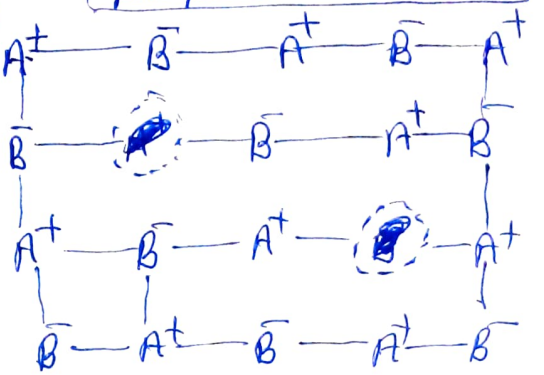
Expression for Schottky Defect:→ Or Schottky defect is proportional to N (1)

N- total number of pairs of cation and ions

n- number of pairs removed or number of Schottky defects.



E_p - energy required to remove a pair of cation and ion

The total number of ways in which we can create n- Schottky defects or n-pairs

$$W = \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

If defect is produced then entropy will increase.

$$S = k_B \ln W$$

↳ Boltzmann constant

$$S = k_B \ln \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

Corresponding change in free energy,

$$F = U - TS$$

↳ Internal energy → entropy

↳ Temp

↳ Free energy - the capacity of a system to do work.

$$F = \underbrace{nE_p}_{U = nE_p} - k_B T \ln \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

↳ energy (internal) produce to produce n-pairs

$$F = nE_p - k_B T \ln \left[\frac{N!}{(N-n)!\,n!}\right]^2$$

Applying Stirling's formula to simplify factorial terms i.e.

$$\ln\left[\frac{N!}{(N-n)!\,n!}\right]^2 = 2\ln\left[\frac{N!}{(N-n)!\,n!}\right]$$

$$= 2\left[\ln N! - \ln(N-n)!\,n!\right]$$

$$= 2\left[\ln N! - \{\ln(N-n)! + \ln n!\}\right] = 2\left[\ln N! - \ln(N-n)! - \ln n!\right]$$

$$= 2\left[N\ln N - N - \{(N-n)\ln(N-n) - (N-n)\} - \{n\ln n - n\}\right]$$

$$= 2\left[N\ln N - N - (N-n)\ln(N-n) + N - n\ln n + n\right]$$

$$= 2\left[N\ln N - (N-n)\ln(N-n) - n\ln n\right]$$

$$F = nE_p - 2k_BT\left[N\ln N - (N-n)\ln(N-n) - n\ln n\right]$$

Diff above eqn wrt n at constn T

$$\left(\frac{\partial F}{\partial n}\right)_T = E_p - 2k_BT\left[0 - \left\{\frac{(N-n)(-1)}{(N-n)} + \ln(N-n)(-1)\right\} - \left\{\frac{n}{n}\cdot\frac{1}{n} + \ln n\right\}\right]$$

$$= E_p - 2k_BT\left[1 + \ln(N-n) - 1 - \ln n\right]$$

$$= E_p - 2k_BT\left[\ln(N-n) - \ln n\right]$$

$$\left(\frac{\partial F}{\partial n}\right)_T = E_p - 2k_BT\ln\frac{(N-n)}{n}$$

Free energy at constant temp T, remains constant So $\left(\frac{\partial F}{\partial n}\right)_T = 0$

$$E_p - 2k_BT\ln\frac{(N-n)}{n} = 0$$

$$\ln\frac{(N-n)}{n} = \frac{E_p}{2k_BT} \Rightarrow n = (N-n)\,e^{-E_p/2k_BT}$$

If $N \gg n$

$$n = N\,e^{-E_p/2k_BT}$$

$n \ll N$

Frenkel Defect :→

N - total number of ions

N_i - interstial ions

E_i - energy required to produce ~~interstial~~ interstitial ions

The total number of ways in which n-Frenkel defects can be produced.

$$W = \frac{N!}{(N-n)!\,n!}\,\frac{N_i!}{(N_i-n)!\,n!}$$

The entropy, $S = K_B \ln W$

$$S = K_B \ln\left[\frac{N!}{(N-n)!\,n!}\,\frac{N_i!}{(N_i-n)!\,n!}\right]$$

Free energy, $F = U - TS$

$$F = nE_i - TK_B \ln\left[\frac{N!}{(N-n)!\,n!}\,\frac{N_i!}{(N_i-n)!\,n!}\right]$$

Differentiating wrt to n and putting equal ~~zero~~ to zero.

$$\left(\frac{\partial F}{\partial n}\right)_T = 0$$

we get

$$\boxed{n = (N N_i)^{1/2}\, e^{-\frac{E_i}{2K_B T}}}$$

It shows that the concentration of Frenkel defect is proportional to $(N N_i)^{1/2}$

Experiment :

