B.Sc. (Honours) Part-II
Paper-IIIA

Topic: Solid State- Braggs Law & Co-ordination Number

UG
Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)

Atoms, molecules or ions are too small to be seen with naked eye. The arrangement of particles in crystalline solids is determined indirectly by X-ray diffraction. In 1912, **Von Laue** showed that any crystal could serve as a three-dimensional grating to the incident electromagnetic radiation with wavelength approximately equal to the internuclear separations ($\simeq 10^{-8}$ cm) of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum.

The apparatus used is shown in Fig. 4.28. A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence θ. At various angles, strong beams of deflected X-rays strike the photographic plate. The photographic plate after developing shows a central spot due to primary beam and a set of symmetrically disposed spots due to deflected X-rays. Different kinds of crystals produce different arrangements of spots.

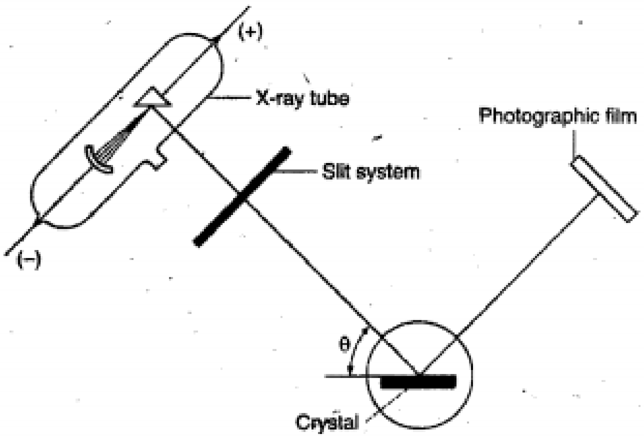


Fig. 4.28 . X-ray diffraction of crystals

In 1913, **Bragg** found that Laue photographs are more easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. Fig. 4.29 illustrates the way by which the crystal spacings can be determined by use of X-rays of a single wavelength, λ. The rays strike the parallel planes of the crystal at angle θ. Some of the rays are reflected from the upper plane, some from the second and some from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase. The waves reflected by different layer planes will be in phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths. OL and OM are the perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

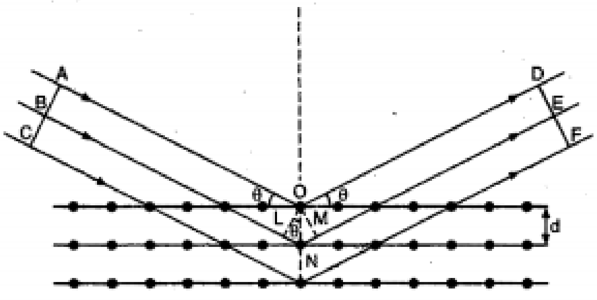


Fig. 4.29 X-ray reflection from crystals

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, the triangles OLN and OMN are congruent, hence $LN = NM$.

So, Path difference = $2LN$

as $LN = d \sin\theta$ where, d is the distance between two planes.

So, Path difference = $2d \sin\theta$

When two reflected waves reinforce each other (maximum reflection), the path difference should be $= n\lambda$ (where, $n = 1, 2, 3, \dots$).

So, for maximum reflection,

$$n\lambda = 2d \sin\theta$$

This relation is called Bragg's equation. Distance between two successive planes d can be calculated from this equation. With X-rays of definite wavelength, reflections at various angles will be observed for a given set of planes separated by a distance d. These reflections correspond to $n = 1, 2, 3$ and so on and are spoken of as first order, second order, third order and so on. With each successive order, the angle θ increases and the intensity of the reflected beam weakens.

The values of θ for the first order reflection from the three faces of sodium chloride crystal were found to be 5.9°, 8.4° and 5.2° respectively. As n and a are same in each case, the distance d between successive planes in three faces will be in the ratio of

$$\frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} = 9.61 : 6.84 : 11.04$$

$$= 1 : 0.70 : 1.14$$

$$= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$$

This ratio corresponds to spacings along the three planes of a face-centred cubic structure. Thus, the NaCl crystal has face-centred cubic structure.

Example 63. *X-rays of wavelength* 1.54 Å *strike a crystal and are observed to be deflected at an angle of* 22.5°. *Assuming that* $n = 1$, *calculate the spacing between the planes of atoms that are responsible for this reflection.*

Solution: Applying Bragg's equation,

$$n\lambda = 2d \sin\theta$$

Given, $n = 1,\ \lambda = 1.54\,\text{Å},\ \theta = 22.5^\circ$.

