_h and the radius of foreign atom occupying octahedral void in an ideal FCC lattice be r_f', then the distance between a host atom and a foreign atom is given by

$$(r_h + r_f') = \dfrac{a}{2}$$

where a is the edge length of ideal FCC lattice.

5. Radius Ratio Rules

So far we have discussed packing of spheres of same size. The arrangement of ions in a crystal is determined by the relative sizes of cations and anions as packing of spheres of different sizes is involved. The ratio of the radii of cation to that of anion is called as radius ratio and it generally determines the crystal structure for an ionic compound. The radius ratio value depends on the coordination number of the ion and is always indicated by a range. Let us consider the case of three coordinate crystal structure. We have shown three arrangements for three coordinate structures.
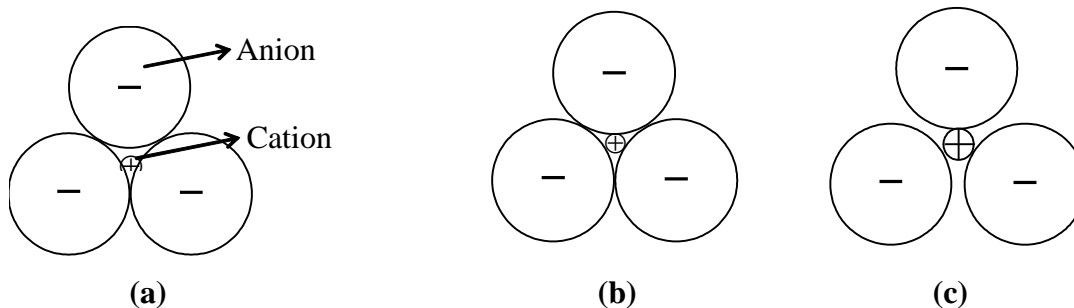
Figure 13

In all the three arrangements, a cation is surrounded by three anions, depicting coordination number 3. But arrangement shown in 13(a) is not possible because cation's position is not fixed and it will keep on rattling in the available space. In arrangement 13(b) and 13(c), since cation is touching all the three anions, there are significant attractions between them, which makes the structures stable and possible. If we calculate the radius ratio value for these two arrangements, it will be different. So, arrangement in which cation touches anions and anions are also in contact with each other yield the critical value of radius ratio. This is also referred to as ideal or limiting radius ratio. Now, from the structure having limiting radius ratio, if the size of cation is increased without changing the size of anion, the radius ratio keeps on increasing and after a while, for a particular size of cation, we will be able to place four anions around it, which will make coordination number 4. At this stage, radius ratio represents limiting radius ratio for coordination number 4. Any value of radius ratio less than this value, will be for the coordination number 3 only. Thus, radius ratio will always be in range for a given coordination number. The radius ratio range for various coordination numbers is tabulated below.

Limiting radius ratio $\frac{r_c}{r_a} = x$	Coordination number	Shape	Example
$x < 0.155$	2	Linear	$BeCl_2$
$0.155 \le x < 0.225$	3	Triangular planar	BCl_3
$0.255 \le x < 0.414$	4	Tetrahedral	ZnS, BeO
$0.414 \le x < 0.732$	4	Square planar	$[PtCl_4]^{2-}$
$0.414 \le x < 0.732$	6	Octahedral	NaCl, CaO
$0.732 \le x < 0.999$	8	Body centered cubic	CsCl
$x = 1$	12	Ideal FCC	Fe, Al, Ag

Coordination number 4 has 2 possible arrangements: tetrahedral and square planar. Each shape will have a different radius ratio range. For coordination number 12, the radius ratio comes out to be one because the distinction between cations and anions will be lost i.e. they will be same in size and will be present as atoms.

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5.1 Radius Ratio for Coordination Number 3 (Triangular Arrangement)

The radius ratio for the triangular arrangement of ions can be obtained as follows.

In triangular arrangement (coordination number 3), a cation of radius, r_c is surrounded by 3 anions of radius, r_a. The cation is touching all the three anions and anions are also in contact with each other, an arrangement which gives limiting radius ratio for coordination number 3. From figure 13(d), it is obvious that

Figure 13(d)

$$AB = BC = AC = 2r_a$$
$$AD = r_c + r_a \text{ and } AE = r_a$$

The angle BAC is 60° and the angle DAE is 30°, then by trigonometry,

$$\text{Cos } 30° = \frac{AE}{AD} = \frac{r_a}{r_c + r_a}$$

$$\frac{\sqrt{3}}{2} = \frac{r_a}{r_c + r_a}$$

Taking reciprocal,

$$\frac{r_c + r_a}{r_a} = \frac{2}{\sqrt{3}}$$

or

$$\frac{r_c}{r_a} + 1 = \frac{2}{\sqrt{3}}$$

$$\frac{r_c}{r_a} = \frac{2}{\sqrt{3}} - 1 = \frac{2 - \sqrt{3}}{\sqrt{3}} = \mathbf{0.155}$$

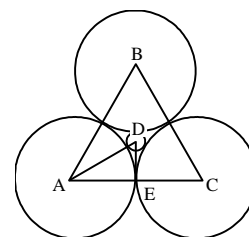## 5.2 Radius Ratio for Coordination Number 4 (Tetrahedral Arrangement)

