

# SOLID STATE

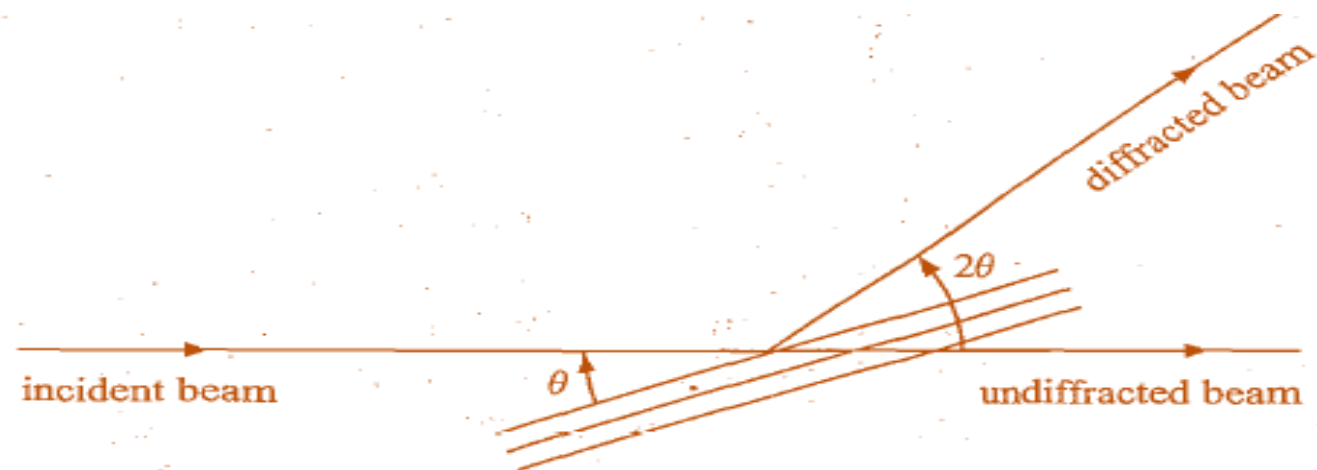
## LECTURE-5

## POWDER METHOD

In the Bragg method, one has to use a fairly large crystal with flat faces carefully oriented in a number of specific directions. All crystalline substances are not available in the above needed form. Another method, which is very convenient to handle, was developed independently by Debye and Scherrer, and Hull. In this method, known as the powder method, the given substance is taken in powder form in a thin-walled capillary tube. It is then irradiated with monochromatic X-rays. The particles in the powder act as tiny crystals and are randomly oriented with respect to the incident X-rays. Since the powder contains a very large number of particles, it is possible that some particles will have their (100) planes correctly oriented so that the Bragg equation is satisfied. Some others will have their (110) planes properly oriented, while there may be some with their (111) planes properly oriented and so on. Thus, the powder provides all types of lattice planes for the reflection of X-rays and hence may be considered equivalent to a single crystal rotated not only about one axis, but about all possible axes at once.