Date
Page No

Derive Relation between Lattice constant a and Density of crystal

$$a = \left(\frac{nM}{N\rho}\right)^{1/3}$$

Let $a \rightarrow$ lattice constant of cubic lattice

$\rho \rightarrow$ density of crystal

If a is the lattice constant of cubic lattice, then

the volume of unit cell $= a^3$

mass of unit cell $= a^3\rho$ — (1)

If m is the molecular weight & N is Avogadro number, then

Mass of each molecule $= \frac{M}{N}$

If n is number of molecules in unit cell, then

mass of unit cell $= \frac{nM}{N}$ — (2)

eq (1) = eq (2)

$$a^3\rho = \frac{nM}{N}$$

$$a = \left(\frac{nM}{\rho N}\right)^{1/3}$$

this is relation b/w density of crystalline material ρ and lattice constant a.

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4.3 CRYSTAL STRUCTURES OF MATERIALS

We know that the atoms, molecules or ions arranged in the fourteen Bravais lattices under seven crystal systems. Each lattice point is occupied by atoms, molecules or ions. For simplicity, the atoms, molecules and ions are assumed to be solid sphere. First, we have to discuss some important parameters, which are used to describe the crystal structure of the materials.

1. ***Number of atoms, molecules or ions per unit cell (n).*** The total number of atoms, molecules or ions present in an unit cell is known as number of atoms per unit cell.
2. **Co-ordination number *(CN).*** It is the number of nearest neighbouring atoms molecules or ions to a particular atom.
3. ***Atomic radius (r).*** It is the radius of an atom. It is also defined as half the distance between two nearest neighbouring atoms in a crystal.
4. ***Atomic packing factor (APF) or Density of packing.*** It is the ratio of volume occupied by the atoms, molecules or ions in a unit cell (v) to the total volume of the unit cell (V).

$$\text{APF} = \frac{\text{Volume occupied by the atoms in an unit cell}}{\text{Volume of the unit cell}}$$

$$\Rightarrow \quad \text{APF} = \frac{\text{Number of atoms present in an unit cell} \times \text{Volume of an atom}}{\text{Volume of the unit cell}}$$

i.e.,

$$\text{APF} = \frac{v}{V} \qquad \ldots(4.4)$$

The above mentioned parameters are discussed for simple cubic (*sc*), body centered cubic (*bcc*), face centered cubic (*fcc*) and hexagonal closed packed (*hcp*) crystal structures in detail in the following sections :

4.3.1 Simple Cubic (sc) Structure

A simple cubic unit cell consists of eight corner atoms as shown in Fig. 4.12. The atoms touch along cube edge.

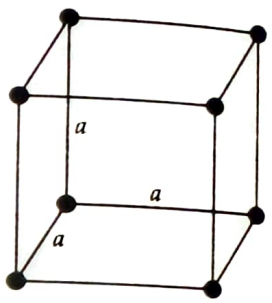

Fig. 4.12 Simple Cubic Structure.

In actual crystals, each and every corner atom is shared by eight adjacent unit cells. The contribution of each and every corner atom to one unit cell is (1/8).

∴ The total number of atoms present in a unit cell

$$= \frac{1}{8} \times 8 = 1$$

Co-ordination Number (CN)

Let us consider any corner atom. For this atom, there are four nearest neighbours in its own plane. There is another nearest neighbour in another plane, which lies just below this atom. Therefore the total number of nearest neighbours is six. Hence the coordination number is 6.

Figure 4.13 shows the coordination number in simple cubic structure.

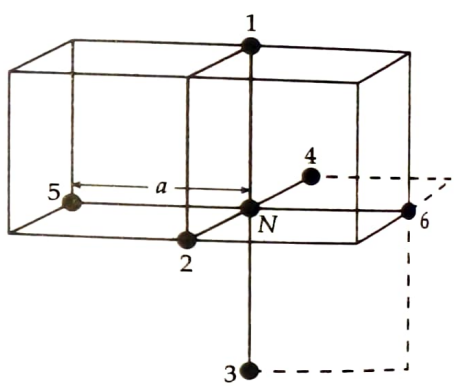

Fig. 4.13 Six atoms in Simple Cubic Structure.

Atomic Radius (*r*)

Since the atoms touch along cube edges, the atomic radius for a simple cubic unit cell is $r = \frac{a}{2}$ (where $a = 2r$ is the lattice constant).