In the limiting tetrahedral arrangement, a cation of radius, r_c is touching all four anions of radius, r_a and the anions are also in contact with each other. From figure13(e), it is obvious that

$$AB = BC = CD = DA = 2r_a = \frac{a}{\sqrt{2}}$$

and

$$AE = BE = CE = DE = r_c + r_a = \frac{\sqrt{3}\,a}{4}$$

$$\therefore \quad \frac{r_c + r_a}{2r_a} = \frac{\sqrt{3}\,a}{4} \times \frac{\sqrt{2}}{a}$$

$$\frac{r_c + r_a}{r_a} = \sqrt{\frac{3}{2}}$$

or

$$\frac{r_c}{r_a} + 1 = \sqrt{\frac{3}{2}}$$

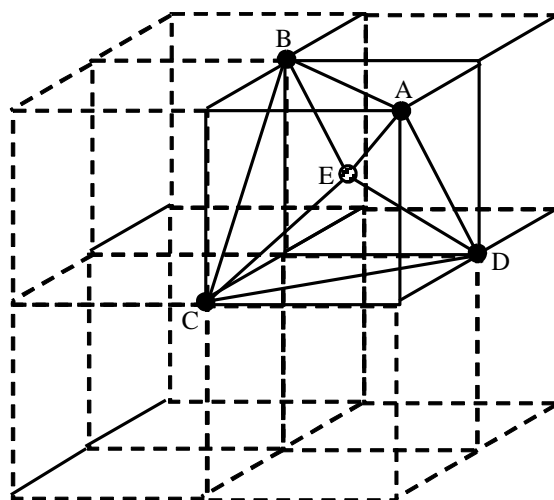$$\frac{r_c}{r_a} = \sqrt{\frac{3}{2}} - 1 = \mathbf{0.225}$$

Figure 13(e)

5.3 Radius Ratio for Coordination Number 6 (Octahedral Arrangement) or Radius Ratio for Coordination Number 4 (Square Planar Arrangement)

In the limiting octahedral arrangement, a cation of radius, r_c is in contact with six anions of radius, r_a and the anions are also in contact with each other.

Draw a right angle triangle passing through the centre of the three anions. The cation will lie in the middle of the hypotenuse. From figure 13(f), it is obvious that
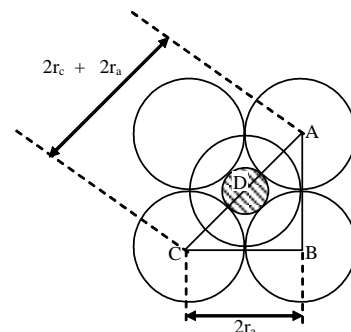
$$BC = AB = 2r_a = \frac{a}{\sqrt{2}}$$

and

$$AC = 2(r_c + r_a) = a$$

$$\therefore \quad \frac{2(r_c + r_a)}{2r_a} = a \times \frac{\sqrt{2}}{a}$$

$$\frac{r_c + r_a}{r_a} = \sqrt{2}$$

or

$$\frac{r_c}{r_a} + 1 = \sqrt{2}$$

$$\frac{r_c}{r_a} = \sqrt{2} - 1 = \mathbf{0.414}$$

Top view of octahedral arrangement
Figure 13(f)

5.4 Radius Ratio for Coordination Number 8 (Body Centered Cubic Crystal)

In the limiting cubical (body centered cubic) arrangement, a cation of radius, r_c is touching all the eight anions of radius, r_a and the anions are also in contact with each other.

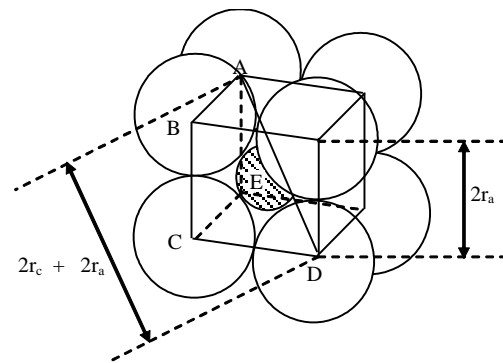From the figure 13(g), it is obvious that

$$AB = BC = CD = 2r_a = a$$

and

$$AD = 2(r_c + r_a) = \sqrt{3}\,a$$

$$\therefore \quad \frac{2(r_c + r_a)}{2r_a} = \frac{\sqrt{3}a}{a}$$

$$\frac{r_c + r_a}{r_a} = \sqrt{3}$$

or

$$\frac{r_c}{r_a} + 1 = \sqrt{3}$$

$$\frac{r_c}{r_a} = \sqrt{3} - 1 = \mathbf{0.732}$$

Figure 13(g)

Radius ratio rules are used for finding out the type of crystal structure in which ionic solids will crystallise, depending on their coordination number. In practice, the radius ratio rules are most reliable when the cation coordination number is 8, less reliable with 6 coordinate cations and unreliable for 4 coordinate cations.

6. Types of Ionic Structures

For any ionic solid of the general formula A_xB_y, in which the molar ratio of cation and anion is $x : y$, the ratio of coordination number of cation to anion would be $y : x$. Thus, using the coordination number ratio of cation and anion, the molar ratio of cation and anion in 1 mole of ionic solid can be obtained, i.e. their general formula can be obtained. The general formula of an ionic structure can also be calculated by finding the number of effective cations & anions per unit cell. In the following structures, cations are indicated by black circles while anions are shown by shaded circles.

6.1 Rock Salt Structure

NaCl exhibits this type of structure. In the rock salt structure, Cl^- ions exists in FCC pattern and Na^+ ions occupy all octahedral voids. There are 4 effective Na^+ ions and 4 effective Cl^- ions in a unit cell of NaCl. So, the general formula is Na_4Cl_4 or NaCl as per the effective ions in a unit cell. The coordination number of Na^+ ion is 6 and coordination number of Cl^- ion is also 6. So, the general formula (using coordination number of ions) is Na_6Cl_6 or NaCl.