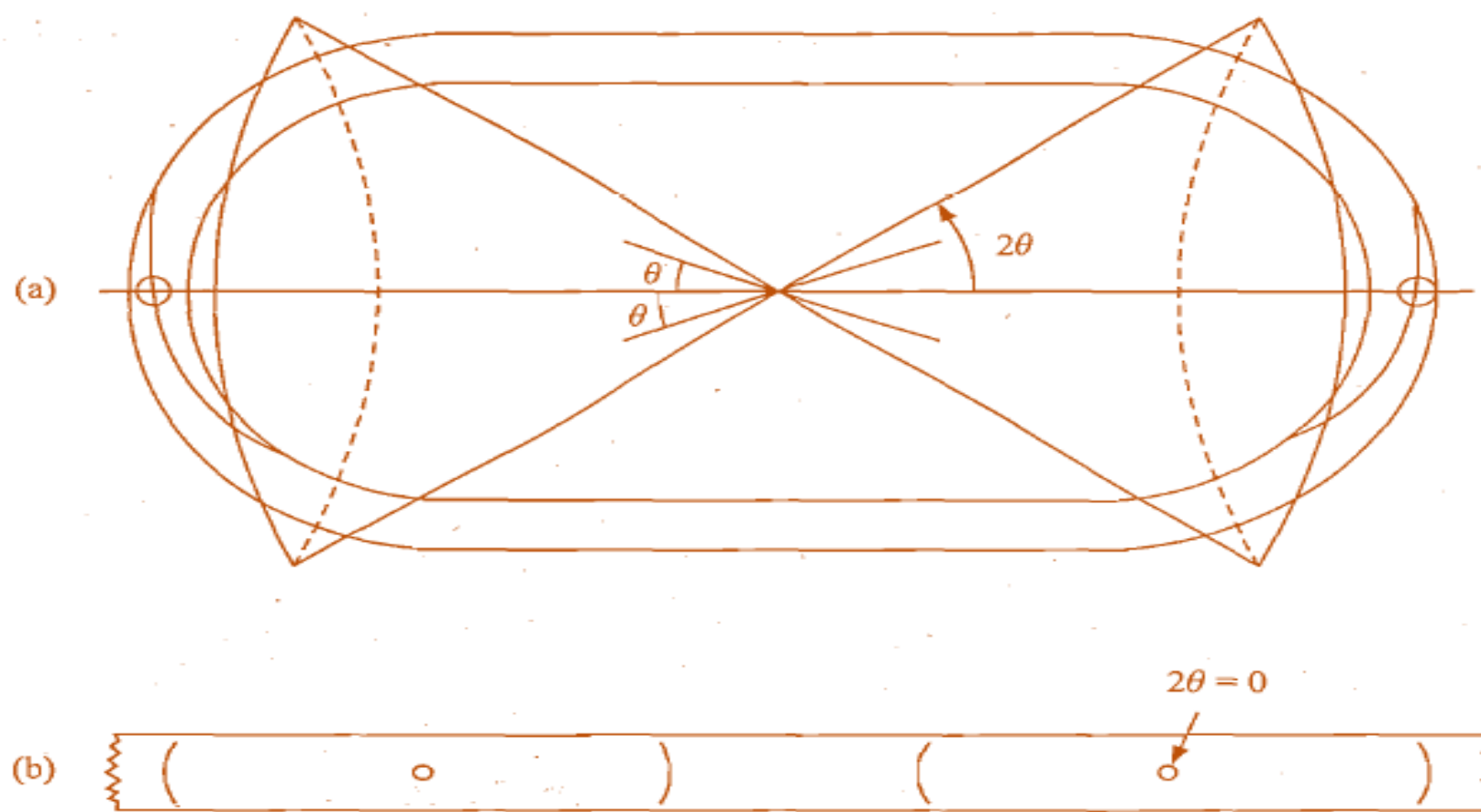
## Experimental Set-up

Consider a set of parallel planes making an angle  $\theta$  with the incident beam of X-rays as shown in Fig. 3.14.1. The reflected beam from these planes will make an angle  $2\theta$  with the unreflected beam. Now, if these planes are rotated around the incident beam, keeping angle  $\theta$  constant, it is obvious that the diffracted beam will travel over the surface of a cone as shown in Fig. 3.14.2a. Since in the powder, a large number of crystals with all types of orientations are available, the above criterion of a crystal to be rotated around the incident beam is



**Fig. 3.14.1** Diffraction of X-ray by a set of parallel planes.

automatically achieved. Thus, one gets a cone of reflected X-rays corresponding to each and every space lattice planes. If a narrow beam of film is now curved into a cylinder around the capillary tube in such a way that the latter lies along the axis of the cylinder, the diffracted beam will leave impressions on the film in the form of either curved or straight lines which on removing would give the diffraction pattern very similar to the one shown in Fig. 3.14.2b. The big holes in the film correspond to the places where the X-ray beam enters or leaves it.



**Fig. 3.14.2** (a) X-ray diffraction by a powdered sample. (b) Diffraction impressions on the film

If  $s$  is the distance of a diffracted beam from the centre of the hole and  $r$  is the distance of the film from the capillary tube, the angle  $2\theta$  of the diffracted beam with the unreflected beam can be calculated using the expression  $2\theta = s/r$ . From this, the incident angle  $\theta$  of X-rays with the planes can be determined. Thus, knowing the wavelength  $\lambda$  of X-rays, we can calculate the interplanar spacing  $d_{hkl}$  using the Bragg equation

$$d_{hkl} = \frac{\lambda}{2 \sin \theta}$$

## Criterion for Obtaining Sharp Diffraction Lines

In order to obtain sharp diffraction lines of uniform thickness, the tiny crystals in the powder must have average dimensions of a few microns. If the crystals are too large, relatively few of them will contribute to a diffraction line and thus the diffraction pattern will consist of a discontinuous set of spots. If the crystals are too small, the diffraction lines become broadened. This is due to the fact that as the size of a crystal decreases, the number of its lattice planes and thus the extent of the orderly arrangement also decreases. The powder method is useful for the crystal systems that have only one or two lattice parameters to be determined (cubic, tetragonal, hexagonal and rhombohedral systems).