Atomic Packing Factor (Atomic Packing Density) APF

$$\text{APF} = \frac{v}{V}$$

$$v = 1 \times \frac{4}{3}\pi r^3 ;$$

$$V = a^3$$

Then $$\text{APF} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4\pi r^3}{3a^3} \quad \ldots(4.5)$$

Substituting $r = \frac{a}{2}$, we get

$$\text{APF} = \frac{4\pi\left(\frac{a}{2}\right)^3}{3a^3} = \frac{4\pi a^3}{8 \times 3a^3} = \frac{\pi}{6}$$

$\therefore$ Packing density $= \frac{\pi}{6} = 0.5233$

$\therefore$ $$\text{APF} = 0.52 \quad \ldots(4.6)$$

Thus 52% of volume of the simple cubic unit cell is occupied by atoms and the remaining 48% volume of the unit cell is vacant or void space.

4.3.2 Body Centered Cubic (*bcc*) Structure

A body centered cubic structure has eight corner atoms and one body centered atom. The atom at centre touches all eight corner atoms. The *bcc* structure is shown in Fig. 4.14.

In *bcc* unit cell, each and every corner atom is shared by eight adjacent unit cells.

So, the total number of atoms contributed by the corner atoms is

$$\frac{1}{8} \times 8 = 1.$$

A *bcc* unit cell has one full atom at the centre of the unit cell.

$\therefore$ Total number of atoms present in *bcc* unit cell

$$= 1 + 1 = 2$$

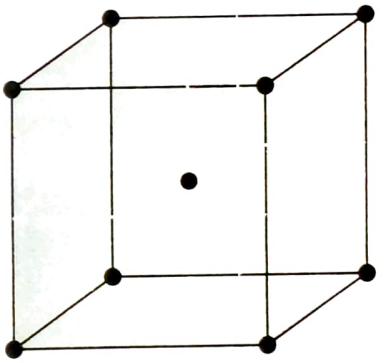

Fig. 4.14 Body Centered Cubic Structure.

Coordination Number (CN)

Let us consider a body centered atom. The nearest neighbour for a body centered atom is a corner atom. A body centered atom is surrounded by eight corner atoms.

Therefore, the coordination number of a *bcc* unit cell = 8.

Figure 4.15 shows 8 atoms in bcc unit cell.

Atomic Radius (r)

For a body centered cubic unit cell, the atomic radius can be calculated by the following way :

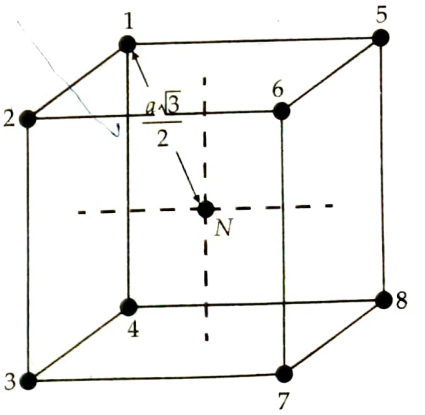

Fig. 4.15 Eight atoms in bcc crystal.

From Fig. 4.16, $AG = 4r$ and $DG = a$

From ΔAGD, $AD^2 + DG^2 = AG^2$ ...(4.7)

For AD, from ΔABD

$$AB^2 + BD^2 = AD^2 \quad \text{...(4.8)}$$

or $$a^2 + a^2 = AD^2 \quad i.e., \quad AD^2 = 2a^2$$

Therefore, $AD = \sqrt{2}\, a$

Substituting the values of AD, AG and DG in Eq. (4.7), we get

$$AD^2 + DG^2 = AG^2$$

or $$2a^2 + a^2 = (4r)^2 \quad i.e., \quad 16r^2 = 3a^2$$

or $$r^2 = \frac{3}{16} a^2$$

Therefore, the atomic radius $r = \frac{\sqrt{3}}{4} a$ ...(4.9)

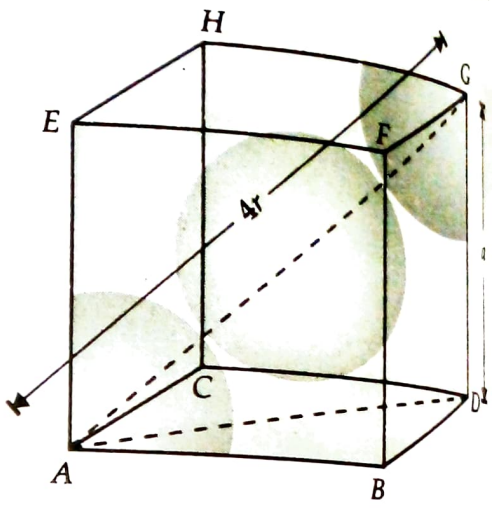

Fig. 4.16 Calculation of atomic radius.

Atomic Packing Factor (APF)/Packing Density

$$\text{APF} = \frac{v}{V}$$

The number of atoms present in an unit cell = 2

$\therefore$ $$v = 2 \times \frac{4}{3} \times \pi r^3 \; ; \quad V = a^3$$

$$\text{APF} = \frac{2 \times \frac{4}{3} \times \pi r^3}{a^3} \quad \text{...(4.10)}$$

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

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

$\Rightarrow$ $$\text{APF} = \frac{\sqrt{3}\pi}{8} = 0.68 \quad \text{...(4.11)}$$

Thus, 68% of the volume of the *bcc* unit cell is occupied by atoms and remaining 32% volume of the unit cell is vacant or void space.