Halides of all alkali metals except cesium and oxides of all alkaline earth metals except beryllium also represent this structure. AgCl, AgBr & AgI also crystallize in this structure. Other examples include TiO, FeO, NiO etc.. Let the radius of Na^+ ion and Cl^- ion be represented by r_c and r_a respectively and 'a' be the edge length of the unit cell, then $r_c + r_a = \dfrac{a}{2}$.
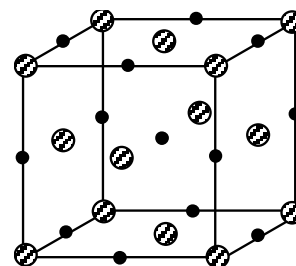

Figure 14(a), Rock salt structure

6.2 Zinc Blende (Sphalerite) Structure

This structure is represented by ZnS. In the zinc blende structure, S^{2-} ions forms FCC lattice and Zn^{2+} ions occupy alternate tetrahedral voids. The effective Zn^{2+} and S^{2-} ions in a unit cell are 4 each, so the general formula is Zn_4S_4 or ZnS. The coordination number of both the ions (Zn^{2+} and S^{2-}) is 4, so the general formula (using coordination number of ions) is also Zn_4S_4 or ZnS.
The zinc blende structure is also exhibited by BeO. Let the radius of Zn^{2+} and S^{2-} ions be r_c and r_a respectively and edge length of the unit cell be 'a', then
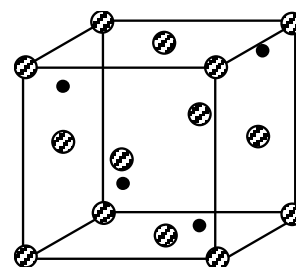

Figure 14(b), Zinc blende structure

$$r_c + r_a = \frac{\sqrt{3}\,a}{4}$$

6.3 Fluorite Structure

This structure is exhibited by CaF_2. In the lattice structure of CaF_2, Ca^{2+} ions exist as FCC and F^- ions occupy all tetrahedral voids. The effective number of Ca^{2+} and F^- ions in a unit cell are 4 and 8 respectively, so the general formula is Ca_4F_8 or CaF_2. The coordination number of F^- ions is 4 (as they are present in tetrahedral voids) and that of Ca^{2+} ions is 8. Thus, the general formula using coordination number of ions is also Ca_4F_8 or CaF_2.

The fluorite structure is also represented by other halides of alkaline earth metals and by ionic compounds of the general formula AB_2 like UO_2, ThO_2, PbO_2, HgF_2 etc.

Let 'a' be the edge length of the unit cell and r_c and r_a be the radius of Ca^{2+} and F^- ions respectively, then

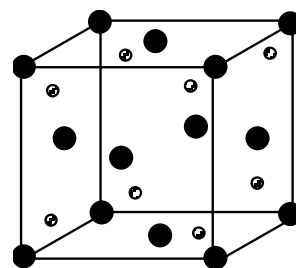$$r_c + r_a = \frac{\sqrt{3}\,a}{4}$$

Figure 14(c), Fluorite structure

6.4   Antifluorite Structure

This structure is shown by Li_2O. In the antifluorite structure, O^{2-} ions forms FCC lattice and Li^+ ions occupy all tetrahedral voids. The effective number of Li^+ and O^{2-} ions in a unit cell are 8 and 4 respectively, so the general formula is Li_8O_4 or Li_2O. Antifluorite structure in just reverse of fluorite structure because the positions of cations and anions are interchanged i.e. cations in fluorite structure occupy FCC lattice sites but the same sites in antifluorite structure are occupied by anions. The coordination number of Li^+ ions is 4 (as they occupy tetrahedral voids) and that of O^{2-} ions is 8.

Thus, the general formula of antifluorite structure using coordination number of ions is also Li_8O_4 or Li_2O. This type of structure is also exhibited by oxides of other alkali metals like Na_2O, K_2O etc.

Let 'a' be the edge length of the unit cell and r_c and r_a represents the radius of cation and anion respectively, so
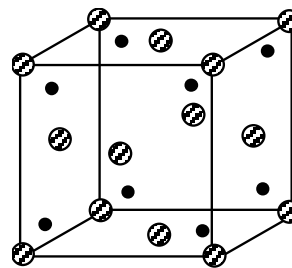
$$r_c + r_a = \frac{\sqrt{3}\,a}{4}$$

Figure 14(d), Antifluorite structure

6.5.   CESIUM HALIDE STRUCTURE

This type of structure is exhibited by cesium chloride. Chloride ions exist as primitive cubic and cesium ions occupy body centered position (cubic void). Overall this structure is referred as BCC−like structure. The effective number of Cs^+ and Cl^- ions are one each, so the general formula is CsCl. The coordination number of both the ions (Cs^+ and Cl^-) is 8, so the general formula using coordination number of ions is Cs_8Cl_8 or CsCl.

This kind of structure is also exhibited by other halides of cesium and by the halides of ammonium like NH_4Cl, NH_4Br etc.