A powder diffraction pattern for a given substance was obtained using X-rays from a Cu target where  $\lambda = 154$  pm. The distance from the capillary to the film was 5.0 cm. Diffracted lines were obtained, two of which were at distances 1.2 and 3.4 cm from the undeflected beam. Calculate the spacings for the planes that give rise to these lines.

Since in the powder method, the diffracted line is observed at angle  $2\theta$  from the incident beam, it is obvious that  $2\theta = s/r$ , where  $s$  is the distance of the diffracted beam from the undiffracted one and  $r$  is the distance of the film from the capillary tube.

$$\text{Thus, } 2\theta_1/\text{radian} = \frac{s}{r} = \frac{1.2 \text{ cm}}{5 \text{ cm}}$$

$$\text{or } \theta_1 = \frac{1.2}{10} \text{ radian} = 0.12 \text{ radian} = (0.12 \text{ radian}) \left( \frac{180^\circ}{\pi \text{ radian}} \right) = 6.9^\circ$$

For second line  $\theta_2 = 19.5^\circ$

Taking the sine of  $\theta_1$  and  $\theta_2$ , we get

$$\sin \theta_1 = 0.120 \quad \text{and} \quad \sin \theta_2 = 0.334$$

Substituting these in the Bragg equation, we have

$$d_1 = \frac{154 \text{ pm}}{2(0.120)} = 640 \text{ pm} \quad \text{and} \quad d_2 = \frac{154 \text{ pm}}{2(0.334)} = 230 \text{ pm}$$

## DIFFRACTION PATTERN OF A CUBIC SYSTEM

### Basic Equation

Since for a cubic crystal

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad (3.15.1)$$

the Bragg's equation

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

becomes  $\lambda = 2 \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \sin \theta_{hkl}$

$$\text{or} \quad \sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

$$\text{or} \quad \sin^2 \theta_{hkl} = K(h^2 + k^2 + l^2) \quad (3.15.2)$$

where  $K = \lambda^2/4a^2$ . This has a constant value for a given cubic crystal and for a given wavelength  $\lambda$  of X-rays.

Equation (3.15.2) can be used to predict the diffraction patterns for the three types of cubic systems. These are described in the following.

## Primitive Cubic Lattice

By assigning consecutive integral values (0, 1, 2, ...) to  $h$ ,  $k$  and  $l$ , we can calculate a series of values of  $d_{hkl}$  and  $\sin^2\theta$  by using Eqs (3.15.1) and (3.15.2), respectively. These are listed in Table 3.15.1

(It can be noted that  $\sin^2\theta$  cannot have the value of  $7K$  because there is no way in which the integer 7 can be written in the form of  $h^2 + k^2 + l^2$ . This is also true of the integers 15, 23, 28, etc.)

We will observe diffraction lines at angles listed in Table 3.15.1. Thus, the predicted diffraction pattern consists of a set of six lines which are equally spaced when plotted against  $\sin^2\theta$  followed by a gap and then another series of lines. The observation of such a set of diffraction lines shows directly that the crystal under study has a primitive cubic lattice.

**Table 3.15.1** Interplanar Distances and the Corresponding Expected Angles of Diffraction for a Primitive Cubic Lattice

	221											
$hkl$	100	110	111	200	210	211	220	300	310	311	222	320
$d_{hkl}$	$a$	$\frac{a}{\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$	$\frac{a}{\sqrt{5}}$	$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{3}$	$\frac{a}{\sqrt{10}}$	$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$	$\frac{a}{\sqrt{13}}$
$\sin^2\theta$	$K$	$2K$	$3K$	$4K$	$5K$	$6K$	$8K$	$9K$	$10K$	$11K$	$12K$	$13K$

## Body-Centred Cubic Lattice

The patterns of lines expected from face-centred and body-centred lattices are different from the pattern of primitive cubic lattice.