Let us study these structures

(i) Face Centered Cubic (fcc) Structure

A face centered cubic cell consists of eight corner atoms and six face centered atoms. A face centered cubic unit cell is shown in Fig. 4.18.

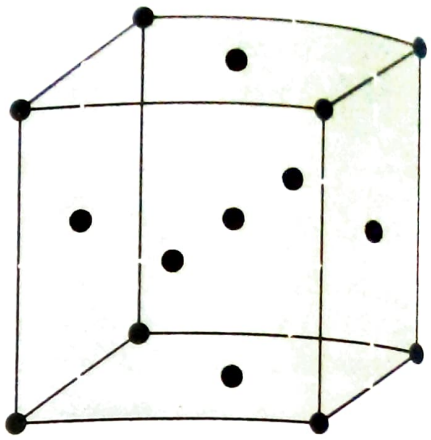

Fig. 4.18 Face centered cubic omit cel

The atom in a *fcc* unit cell touches along the face diagonal. Each and every corner atom is shared by eight adjacent unit cells. Therefore each and every corner atoms contributes 1/8 of its part to one unit cell.

So, the number of atoms contributed by the corner atoms $= \frac{1}{8} \times 8 = 1$.

Two unit cells share each and every face centered atom. Therefore, the contribution of centered atom to unit cell is ½. So the total number of atoms contributed by face centered at $\frac{1}{2} \times 6 = 3$.

$\therefore$ Total number of atoms present in a *fcc* unit cell $= 1 + 3 = 4$.

Coordination Number (CN)

Let us consider a corner atom. In its own plane it touches four face centered atoms. These face centered atoms are its nearest neighbours. In a plane, which lies just above this corner atom, it has four more face centered atoms as nearest neighbours. Similarly, in a plane, which lies just below this corner atom, it has yet four more face centered atoms as its nearest neighbours.

Therefore, the number of nearest neighbour *i.e.*, coordination number for *fcc* unit cell $= 4 + 4 + 4 = 12$. These CN are shown in Fig. 4.19.

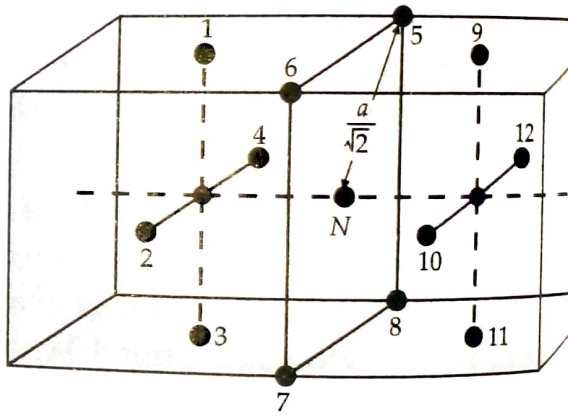

Fig. 4.19 Atoms in fcc crystal.

Atomic Radius (*r*)

The atomic radius can be calculated from Fig. 4.20 as follows :

Consider ΔABC,

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

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

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

The atomic radius

$$r = \frac{a}{2\sqrt{2}} \qquad \ldots(4.12)$$

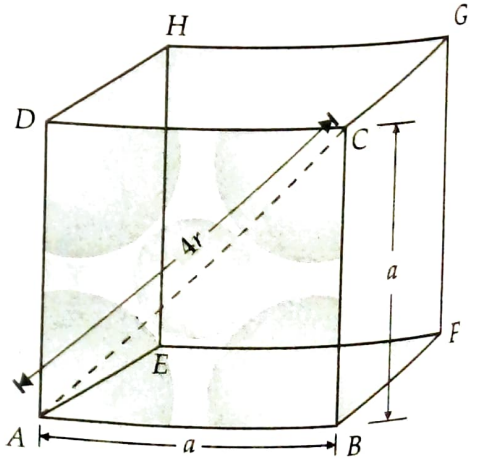

Fig. 4.20 Calculation of atomic radius of *fcc*

Atomic Packing Factor (APF)/Packing Density

$$\text{APF} = \frac{v}{V}$$

$$v = 4 \times \frac{4}{3} \times \pi r^3 \; ; \quad V = a^3$$

$$\text{APF} = \frac{4 \times 4\pi r^3}{3a^3}$$

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

$$\text{APF} = \frac{\pi}{3\sqrt{2}} = 0.74 \qquad \ldots(4.13)$$

Thus 74% of the volume of the *fcc* unit cell is occupied by atoms and the remaining 26%