Let the radius of Cs^+ and Cl^- be r_c and r_a respectively and the edge length of the unit cell be 'a', then
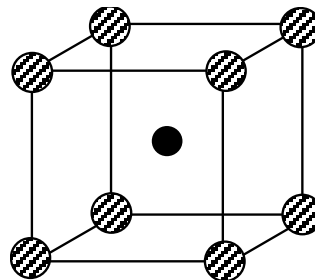
$$r_c + r_a = \frac{\sqrt{3}\,a}{2}$$

Figure 14(f), Cesium chloride structure

Illustration 5

NH$_4$Cl crystallizes as body centered cubic lattice with unit cell distance of 387 pm. Calculate
(a) the distance between the oppositely charged ions in the lattice and
(b) the radius of the NH_4^+ ion, the radius of the Cl^- ion is 181 pm.

Solution:

(a) In bcc lattice, oppositely charged ions touch each other along the body diagonal of the cube.

$$\therefore \quad \sqrt{3}\, a = 2r^+ + 2r^-$$

$$(r^+ + r^-) = \frac{\sqrt{3}\,a}{2} = \textbf{335.15 pm}$$

(b) $\because \quad r^- = 181$ pm

$$r^+ = (335.15 - 181) = \textbf{154.15 pm.}$$

6.6 Corundum Structure

This type of structure is exhibited by Al$_2$O$_3$. The oxides of trivalent metal cations crystallize in corundum structure. The oxide ions form hexagonal primitive lattice and trivalent cations (A^{3+}) fill two–third of the octahedral voids. So, the general formula is $A_{\frac{2}{3}\times 6}O_6$ or A$_2$O$_3$. Examples include Fe$_2$O$_3$, Al$_2$O$_3$, Cr$_2$O$_3$, Mn$_2$O$_3$ etc.

6.7 Rutile Structure

This type of structure is represented by TiO$_2$. In the rutile structure, O^{2-} ions exists in hexagonal primitive while Ti^{4+} ions occupy half of the octahedral voids. The effective number of Ti^{4+} and O^{2-} ions in a unit cell are 3 and 6 respectively, so the general formula is Ti$_3$O$_6$ or TiO$_2$. The coordination number of Ti^{4+} ion is 6 while that of O^{2-} ion is 3. Thus, from an alternative view point (using coordination number of ions), the general formula is Ti$_3$O$_6$ or TiO$_2$.
Examples include MnO$_2$, SnO$_2$, MgF$_2$, NiF$_2$ etc.

6.8 Pervoskite Structure

This type of structure is exhibited by CaTiO$_3$ and is a prototype of the ABO$_3$ type of solids, with A as a divalent cation and B as tetravalent cation. The bivalent ions (A^{2+}) are present in primitive cubic lattice with O^{2-} ions on all the face centres. A^{2+} and O^{2-} ions combindly form FCC–like structure. The tetravalent cation (B^{4+}) occupy the central octahedral void (in the centre of the unit cell). So, the general formula is ABO$_3$. Other examples include BaTiO$_3$, SrTiO$_3$ etc.

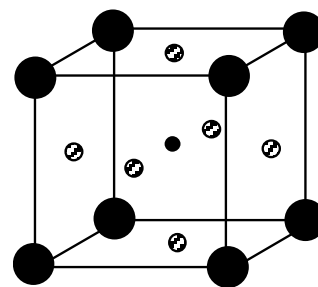**Figure 14(g), Pervoskite structure**

6.9 Spinel and Inverse Spinel Structure

Spinel itself is the mineral MgAl$_2$O$_4$ and spinels in general have the formula AB$_2$O$_4$ where A is a divalent cation and B is a trivalent cation. The spinel structure consists of an FCC arrangement of O^{2-} ions in which the

divalent cation occupies one–eight of the tetrahedral voids and trivalent cation occupies one–half of the octahedral voids. Examples include $ZnAl_2O_4$, $Fe^{II}Fe_2^{III}O_4$, $Co^{II}Co_2^{III}O_4$, $Mn^{II}Mn_2^{III}O_4$, $FeCr_2O_4$, $FeAl_2O_4$ etc.

Many substances of the type $A[B_2]O_4$ also have this structure in which A is a tetravalent cation and B is a divalent cation. Square brackets denote the species, which occupy octahedral void.

In an inverse spinel structure, O^{2-} ions form FCC lattice, A^{2+} ions occupy one–eight of the tetrahedral voids and trivalent cation occupies one–eight of the tetrahedral voids and one–four of the octahedral voids.

7.   Crystals Defects

Till now, we have assumed that all lattice structures were perfect or ideal but in real practice, crystal lattices have substantial number of defects. These defects affect the mechanical, electrical and optical properties of the solids.

We will discuss about the crystal defects (lattice imperfections) in lattices made up of atoms only and also in ionic lattices. Let us first consider lattice imperfections in lattices made up of atoms only. The lattice imperfections are classified according to their geometric characteristics. There are crystal defects of four types in such lattices. These are

(a) Vacancy   (b) Self interstitial
(c) Substitutional impurity   (d) Interstitial impurity

If an atom is missing from a lattice site, it creates a vacancy. Due to vacancy, density of the crystal decreases. Due to absence of atoms from lattice sites, the occupancy of the lattice sites decreases and the percentage occupancy of such crystals can be determined as

$$\text{Percentage occupancy} = \frac{No.\,of\,atoms\,actually\,present\,at\,the\,lattice\,site}{No.\,of\,atoms\,theoretically\,present\,at\,the\,lattice\,site\,assuming\,no\,vacancy\,defect}$$

$$= \frac{\text{Observed density}}{\text{Theoretical density}} \times 100$$

If an atom leaves its lattice site and occupies some interstitial space, then the defect is referred as self interstitial defect. Due to this defect, density of the crystal remains unaffected.