It can be seen from Fig. (3.9.3) that in (100) planes of a body-centred lattice, only half of the atoms lie in these planes, the remainder lie in the (200) planes which are located half-way between adjacent (100) planes. As a consequence of this, the X-rays scattered at the Bragg angle for reflection from the (100) planes will be out of phase with those scattered by the (200) planes, with the result that destructive interference will occur, and the diffraction line corresponding to the (100) planes will be absent. On the other hand, at the Bragg angle for reflection from the (200) planes all scattered X-rays will be in phase and thus a strong diffraction line will be observed.

It can be shown, in general, that for a body-centred cubic lattice, all diffraction lines for which  $(h + k + l)$  is an odd integer must be absent.<sup>†</sup> Thus, we will observe diffraction lines at angles listed in Table 3.15.2.

## Face-Centred Cubic Lattice

Again from Fig. 3.9.3, it can be seen that only half the atoms lie in the (100) and the (110) planes. Thus, it is expected that the diffraction from these planes will be absent. On the other hand, all atoms lie in (111), (200) and (220)

**Table 3.15.2** Angles at which Diffraction Lines are Observed for a Body-Centred Cubic Lattice

$hkl$	100	110	111	200	210	211	220	221	300	310	311	222	320
$d_{hkl}$		$\frac{a}{\sqrt{2}}$		$\frac{a}{2}$		$\frac{a}{\sqrt{6}}$	$\frac{a}{2\sqrt{2}}$			$\frac{a}{\sqrt{10}}$		$\frac{a}{\sqrt{12}}$	
$\sin^2\theta$		$2K$		$4K$		$6K$	$8K$			$10K$		$12K$	

planes and thus the corresponding diffraction lines will be observed. It can be shown, in general, that for a face-centred cubic lattice, the strong diffraction lines are observed only from those planes for which the values of  $h$ ,  $k$  and  $l$  are either all even or all odd. Thus, one would observe diffraction lines at angles listed in Table 3.15.3



**Table 3.15.3** Angles at which Diffraction Lines are Observed for a Face-Centred Cubic Lattice

<i>hkl</i>	100	110	111	200	210	211	220	221	300	310	311	222
$d_{hkl}$			$\frac{a}{\sqrt{3}}$	$\frac{a}{2}$			$\frac{a}{2\sqrt{2}}$				$\frac{a}{\sqrt{11}}$	$\frac{a}{\sqrt{12}}$
$\sin^2\theta$			$3K$	$4K$			$8K$				$11K$	$12K$

**Summary of Diffraction Pattern for Cubic Systems**

The predicted patterns for three types of cubic lattices are also shown in Fig. 3.15.1.

Planes	100	110	111	200	210	211		220	221, 300	310	311	222	320	321		400
	1K	2K	3K	4K	5K	6K	7K	8K	9K	10K	11K	12K	13K	14K	15K	16K
Primitive																
Body																
Face																

**Fig. 3.15.1** A typical X-ray diffraction pattern of a cubic system (The presence of a reflection is indicated by a line)

## Importance of Missing Reflections

The difference between the three diffraction patterns clearly indicates the usefulness of missing reflections in distinguishing different lattice types. In general, the search for missing reflections is an important step in the determination of crystal structures. It may be mentioned, however, that the distinction between the primitive and the body-centred cubic systems cannot be made on the basis of the first six lines, since spacing of the lines in the individual diffraction pattern will be same ( $K$  in case of primitive and  $2K$  in body-centred). If more lines are included only then the distinction can be made since, in the primitive structure, there will be a gap after the sixth line whereas no such gap will be observed in the body-centred cubic system.

## Computing Edge Length of Unit Cell

Once the diffraction pattern has been identified, it is then possible to assign each and every line with the correct values of  $h$ ,  $k$ , and  $l$ . From the measurement of  $\theta$  for any one of these lines, the edge length  $a$  of the cube can be computed from the equation

$$a = \frac{1}{2 \sin \theta_{hkl}} (h^2 + k^2 + l^2)^{1/2}$$

If the indexing of the lines has been done correctly, the same value of  $a$  will be obtained from all values of  $\sin \theta_{hkl}$ .