Using relation $n\lambda = 2d \sin\theta$,

$$d = \frac{1.54}{2 \sin 22.5^\circ} = \frac{1.54}{2 \times 0.383} = 2.01\,\text{Å}$$

Example 64. *The first order reflection of a beam of X-rays of wavelength* 1.54 Å *from the* (100) *face of a crystal of the simple* *cubic type occurs at an angle of* 11.29°. *Calculate the length of the unit cell.*

Solution: Applying Bragg's equation,

$$2d \sin \theta = n\lambda$$

Given, $\theta = 11.29°$, $n = 1$, $\lambda = 1.54$ Å $= 1.54 \times 10^{-8}$ cm

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 11.29°} = \frac{1.54 \times 10^{-8}}{2 \times 0.1957} = 3.93 \times 10^{-8} \text{ cm}$$

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

$$a = 3.93 \times 10^{-8} \text{ cm} = \text{length of the unit cell}$$

Example 65. *When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction* (sin 7.75° = 0.1349)?

Solution: According to Bragg's equation:

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 2.64 \sin 7.75° = 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712 \text{ Å}$$

Energy difference between *K* and *L*-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15} \text{ J}$$

4.21 ANALYSIS OF CUBIC SYSTEMS

The following characteristics are reflected by cubic systems when analysed mathematically:

(i) Atomic Radius

It is defined as half the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge '*a*' of the unit cell of the crystal.

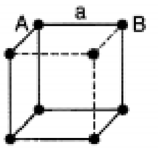


Fig. 4.30
Simple cubic unit cell

(a) Simple cubic unit cell : In a simple cubic unit cell, atoms at the corners touch each other along the edge.

Distance between the nearest neighbours,

$$d = AB = a = 2r$$

(where r = radius of the atom)

or Atomic radius,

$$r = \frac{a}{2} = 0.5\,a$$

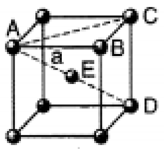


Fig. 4.31
Body-centred cubic unit cell

(b) Body-centred cubic unit cell : The distance between the two nearest neighbours is represented by length *AE* or *ED*, *i.e.*, half of the body diagonal, *AD*.

$$d = AE = ED = \frac{AD}{2}$$

In Δ *ABC*,

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

or $AC = \sqrt{2}a$

Now, in Δ *ADC*,

$$AD^2 = AC^2 + CD^2 = (\sqrt{2}a)^2 + a^2 = 3a^2$$

or $AD = \sqrt{3}a$

$$\therefore \quad d = \frac{\sqrt{3}}{2}a$$

$$d = 2r = \frac{\sqrt{3}}{2}a$$

or Atomic radius, $r = \frac{\sqrt{3}}{4}a$

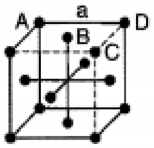


Fig. 4.32
Face-centred cubic unit cell

(c) Face-centred cubic unit cell : The distance between the two nearest neighbours is represented by length *AB* or *BC*, *i.e.*, half of the face diagonal, *AC*.

$$d = AB = BC = \frac{AC}{2}$$

In Δ*ACD*, $AC^2 = CD^2 + AD^2 = a^2 + a^2 = 2a^2$

$$AC = \sqrt{2}a$$

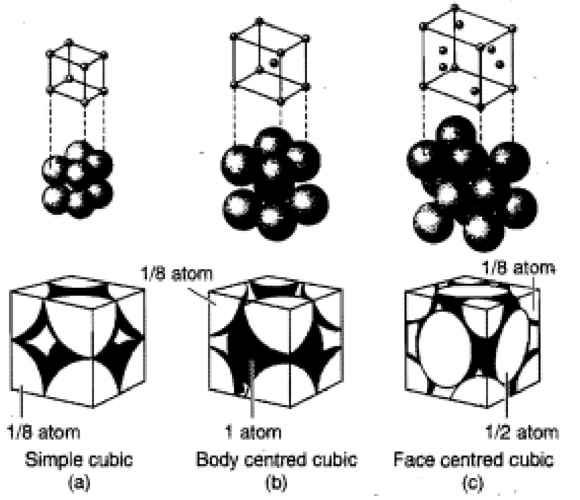
or $d = \frac{AC}{2} = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$

$$d = 2r = \frac{1}{\sqrt{2}}a$$

or Atomic radius, $r = \frac{1}{2\sqrt{2}}a$

(ii) No. of Atoms Per Unit Cell

Different types of cubic unit cells are given in following figure:



Simple cubic (a) Body centred cubic (b) Face centred cubic (c)

Fig. 4.33 (a) Simple or primitive cubic lattice; (b) Body-centred cubic lattice; (c) Face-centred cubic lattice

(a) Simple cubic structure: Since, each corner atom is shared by eight surrounding cubes, therefore, it contributes for $\frac{1}{8}$ of an atom.