If a foreign atom displaces or substitutes a host atom (which forms lattice) and occupies its lattice site, the defect is called substitutional impurity. Such defects can alter the density of the crystal depending upon the mass of the replacing atom relative to replaced atom.

If the foreign atoms do not occupy a lattice site but occupies some interstitial space, then the defect is referred as interstitial impurity. Due to such defects, the density of the crystal increases.
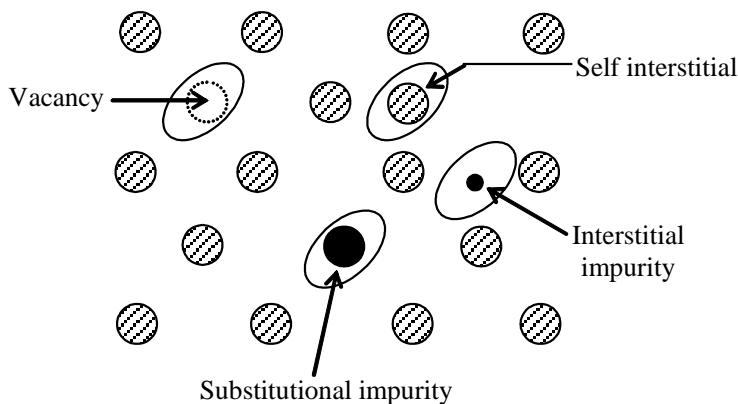

Figure 15(a), Type of crystal defects in a lattice made up of atoms only.

Now, let us consider these crystal imperfections in ionic crystals.

A vacancy at a cation site is mostly accompanied by a vacancy at a nearby anion site. Such paired cation−anion vacancies are referred as **Schottky defect**. Such defect preserves the electrical neutrality of the crystal but the density of crystal decreases.

When an ion (cation or anion) leaves its lattice point and occupies some interstitial space, the defect is called **Frenkel defect.** This defect also preserves the electrical neutrality of the crystal and the density of the crystal also remains unaltered.

Frenkel defects arise easily when the anions are larger and the cations are smaller in size or when the crystal structure is of an open type with large interstitial spaces.

Let us have a solution containing Ba^{2+} ions, contaminated with some Sr^{2+} ions and we want to crystallize $BaSO_4$ by adding SO_4^{2-} ions to the solution. Since, Ba^{2+} and Sr^{2+} ions have same charge and nearly similar size, so during the formation of $BaSO_4$ lattice, inevitably some Sr^{2+} will also be incorporated in place of Ba^{2+}. Thus, Ba^{2+} is substituted by Sr^{2+} in $BaSO_4$ lattice. Such defects are called substitutional impurity defect. Due to such defects, the electrical neutrality is preserved but the density of crystal changes. Such substitutional impurity defects are very common in ionic compounds of the transition metals, as many of the transition metal ions are of the same charge and are very nearly of the same size.

In a crystal lattice of titanium carbide, in which C^{4-} forms FCC lattice and Ti^{4+} occupies all octahedral voids, when hydrogen gas is passed through such crystal, it is trapped in the tetrahedral voids. So, H_2 acts as an interstitial impurity in TiC lattice. Due to such defects, density of the crystal lattice increases.

A simple anion vacancy in an ionic crystal creates an excess of positive charge. An electron can be trapped and migrate to this anionic vacancy site, which in effect replaces the absent negative ion. The presence of a number of such defects imparts colour to an otherwise colourless crystal. This type of imperfection is called F−centre (F stands for Farbe, a German word for colour).
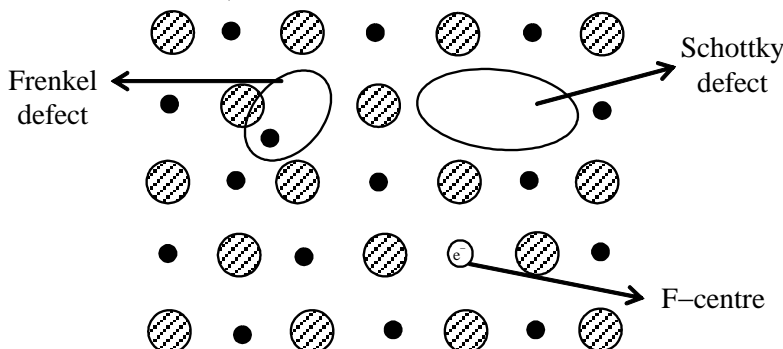
Figure 15(b), Type of crystal defects in an ionic lattice

Illustration 6

Li forms a body centered cubic lattice. If the edge length of the lattice is 3.5×10^{-10} m and the observed density is 5.3×10^2 kg m^{-3}, calculate the percentage occupancy of lattice points by Li metal.

Solution:

Theoretical density obtained by $\dfrac{n \times M}{N_{AV} \times V}$ is with the assumption that each lattice point is occupied by the constituent species. But generally, some lattice points are not occupied by the constituent particles due to some defect in the crystal lattice. These points are called vacancies. The density obtained considering vacancies is called observed density and is surely less than the theoretical density.

Theoretical density $= \dfrac{2 \times 7 \times 10^{-3}}{6.023 \times 10^{23} \times (3.5 \times 10^{-10})^3} = 5.42 \times 10^2$ kg m^{-3}

% occupancy $= \dfrac{\text{Observed density}}{\text{Theoretical density}} \times 100$

% occupancy $= \dfrac{5.3 \times 10^2}{5.42 \times 10^2} \times 100 = \mathbf{97.78\%}$

Illustration 7

Calcium crystallizes in a face−centered cubic unit cell with a = 0.556 nm. Calculate the density if

(i) it contains 0.1% Frenkel defects   (ii) it contains 0.1% Schottky defects.