Silver is known to be crystallized in cubic form. The Bragg angles, using copper  $K_{\alpha}$  X-rays with  $\lambda = 154.1$  pm, for the first six diffraction lines are as follows:

$\theta$	$19.08^\circ$	$22.17^\circ$	$32.26^\circ$	$38.74^\circ$	$40.82^\circ$	$49.00^\circ$
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- What is the type of cubic crystal formed by silver?
- What is the length of a side of the unit cell?
- What is the interplanar distance of the planes (111)?

### Solution

(a) Type of cubic crystal

$\theta$	$19.08^\circ$	$22.17^\circ$	$32.26^\circ$	$38.74^\circ$	$40.82^\circ$	$49.00^\circ$
$\sin \theta$	0.326 8	0.377 3	0.533 8	0.625 7	0.653 6	0.754 7
$\sin^2 \theta$	0.106 7	0.142 4	0.284 8	0.391 5	0.427 2	0.569 7
	3K	4K	8K	11K	16K	

where  $K = 0.035 6$

Thus, silver crystallizes in the face-centred cubic lattice.

(b) The edge-length of the cube can be calculated from the following expression.

$$a = \frac{\lambda}{2 \sin \theta_{hkl}} \sqrt{(h^2 + k^2 + l^2)}$$

The reflection at  $19.08^\circ$  is due to (111) planes. Hence

$$a = \frac{154.1 \text{ pm}}{2 \times 0.326 8} \sqrt{1^2 + 1^2 + 1^2} = 408.6 \text{ pm}$$

(c) Distance between (111) planes is

$$d_{111} = \frac{408.6 \text{ pm}}{\sqrt{3}} = 235.9 \text{ pm}$$

Gold has a face-centred cubic lattice with an edge length of the unit cube of 407 pm. Calculate the diffraction pattern when copper X-rays of wavelength 154 pm is used.

In a face-centred lattice, the reflection of X-rays will occur from the planes for which the Miller indices ( $hkl$ ) are either all even or all odd. Thus, we will have reflections from (111), (200), (220), (311), (222), (400), etc., planes

For a cubic crystal, we have

$$\sin \theta = \frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2}$$

Thus, the diffraction pattern of Au will exhibit reflections at the following angles:

Plane	$\sin \theta$	$\theta$
111	$\frac{\sqrt{3}\lambda}{2a} = \frac{1.732(154 \text{ pm})}{2(407 \text{ pm})} = 0.3280$	$19^\circ 9'$
200	$\frac{\lambda}{a} = \frac{(154 \text{ pm})}{(407 \text{ pm})} = 0.3784$	$22^\circ 14'$
220	$\frac{\sqrt{2}\lambda}{a} = \frac{1.414(154 \text{ pm})}{(407 \text{ pm})} = 0.5350$	$32^\circ 52'$
311	$\frac{\sqrt{11}\lambda}{2a} = \frac{3.317(154 \text{ pm})}{2(407 \text{ pm})} = 0.6274$	$38^\circ 51'$
222	$\frac{\sqrt{12}\lambda}{2a} = \frac{3.464(154 \text{ pm})}{2(407 \text{ pm})} = 0.6554$	$40^\circ 51'$
400	$\frac{\sqrt{16}\lambda}{2a} = \frac{4(154 \text{ pm})}{2(407 \text{ pm})} = 0.7568$	$49^\circ 12'$

When an X-ray powder pattern of crystalline copper is obtained using X-rays from copper target (the wavelength of the  $K_{\alpha}$ -line is 154.05 pm), reflections are found at  $21.65^{\circ}$ ,  $25.21^{\circ}$ ,  $37.06^{\circ}$ ,  $44.96^{\circ}$ ,  $47.58^{\circ}$  and other angles.

- What is the type of cubic crystal formed by copper?
- What is the length of a side of the unit cell?
- Determine the value of Avogadro constant if density of copper is  $8.812 \text{ g cm}^{-3}$ .
- Calculate the radius of copper atom.