Thus, for simple cube $= 8 \times \frac{1}{8} = 1$ atom per unit cell

(b) Face-centred cubic structure: Since, the structure possesses 8 corner atoms and six at the centre of each face, the contribution will be

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \quad \text{(Face atom is shared by two cubes)}$$

$$= 1 + 3 = 4 \text{ atoms per unit cell}$$

(c) Body-centred cubic structure: Since, the structure possesses 8 corner atoms and one body-centre, the contribution will be $= 8 \times \frac{1}{8} + 1 = 2$ atoms per unit cell.

(iii) Coordination Number

It is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

(a) Simple cubic structure: Coordination number = 6

(b) Face-centred cubic structure: Coordination number = 12

(c) Body-centred cubic structure: Coordination number = 8

(iv) Density of Lattice Matter

Knowing the unit cell dimensions, the theoretical density of a crystal can be calculated as:

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

Mass of the unit cell = number of atoms in the unit cell × mass of each atom

$$\text{Mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{So, density of a unit cell} = \frac{Z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3} \quad \text{(For a cube)}$$

where, Z is the number of atoms in a unit cell and V is the volume of unit cell.

For a cube $V = a^3$ where, a is the edge length of the cubic unit cell.

(v) Packing Fraction or Density of Packing

It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

(a) Simple cubic structure: Let a be the cube edge and r the atomic radius.

$$V = \text{volume of the unit cell} = a^3$$

Since, one atom is present in a unit cell, its

$$\text{Volume, } v = \frac{4}{3}\pi r^3 \qquad (r = a/2)$$

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

$$\text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3/6}{a^3} = \frac{\pi}{6} = 0.52$$

i. e., 52% of the unit cell is occupied by atoms and 48% is empty.

(b) Face-centred cubic structure: Since, four atoms are present in a unit cell, their volume is

$$v = 4 \times \left(\frac{4}{3}\pi r^3\right)$$

Putting the value of $r = \frac{a}{2\sqrt{2}}$,

$$v = \frac{16}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3 = \frac{\pi}{3\sqrt{2}}a^3$$

Volume of unit cell, $V = a^3$

$$\text{Packing fraction} = \frac{\pi a^3}{3\sqrt{2}a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

i. e., 74% of unit cell is occupied by atoms and 26% is empty.

(c) Body-centred cubic structure: Since, two atoms are present in a unit cell, their volume is

$$v = 2 \times \left(\frac{4}{3}\pi r^3\right)$$

Putting the value of $r = \frac{\sqrt{3}}{4}a$, $'v' = 2 \times \frac{4}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3$

$$= \frac{\sqrt{3}\pi a^3}{8}$$

Volume of unit cell, $V = a^3$

$$\text{Packing fraction} = \frac{\sqrt{3}\pi a^3}{8a^3} = \frac{\sqrt{3}}{8}\pi = 0.68$$

i. e., 68% of the unit cell is occupied by atoms and 32% is empty.

Characteristics of cubic unit cells are summerised in following tables :

	Simple	**Body-centered**	**Face-centered**
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2$ $= 0.866a$	$a/2^{1/2}$ $= 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction	$\frac{1}{6}\pi$ $= 0.524$	$\frac{1}{6}\pi\sqrt{3}$ $= 0.680$	$\frac{1}{6}\pi\sqrt{2}$ $= 0.740$

Hexagonal Unit Cell

Let us consider hexagonal unit cell of height 'h'; its constituent units are spherical having radius 'r'.

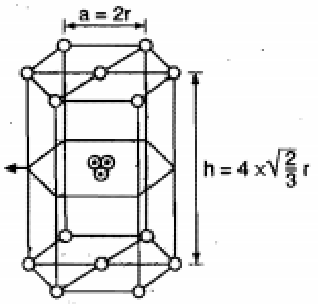


Fig. 4.34 Hexagonal unit cell

Number of constituent units in the hexagonal unit cell = 6.