Solution:

The density of crystal is unaffected due to Frenkel defect as the atom only occupies an interstitial position instead of lattice site while Schottky defect changes the density of crystal.

(i) The density of crystal when the crystal contained 0.1% Frenkel defects, would thus be

$$\rho = \dfrac{n \times M}{N_{AV} \times a^3} = \dfrac{4 \times 40}{6.023 \times 10^{23} \times (0.556 \times 10^{-7})^3}$$

$$\rho = \mathbf{1.5455 \ g/cm^3}$$

(ii) Since the crystal contains 0.1% Schottky defect (in which the atoms are missing from lattice site), so the mass of crystal decreases by 0.1% assuming the volume of crystal remain same. Thus, the density of the crystal also decreases by 0.1%.

$$\therefore \qquad \rho' = \rho\left(1 - \dfrac{0.1}{100}\right) = 0.999 \ \rho = 0.999 \times 1.5455$$

$$\rho' = \mathbf{1.5439 \ g/cm^3}$$

8   Solved Fundamental Examples

Example 1

A substance form face−centered cubic crystals. Its density is 1.984 g cm^{-3} and edge length of the unit cell is 630 pm. Calculate the molar mass of the substance.

Solution:

Since $\rho = \dfrac{n \times M}{N_{AV} \times a^3}$, we get $M = \dfrac{\rho \times a^3 \times N_{AV}}{n}$

Substituting the values, we have

$$M = \dfrac{1.984 \times (6.30 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = 74.7 \ \text{g mol}^{-1}$$

Example 2

Use the data given below to find the type of cubic lattice to which the crystal belongs:

	Fe	V	Pd
a/pm	286	301	388
ρ/g cm^{-3}	7.86	5.96	12.16

Solution:

The density of a cubic unit cell is given by

$$\rho = \dfrac{n \times M}{N_{AV} \times a^3}$$

$$\therefore \qquad n = \dfrac{\rho \times a^3 \times N_{AV}}{M}$$

For Fe, $n_{Fe} = \dfrac{7.86 \times (2.86 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{55.85} = 1.982 \approx 2$

Hence, the cubic lattice of Fe is body−centered.

For V, $n_V = \dfrac{5.96 \times (3.01 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{50.94} = 1.921 \approx 2$

Hence, the cubic lattice for V is body–centered.

For Pd $n_{Pd} = \dfrac{12.16 \times (3.88 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{106.4} = 4.02 \approx 4$

Hence, the cubic lattice for Pd is face–centered.

Example 3

(a) Spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one–eight of the tetrahedral holes occupied by one type of metal ion and one–half of the octahedral holes occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-} with Zn^{2+} in the tetrahedral holes. Give formula of the spinel.
(b) If all the species in problem (a) touch each other, determine the fraction of the volume occupied by ions in the unit cell.

Solution:

(a) Number of oxide ions per unit cell $= \left(\dfrac{1}{8} \times 8\right) + \left(\dfrac{1}{2} \times 6\right) = 4$,

Number of Zn^{2+} ions per unit cell $= \left(\dfrac{1}{8} \times 8\right) = 1$

and number of Al^{3+} ions per unit cell $= \left(\dfrac{1}{2} \times 4\right) = 2$

Thus, the formula of spinel is $ZnAl_2O_4$.

(b) For FCC lattice, $4r_{O^{2-}} = \sqrt{2}\, a$,

For octahedral void, $(r_{O^{2-}} + r_{Al^{3+}}) = \dfrac{a}{2}$

and for tetrahedral void, $(r_{O^{2-}} + r_{Zn^{2+}}) = \dfrac{\sqrt{3}\, a}{4}$

$\therefore \quad a = 2\sqrt{2}\, r_{O^{2-}}$,

$r_{O^{2-}} + r_{Al^{3+}} = \sqrt{2}\, r_{O^{2-}}$

$\therefore \quad r_{Al^{3+}} = (\sqrt{2} - 1)\, r_{O^{2-}} = 0.414\, r_{O^{2-}}$

and $r_{O^{2-}} + r_{Zn^{2+}} = \dfrac{\sqrt{3} \times 2\sqrt{2}\, r_{O^{2-}}}{4} = \sqrt{\dfrac{3}{2}}\, r_{O^{2-}} = 1.225\, r_{O^{2-}}$

$\therefore r_{Zn^{2+}} = 0.225\, r_{O^{2-}}$

Packing fraction $= \dfrac{\left[4 \times \dfrac{4}{3}\pi(r_{O^{2-}})^3\right] + \left[1 \times \dfrac{4}{3}\pi(0.225\, r_{O^{2-}})^3\right] + \left[2 \times \dfrac{4}{3}\pi(0.414\, r_{O^{2-}})^3\right]}{(2\sqrt{2}\, r_{O^{2-}})^3}$

$= \dfrac{\dfrac{4}{3}\pi(r_{O^{2-}})^3\left[4 + (0.225)^3 + 2(0.414)^3\right]}{16 \times \sqrt{2} \times (r_{O^{2-}})^3} = \dfrac{\pi \times 4.15329}{12\sqrt{2}} = 0.77$

Example 4

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

Solution:

Due to addition of $SrCl_2$, each Sr^{2+} ion replaces two Na^+ ions, but occupies only one Na^+ lattice point. This creates one cationic vacancy.