(a) *Type of cubic crystal*      Calculating  $\sin^2 \theta$ , we have

Angle	$\sin \theta$	$\sin^2 \theta$
$21.65^{\circ}$	0.368 9	0.136 1
$25.21^{\circ}$	0.425 8	0.181 3
$37.06^{\circ}$	0.602 4	0.362 9
$44.96^{\circ}$	0.706 5	0.499 1
$47.58^{\circ}$	0.738 1	0.544 8

Taking the ratios of  $\sin^2 \theta$ , we get

$$0.136 \ 1 : 0.181 \ 3 : 0.362 \ 9 : 0.499 \ 1 : 0.544 \ 8$$

or  $3 \times 0.045 : 4 \times 0.045 : 8 \times 0.045 : 11 \times 0.045 : 12 \times 0.045$

that is,  $3K : 4K : 8K : 11K : 12K$ , where  $K = 0.045$

From these ratios, it is obvious that copper has face-centred cubic crystal.

(b) *Length of the side of the unit cell*      Since

$$K = \frac{\lambda^2}{4a^2}$$

therefore,

$$a = \left( \frac{\lambda^2}{4K} \right)^{1/2} = \frac{\lambda}{2} \cdot \frac{1}{\sqrt{K}} = \frac{154.05 \text{ pm}}{2 \times \sqrt{0.045}} = \frac{154.05 \text{ pm}}{2 \times 0.2121} = 363.2 \text{ pm}$$

(c) *Avogadro constant* Since

$$\rho = \frac{nM}{a^3 N_A}, \quad \text{therefore,} \quad N_A = \frac{nM}{a^3 \rho}$$

Substituting the values, we have

$$N_A = \frac{4(63.54 \text{ g mol}^{-1})}{(363.2 \times 10^{-10} \text{ cm})^3 (8.812 \text{ g cm}^{-3})} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

(d) *Radius of Cu atom* In a face-centred cubic lattice, atoms touch one another along the face-diagonal of the cubic unit cell.

Therefore,

$$4r = \sqrt{2}a \quad \text{or} \quad r = \frac{\sqrt{2}a}{4}$$

Substituting the values, we have

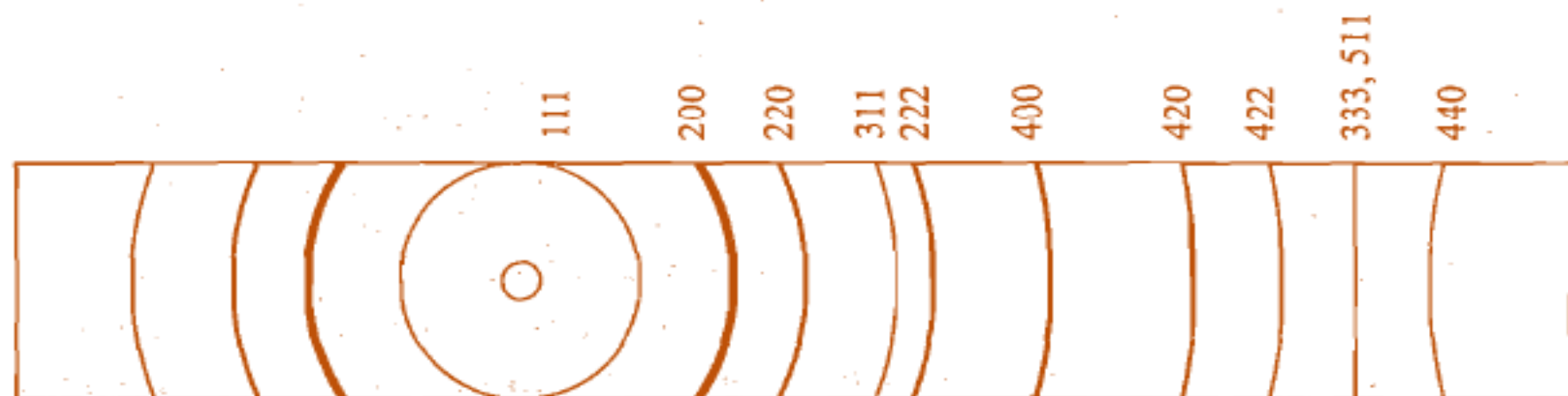
$$r = \frac{(1.414)(363.2 \text{ pm})}{4} = 128.3 \text{ pm}$$

## CRYSTAL STRUCTURE OF SODIUM CHLORIDE

The unit lattice of sodium chloride, like the macroscopic crystal, must be a cube and thus the sodium and chloride ions must be arranged in some combination of only three possible space-lattices.

Schematic representation of the powder pattern of sodium chloride is given in Fig. 3.16.1.