Thus, occupied volume in the unit cell $= 6\times\frac{4}{3}\pi r^3$

Volume of unit cell = Area of base × height

$$= 6\times \text{Area of equilateral triangle} \times \text{height}$$

$$= 6\times\frac{\sqrt{3}}{4}a^2\times 4r\sqrt{\frac{2}{3}}$$

$$= 6\times\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}$$

(Height of the unit cell can be calculated geometrically)

$$\text{Percentage occupied space} = \frac{\text{occupied volume}}{\text{volume of unit cell}}\times 100$$

$$= \frac{6\times\frac{4}{3}\pi r^3}{6\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}}\times 100 = 74.06\%$$

SOME SOLVED EXAMPLES

Example 66. *A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound ?*

Solution: An atom at the corner of the cube contributes $\frac{1}{8}$ to the unit cell. Hence, number of atoms of A in the unit cell $= 8\times\frac{1}{8} = 1$.

An atom at the face of the cube contributes $\frac{1}{2}$ to the unit cell. Hence, number of atoms of B in the unit cell $= 6\times\frac{1}{2} = 3$.

Thus, the formula is AB_3.

Example 67. *At room temperature, sodium crystallises in body-centred cubic lattice with $a = 4.24$ Å. Calculate the theoretical density of sodium (At. mass of Na = 23.0).*

Solution: A body-centred cubic unit cell contains 8 atoms at the 8 corners and 1 in the centre.

Hence,

$$\text{Total number of atoms in a unit cell} = 8\times\frac{1}{8}+1 = 2$$

$$\text{Volume of unit cell} = a^3 = (4.24\times 10^{-8})^3\ \text{cm}^3$$

$$\text{So, Density} = \frac{Z\times M}{N_0\times V} = \frac{2\times 23}{(6.023\times 10^{23})(4.24\times 10^{-8})^3}$$

$$= 1.002\ \text{g cm}^{-3}$$

Example 68. *The density of KCl is 1.9893 g cm^{-3} and the length of a side of unit cell is 6.29082 Å as determined by X-ray diffraction. Calculate the value of Avogadro's number.*

Solution: KCl has face-centred cubic structure,

i.e., $Z = 4$

$$\text{Avogadro's number} = \frac{Z\times M}{d\times V}$$

Given that, $d = 1.9893$; $M = 74.5$; $V = (6.29082\times 10^{-8})^3\ \text{cm}^3$

$$\text{Avogadro's number} = \frac{4\times 74.5}{1.9893\times(6.29082\times 10^{-8})^3}$$

$$= 6.017\times 10^{23}$$

Example 69. *Silver crystallises in a face-centred cubic unit cell. The density of Ag is 10.5 g cm^{-3}. Calculate the edge length of the unit cell.*

Solution: For face-centred cubic unit, $Z = 4$.

We know that, $V = \frac{Z\times M}{N_0\times d}$

$$= \frac{4\times 108}{(6.023\times 10^{23})\times 10.5} = 6.83\times 10^{-23}$$

$$= 68.3\times 10^{-24}$$

Let a be the edge length of the unit cell.

So, $V = a^3$

or $a^3 = 68.3\times 10^{-24}$

$$a = (68.3\times 10^{-24})^{1/3}\text{cm}$$

$$= 4.09\times 10^{-8}\ \text{cm}$$

$$= 409\ \text{pm}$$

Example 70. *An element occurs in bcc structure with a cell edge of 288 pm. The density of metal is 7.2 g cm^{-3}. How many atoms does 208 g of the element contain?*

Solution: Volume of the unit cell $= (288\times 10^{-10})^3$

$$= 23.9\times 10^{-24}\ \text{cm}^3$$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88\ \text{cm}^3$$

$$\text{Number of unit cells in } 28.88\ \text{cm}^3 = \frac{28.88}{23.9\times 10^{-24}}$$

$$= 12.08\times 10^{23}\ \text{unit cells}$$

Each bcc structure contains 2 atoms.

So, Total atoms in 12.08×10^{23} unit cells

$$= 2 \times 12.08 \times 10^{23}$$

$$= 24.16 \times 10^{23}$$

Example 71. *Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is* $351\,pm$.