Number of moles of Sr^{2+} present in 100 mole of NaCl $= 10^{-3}$

Number of moles of cation vacancy in 100 mole of NaCl $= 10^{-3}$

Number of moles of cation vacancies in 1 mol $= \dfrac{10^{-3}}{100} = 10^{-5}$ mol

Total cationic vacancies $= 10^{-5} \times N_{AV} = 10^{-5} \times 6.02 \times 10^{23} = 6.02 \times 10^{18}$

Example 5

In diamond, carbon atoms occupy FCC lattice points as well as alternate tetrahedral voids. The edge length of the unit cell is 356.7 pm. Calculate

(a) the closest distance between carbon atoms and

(b) the fraction of total volume occupied by carbon atoms.

Solution:

If a sphere is present in a tetrahedral void surrounded by same kind of spheres, then the spheres present at corners of tetrahedron will not touch each other but the sphere in tetrahedral void touches all spheres present at the corner of the tetrahedron.

$\therefore \qquad 2r_c = \dfrac{\sqrt{3}\,a}{4}$

$2r_c = \dfrac{\sqrt{3} \times 356.7}{4} = 154.45$ pm

$\therefore$ Radius of carbon atom $= \dfrac{154.45}{2} = 77.225$ pm

Fraction of total volume occupied by carbon atoms $= \dfrac{8 \times \dfrac{4}{3} \times \dfrac{22}{7} \times (77.225 \times 10^{-12})^3}{(356.7 \times 10^{-12})^3} = 0.34$

Example 6

Metallic gold crystallises in FCC lattice. The edge length of the cubic unit cell is 4.07Å.

(a) What is the closest distance between gold atoms?

(b) How many "nearest neighbours" does each gold atom have at the distance calculated in (a)?

(c) What is the density of gold?

(d) Prove that the packing fraction of gold is 0.74.

Solution:

(a) In FCC lattice, the face centered atom touches four corner atoms of that face.

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

or, $\qquad 2r = \dfrac{\sqrt{2}\,a}{2} = \dfrac{a}{\sqrt{2}}$

Closest distance between two gold atoms $= 2r = \dfrac{a}{\sqrt{2}} = \dfrac{4.07}{\sqrt{2}} = 2.87$ Å

(b) If we consider a face centered gold atom, it has four corner and eight adjacent face centre atoms present at $\dfrac{a}{\sqrt{2}}$ distance. Therefore, there are 12 nearest neighbours.

(c) Density $(\rho) = \dfrac{n \times M}{N_{AV} \times a^3} = \dfrac{4 \times 197}{6.023 \times 10^{23} \times (4.07 \times 10^{-8})^3} = 19.4$ g/cc

(d) Packing fraction $= \dfrac{4 \times \dfrac{4}{3} \pi r^3}{\left(\dfrac{4r}{\sqrt{2}}\right)^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74$

Example 7

In a face–centered unit cell with all the lattice positions occupied by A atoms, the body–centered octahedral hole in it is occupied by atom B of appropriate size. For such a crystal, calculate the void space per unit volume of unit cell. Also predict the formula of the compound.

Solution:

Let 'a' be the edge length of the cube. For FCC unit cell,

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

or $\qquad\qquad a = 2\sqrt{2}\, r_A$

Now, since the atom B occupies body–centered octahedral hole, it is obvious that

$\qquad 2r_A + 2r_B = a$

or $\qquad\qquad 2r_A + 2r_B = 2\sqrt{2}\, r_A$

or $\qquad\qquad 2r_B = (\sqrt{2}-1)2r_A$

or $\qquad \dfrac{r_B}{r_A} = \sqrt{2} - 1 = 1.414 - 1.0 = 0.414$

Volume of the cube $= a^3 = 16\sqrt{2}\, r_A^3$

Volume occupied by A and B atoms $= \left(4 \times \dfrac{4}{3} \pi r_A^3\right) + \left(\dfrac{4}{3} \pi r_B^3\right) = \dfrac{4}{3} \pi (4r_A^3 + r_B^3)$

Volume occupied by atoms per unit volume of unit cell is given by

Packing fraction $= \dfrac{\dfrac{4}{3} \pi (4r_A^3 + r_B^3)}{16\sqrt{2}\, r_A^3} = \dfrac{\pi}{12\sqrt{2}} \times \dfrac{[4r_A^3 + (0.414 r_A)^3]}{r_A^3} = \dfrac{\pi \times r_A^3 [4 + (0.414)^3]}{12\sqrt{2} \times r_A^3} = 0.754$

$\therefore$ Void fraction $= 1 - 0.754 = \mathbf{0.246}$

Number of effective A per unit cell $= \left(\dfrac{1}{8} \times 8\right) + \left(\dfrac{1}{2} \times 6\right) = 4$

Number of effective B per unit cell $= 1$

$\therefore$ Formula of the compound $= \mathbf{A_4B}$

Example 8:

A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.