Table 3.16.1 Records values of the angle  $\theta$ ,  $\sin \theta$ ,  $\sin^2 \theta$  and the relative intensities for some of the lines of NaCl using  $K_{\alpha}$  line from palladium.



### Data from Diffraction Pattern

Fig. 3.16.1 Diffraction pattern (only schematic) of sodium chloride

### Type of Cubic Lattice

It is obvious from the fifth column of Table 3.16.1 that NaCl crystal must belong to the face-centred cubic crystal. Designation of the plane as given in the first column follows this recognition. This can also be checked by finding out the ratio of the first three planes (200), (220) and (111). This ratio is

**Table 3.16.1** Details of Diffraction Pattern of NaCl

<i>Planes</i>	$\theta/\text{degree}$	$\sin \theta$	$\sin^2 \theta$	$K = 0.002\ 73$	<i>Relative Intensities</i>	
111	5.2	0.091	0.008 2	3K	9.0	
200	5.9	0.103	0.010 6	4K	100	
220	8.4	0.146	0.021 3	8K	50.4	
311	8.7	0.151	0.022 8	11K		
222	10.5	0.182	0.033 6	12K	33.1	Second order reflection of (111)
333	15.8	0.273	0.074 5	27K	0.58	Third order reflection of (111)
444	21.3	0.364	0.132 5	48K	2.82	Fourth order reflection of (111)
555	27.1	0.455	0.207 0	75K	0.14	Fifth order reflection of (111)
400	11.9	0.208	0.043 2	16K	19.90	Second order reflection of (200)
600	18	0.309	0.095 5	36K	4.87	Third order reflection of (200)
800	24.3	0.412	0.169 7	64K	0.79	Fourth order reflection of (200)
440	17.0	0.292	0.085 3	32K	6.10	Second order reflection of (220)
660	26	0.438	0.191 8	72K	0.71	Third order reflection of (220)



$$\begin{aligned}
 d_{200} : d_{220} : d_{111} &= \frac{1}{\sin(5.9^\circ)} : \frac{1}{\sin(8.4^\circ)} : \frac{1}{\sin(5.2^\circ)} \\
 &= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.0906} \\
 &= 1 : 0.705 : 1.137
 \end{aligned}$$

This agrees with the theoretical ratio given in Section 3.10, thus confirming the existence of the face-centred cubic crystal system. The indicated indexing of the diffraction lines also lead to a single value of the edge length of the unit cube. Thus, sodium and chloride ions are arranged in a crystal as a face-centred cubic lattice.

### Arrangement of Na<sup>+</sup> and Cl<sup>-</sup> ions

The actual arrangement of Na<sup>+</sup> and Cl<sup>-</sup> in this face-centred cubic lattice can be determined by the relative intensities of the reflection maxima for the different orders and planes.

The intensity of a diffracted beam depends upon two factors:

(i) *Number of electrons in the atom* The scattering power of atoms for X-ray depends on the number of electrons in the atom and is roughly proportional to the atomic number.

(ii) *The order of diffraction* Intensity decreases in a definite manner with increase in the order of reflection.

It can be seen from Table 3.16.1 that in the (200) and (220) planes the intensities decrease progressively with order.

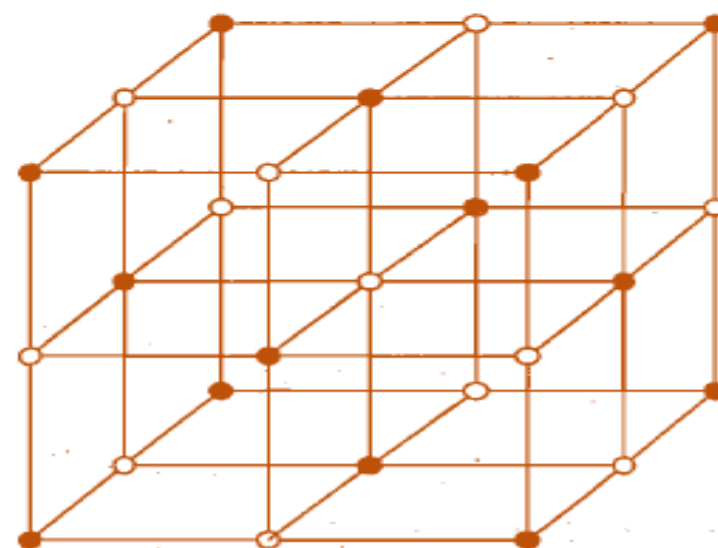
<i>n</i>	1	2	3	4
(200)	100	19.90	4.87	0.79
(220)	50.4	6.10	0.71	

This systematic decrease can be accounted for quantitatively by assuming that such planes contain equal numbers of sodium and chloride ions. In the (111) planes, an alternation of intensities is observed.