Solution: In body-centred cubic crystals,

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

$$= \frac{\sqrt{3}}{4} \times 351\,\text{pm} = 151.98\,\text{pm}$$

Example 72. *Ammonium chloride crystallises in a body-centred cubic lattice with a unit distance of 387 pm. Calculate* (a) *the distance between oppositely charged ions in the lattice and* (b) *the radius of the* NH_4^+ *ion if the radius of* Cl^- *ion is* $181\,pm$.

Solution: (a) In a body-centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube.

So, $$2r_c + 2r_a = \sqrt{3}a$$

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

$$= \frac{\sqrt{3}}{2} \times 387 = 335.15\,\text{pm}$$

(b) Given that, $$r_a = 181\,\text{pm}$$

$$r_c = 335.15 - 181.0 = 154.15\,\text{pm}$$

Example 73. *The unit cell cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.*

Solution: In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

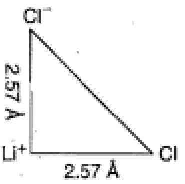
$$4r_{Cl^-} = \sqrt{2}a$$

$$r_{Cl^-} = \frac{\sqrt{2}}{4} a$$

$$= \frac{\sqrt{2}}{4} \times 5.14 = 1.82\,\text{Å}$$

Alternative: Distance between Li^+ and Cl^- ion

$$= \frac{5.14}{2} = 2.57\,\text{Å}$$



Thus, distance between two chloride ions

$$= \sqrt{(2.57)^2 + (2.57)^2}$$

$$= 3.63\,\text{Å}$$

Hence,

$$\text{radius of } Cl^- = \frac{3.63}{2} = 1.82\,\text{Å}$$

Example 74. *The density of crystalline sodium chloride is* $2.165\,g\,cm^{-3}$. *What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of NaCl?*

Solution: We know that,

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

where, ρ = density = $2.165\,\text{gcm}^{-3}$

M = molar mass = 58.5

N_A = Avogadro's number = 6.023×10^{23}

N = number of formula unit per unit cell

= 4 (for fcc)

$$a^3 = \frac{N}{\rho}\left(\frac{M}{N_A}\right) = \frac{4}{2.165}\left[\frac{58.5}{6.023 \times 10^{23}}\right]$$

$$= 1.794 \times 10^{-22}$$

$$a = 5.64 \times 10^{-8}\,\text{cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length } (a) = \left[\frac{58.8}{2.165}\right]^{1/3} = 3\,\text{cm}$$

Example 75. *The density of potassium bromide crystal is* $2.75\,g\,cm^{-3}$ *and the length of an edge of a unit cell is* $654\,pm$. *The unit cell of KBr is one of three types of cubic unit cells. How many formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or CsCl structure?*

Solution: We know that,

$$\rho = \frac{N}{a^3}\left[\frac{M}{N_A}\right]$$

$$N = \frac{\rho \times a^3 \times N_A}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119} = 3.89 = 4$$

Number of mass points per unit cell = 4

It is NaCl type crystal, *i.e.*, fcc structure.

Example 76. *A unit cell of sodium chloride has four formula units. The edge length of unit cell is* 0.564 *nm. What is the density of sodium chloride?* **(IIT May 1997)**

Solution: $$\rho = \frac{ZM}{a^3 N} = \frac{4 \times 58.5}{(5.64 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$= 2.16\,\text{g cm}^{-3}$$

Example 77. *Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in* g/cm^3 ? **(IIT July 1997)**

Solution: In body-centred cubic unit cell,

$$a\sqrt{3} = 4r$$

where, a = edge length, r = radius of atom

$$r = \frac{a\sqrt{3}}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.8574 \text{ Å}$$

Example 78. *When heated above 916°C, iron changes its crystal structure from body-centred cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.*

Solution: In body-centred packing, the efficiency of packing is 67.92%. In the cubic closed packing, the packing efficiency is 74.02%.