Solution:

We have to assume here that the decrease in density is not due to volume change but due to loss of Ge atoms only. Let x be the total number of Ge atoms missing and y be the number of boron atoms replacing germanium atoms. Assuming volume of the crystal remaining same, then 4% decrease in density will also decrease weight of the crystal (sample) by 4%.

$$\therefore \quad 1 - \left(x \times \frac{72.6}{N_{AV}} \right) + \left(y \times \frac{11}{N_{AV}} \right) = 0.96$$

$$0.04 = \left(x \times \frac{72.6}{N_{AV}} \right) - \left(y \times \frac{11}{N_{AV}} \right)$$

$$\text{where } y = \left(\frac{150\, N_{AV}}{10^6 \times 11} \times 0.96 \right)$$

$$\text{or} \quad \frac{y \times 11}{N_{AV}} = \frac{150 \times 0.96}{10^6}$$

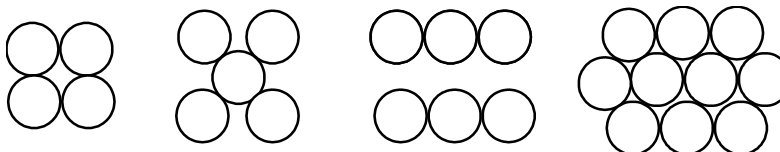$$0.04 = \left(x \times \frac{72.6}{N_{AV}} \right) - \left(\frac{150 \times 0.96}{10^6} \right)$$

$$\therefore \quad x = \frac{(0.04 + 1.44 \times 10^{-4})\, N_{AV}}{72.6} \simeq \frac{0.04 N_{AV}}{72.6}$$

$$\therefore \quad \frac{y}{x} = \frac{150\, N_{AV} \times 0.96 \times 72.6}{10^6 \times 11 \times 0.04 N_{AV}} = 2.376 \times 10^{-2}$$

$$\therefore \quad \frac{y}{x} \times 100 = 2.376 \times 10^{-2} \times 100 = \mathbf{2.376\%}$$
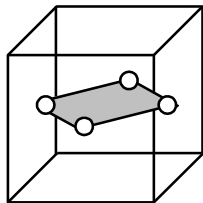
Example 9.

Iron crystallizes in FCC lattice. The figures given below shows the iron atoms in four crystallographic planes.
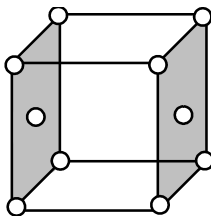
Draw the unit cell for the corresponding structure and identify these planes in the diagram. Also report the distance between two such crystallographic planes in each case in terms of the edge length (a) of the unit cell.
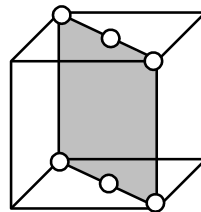
Solution:

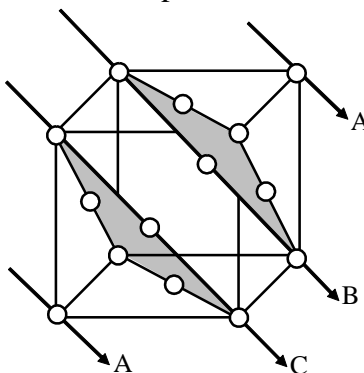| Distance between two such planes = a | Distance between two such planes = a | Distance between two such planes = a |

Distance between two such planes = $\dfrac{\sqrt{3}\,a}{3} = \dfrac{a}{\sqrt{3}}$

Example 10.

Marbles of diameter 10 mm are to be placed on a flat square surface (side = 40 mm), such that each marble has centre within the square. Find the maximum number of marbles per unit area and sketch the diagram. Derive an expression for the number of marbles per unit area.
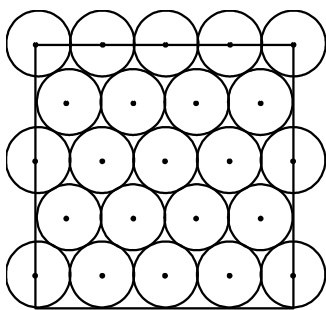
Solution:

(b)

Fig.1

There are 18 marbles effectively present with centres within the square. Therefore the number of marbles per unit area is $\dfrac{18}{(40)^2} = \dfrac{18}{1600}$ marbles/sq.mm

It can be seen from figure 1 that every circle is surrounded by 6 circles (for maximum packing) of equal size. Consider figure 2. If we join the centres of all the circles we get a hexagon. Let us find the number of effective circles in a hexagon. Each corner circle. (whose centres are marked as A, B, C, D, E, & F) would contribute 1/3 of their area to the hexagon. The central circle would contribute completely. Therefore, the effective number of circles in a hexagon of the type shown

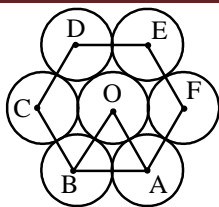is $\left(\dfrac{1}{3}\times 6\right)+1=3$.

Fig. 2

Area of hexagon is six times the area of an equilateral triangle ABO.

Area of one equilateral triangle $= \dfrac{\sqrt{3}}{4} \times d^2$ where d is the diameter of marble. Therefore, area of hexagon ABCDEF $= 6 \times \dfrac{\sqrt{3}}{4} d^2$. Therefore,

number of spheres in unit area $= \dfrac{3}{6 \times \dfrac{\sqrt{3}}{4} \times d^2} = \dfrac{2}{\sqrt{3} d^2}$.

Example 11.

A compound AB has a rock salt type structure with A : B = 1 : 1. The formula weight of AB is 6.023 Y amu and the closest A–B distance is $Y^{1/3}$ nm.

(i) Find the density of lattice.

(ii) If the density of lattice is found to be 20 kg m^{-3}, then predict the type of defect.

Solution:

Edge length of unit cell of AB $= 2Y^{1/3} \times 10^{-9}$ m

(i) Density of AB $= \dfrac{Z \times M}{N_o \times V} = \dfrac{4 \times 6.023 Y \times 10^{-3}}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9})^3}$ kg m^{-3} = **5.0 kg m^{-3}**.

(ii) Since, the observed density (20 kg m^{-3}) of AB is higher than theoretical density, the compound AB has either interstitial impurity defect or substitutional impurity defect.