$n$	1	2	3	4	5
(111)	9.0	33.1	0.58	2.82	0.14

This can be accounted for by postulating that the planes (111) are composed alternately of sodium and chloride ions.

The possible arrangement which satisfies the above facts is given in Fig. 3.16.2.



**Fig. 3.16.2** Crystal structure of sodium chloride,  $\text{Na}^+$  black circles—located at the corners of the cube and at the centre of each of the six faces;  $\text{Cl}^-$  open circles—located halfway between two sodium ions

The structure shown in Fig. 3.16.2 suggests that it consists essentially of two interpenetrating face-centred cubic lattices, one composed entirely of  $\text{Na}^+$  ions and the other of  $\text{Cl}^-$  ions.

## Comment

From the above analysis, it is revealed that the designation 'molecule of sodium chloride' loses a great deal of its definitive meaning. It can hardly be said that any particular chloride ion belongs to any definite sodium ion; rather, each sodium ion is shared equally by six chloride ions, and each chloride ion by six sodium ions. All that can be said is that to each sodium corresponds one-sixth of six chloride ions, so that each sodium has the equivalent of a chloride but not any one ion exclusively.

The first order reflection from (200) planes of NaCl using X-rays of wavelength 58 pm ( $K_{\alpha}$  line from palladium) occurs at an angle of  $5.9^{\circ}$ . Calculate (i) edge length of the unit cell, (ii) volume of the unit cell, (iii) molar volume, and (iv) density of solid NaCl.

(i) Using Bragg's law, we have

$$\lambda = 2 d_{hkl} \sin \theta$$

Thus 
$$d_{200} = \frac{\lambda}{2 \sin \theta} = \frac{58 \text{ pm}}{2 \sin (5.9)} = \frac{58 \text{ pm}}{2 \times 0.103} = 281.6 \text{ pm}$$

The edge length of the unit cell =  $2 \times d_{200} = 563.2 \text{ pm}$

(ii) The volume of unit cell =  $(563.2 \text{ pm})^3 = 1.786 \times 10^{-28} \text{ m}^3$ .

(iii) In order to calculate molar volume, we must know the number of molecules of NaCl which belong to one unit cell. In one unit cell of NaCl, we have the following arrangements:

(a) Eight  $\text{Na}^+$  (or  $\text{Cl}^-$ ) at the end of edges, each of which is shared by eight such unit cells. Thus, contribution from the edges is one  $\text{Na}^+$  (or  $\text{Cl}^-$ ).

(b) Six  $\text{Na}^+$  (or  $\text{Cl}^-$ ) are present in the centres of the faces, each is shared by two cubes, thus contributing three  $\text{Na}^+$  (or  $\text{Cl}^-$ ) ions.

(c) Twelve  $\text{Cl}^-$  (or  $\text{Na}^+$ ) are present along the edges, each of which is shared by four cubes, thus contributing three  $\text{Cl}^-$  (or  $\text{Na}^+$ ).

(d) One  $\text{Cl}^-$  (or  $\text{Na}^+$ ) is present at the centre of the cube.

Thus, we have on an average four  $\text{Na}^+$  ions and four  $\text{Cl}^-$  ions per unit cell, or a total equivalent to four molecules of sodium chloride. The volume allotted to these molecules is the volume of one unit cell. Thus, the molar volume is given by

$$\begin{aligned} V_m &= \frac{\text{volume of one unit cell}}{4} \times N_A \\ &= \frac{(1.786 \times 10^{-28} \text{ m}^3)}{4} \times (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= 2.689 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

(iv) The density of NaCl is

$$\rho = \frac{M}{V_m} = \frac{(58.443 \text{ g mol}^{-1})}{(2.689 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})} = 2.173 \times 10^6 \text{ g m}^{-3} = 2.173 \text{ g cm}^{-3}$$

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