Let d_1 be the density when packing efficiency is 74.02% and d_2 is the density when packing efficiency is 74.02%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

30. An element 'A' has face-centred cubic structure with edge length equal to 361 pm. The apparent radius of atom 'A' is:

(a) 127.6 pm	(b) 180.5 pm
(c) 160.5 pm	(d) 64 pm

[Ans. (a)]

[Hint: For face-centred unit cell,

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

$$\frac{361 \times 1.414}{4} = r$$

$$\therefore \quad r = 127.6 \text{ pm}]$$

31. The packing fraction of the element that crystallises in simple cubic arrangement is:

(a) $\frac{\pi}{4}$ (b) $\frac{\pi}{6}$ (c) $\frac{\pi}{3}$ (d) $\frac{\pi}{2}$

[Ans. (b)]

[Hint: In simple unit cell $a = 2r$

$$Z = 1$$

$$\therefore \quad \text{Packing fraction} = \frac{\text{Occupied volume}}{\text{Total volume}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}]$$

32. How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?

(a) N_A (b) $\frac{N_A}{4}$ (c) $0.5\ N_A$ (d) $0.75\ N_A$

[Ans. (c)]

[Hint: Number of atoms $= \frac{\text{Mass}}{\text{Atomic mass}} \times N_A$

$$= \frac{39}{39} \times N_A = N_A$$

In bcc unit cell, $Z = 2$

$\therefore$ Number of unit cells $= \frac{N_A}{2} = 0.5\ N_A$]

33. Sodium metal exists in bcc unit cell. The distance between nearest sodium atoms is 0.368 nm. The edge length of the unit cell is:

(a) 0.368 nm	(b) 0.184 nm
(c) 0.575 nm	(d) 0.424 nm

[Ans. (d)]

[Hint: In bcc unit cell, $a\sqrt{3} = 4r$

$$a = \frac{4r}{\sqrt{3}} = \frac{2}{\sqrt{3}} \times 2r$$

$$= \frac{2}{\sqrt{3}} \times 0.368 = 0.425 \text{ nm}]$$

34. If the distance between Na^+ and Cl^- ions in NaCl crystal is 265 pm, then edge length of the unit cell will be?

(a) 265 pm (b) 530 pm (c) 795 pm (d) 132.5 pm

[Ans. (b)]

[Hint: In NaCl:

Edge length = 2 × distance between Na^+ and Cl^- ions

= 2 × 265 = 530 pm]

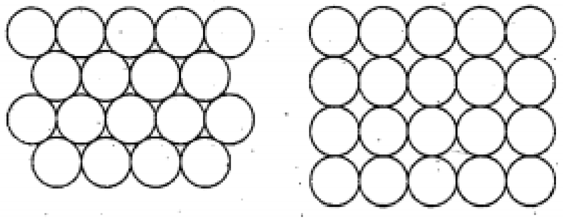
35. The interionic distance for caesium chloride crystal will be: **[PMT (MP) 2007]**

(a) a (b) $\frac{a}{2}$ (c) $\frac{a\sqrt{3}}{2}$ (d) $\frac{2a}{\sqrt{3}}$

[Ans. (c)]

4.22 PACKING OF IDENTICAL SOLID SPHERES

The constituent particles in the formation of crystals are either atoms, ions or molecules. These particles may be of various shapes and thus, the mode of packing of these particles will change according to their shapes. The simplest way will be to consider these particles as spheres of equal size. The packing of spheres is done in such a way as to use the available space in the most economical manner.



Arrangement (i) Arrangement (ii)

Fig. 4.35 Two common ways of packing spheres of equal size

There are two common ways in which spheres of equal size can be packed. This has been shown in Fig. 4.35. The arrangement (i) is more economical in comparison to arrangement (ii) as 60.4% volume is occupied in arrangement (i) and 52.4% volume in arrangement (ii). Arrangement (i) represents a close packing of spheres.

In arrangement (i), the spheres are packed in such a manner that their centres are at the corners of an equilateral triangle. Each sphere is surrounded by six other similar spheres as shown in Fig. 4.36. This arrangement can be extended in three dimensions by adjusting spheres on the top of hollows or voids of the two-dimensional layer which is called the first layer or '*A*' layer. There are two types of hollows in the first layer which have been marked by dots (·) and cross (×). All the hollows are equivalent. The spheres of the second layer may be put either on hollows marked by dots or by crosses. Half of the hollows remain unoccupied in the second layer (Fig. 4.37). The second layer is marked as '*B*' layer. The spheres have been placed on the hollows marked by dots.

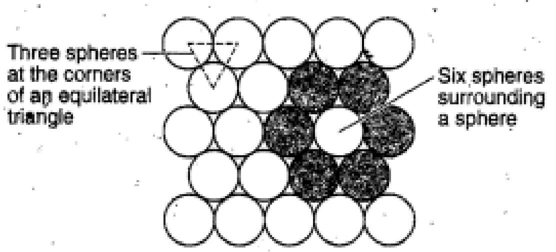


Fig. 4.36 Close packing of spheres

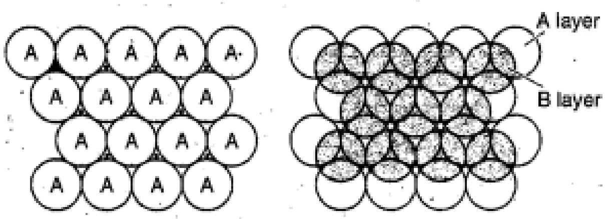


Fig. 4.37 Building of second layer (B, shown shaded) covering hollows marked by dots (•). The hollows marked by a cross (×) unoccupied

To build up the third layer of spheres, there are two alternative ways. In the first way the spheres are placed on the hollows of second layer. It is observed that each sphere of third layer lies exactly above the spheres of first layer. When this arrangement is continued indefinitely, the system obtained is found to possess hexagonal symmetry and is called hexagonal close packing of spheres and is abbreviated as hcp or *ABABAB* . . . This is shown in Fig. 4.38. In the second way, spheres are placed on the unoccupied hollows of the first layer, marked by 'crosses'. It is observed that spheres of the third layer do not come over those of first layer. This arrangement of close packing is referred to as *ABC*. However, it is noted that spheres in the fourth layer will correspond with those in the first layer. When such an arrangement is continued indefinitely, the system is found to possess cubic symmetry and called cubic close packing of spheres and is abbreviated as **ccp** or *ABCABC* . . . This is shown in Fig. 4.39. The system *ABCABC* . . . shows that there is a sphere at the centre of each face of the unit cube and thus, this system is also referred to as face-centred cubic or **fcc.**

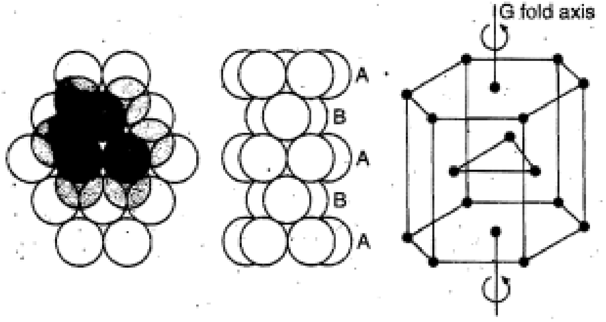
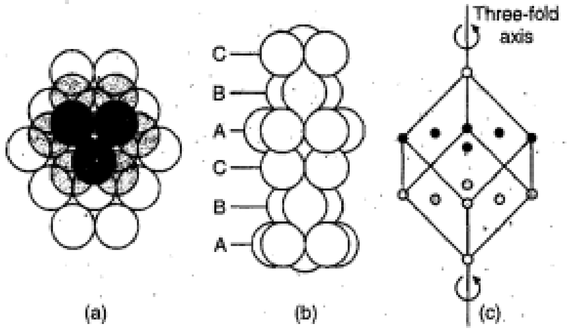


Fig. 4.38 *ABABAB* . . . or hexagonal close packing (hcp) o spheres



(a) (b) (c)

Fig. 4.39 *ABC ABC A* . . . or cubic close packing (ccp) of spheres

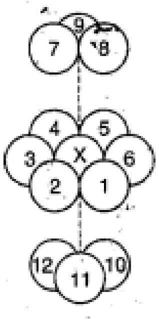


Fig. 4.40 Coordination number in hcp and ccp structure

It is noted that in both the above systems **hcp** or **ccp,** each sphere is surrounded by twelve other spheres shown in Fig. 4.40. There is a third arrangement of packing of spheres which is known as **body-centred cubic** arrangement (bcc). This arrangement is obtained when the spheres in the first layer are slightly opened up, *i.e.*, none of the spheres touches each other. In the second layer, the spheres are placed at the top of hollows in the first layer. In the third layer, spheres are placed exactly above the first layer. Each sphere in this system of packing is in contact with eight spheres, four in the lower layer and four in the upper layer. This arrangement has been shown in Fig. 4.41.

Most of the metals belonging to *s*-block and *d*-block elements possess any one of the following close packing arrangements:

(i) Cubic closed packed, (ii) Hexagonal closed packed and (iii) Body-centred cubic packed.

Examples:

Metals	Structure
Mg, Zn, Mo, V, Cd	hcp
Cu, Ag, Au, Ni, Pt	ccp or fcc
Li, Na, K, Rb, Cs, Ba	bcc