(iii)	a	b	c	
	6	3	3	intercepts
	1/6	1/3	1/3	reciprocals
	1	2	2	clear fractions

(iv)	a	b	c	
	2	–3	–3	intercepts
	1/2	–1/3	–1/3	reciprocals
	3	–2	–2	clear fractions

Hence, the Miller indices are (122).

Hence, the Miller indices are $(3\,\bar{2}\,\bar{2})$

Note. The negative sign in the Miller indices is indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses.

Interplanar Spacing in a Crystal System. It can be shown that in a crystal, the interplanar distance d_{hkl} is given by

$$1/(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2$$

...(12)

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

For a *cubic system*, $a = b = c$ so that from Eq. 12,

$$d_{hkl} = a/[h^2 + k^2 + l^2]^{1/2}$$

...(13)

For a *tetragonal system*, $a = b \ne c$ so that

$$1/(d_{hkl})^2 = (h^2 + k^2)/a^2 + l^2/c^2$$

...(14)

For an *orthorhombic system*, $a \ne b \ne c$ so that

$$1/(d_{hkl})^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$$

...(15)

Example 12. The parameters of an orthorhombic unit cell are $a=50$ pm, $b=100$ pm, $c=150$ pm. Determine the spacing between the (123) planes.

Solution : For an orthorhombic unit cell, the interplanar distance, d_{hkl}, is given by

$$1/(d_{hkl})^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$$

...(Eq. 15)

$$1/(d_{hkl})^2 = 1/(d_{123})^2 = (1/50 \text{ pm})^2 + (2/100 \text{ pm})^2 + (3/150 \text{ pm})^2 = 3(1/50 \text{ pm})^2$$

$$1/d_{123} = \sqrt{3}\,/50 \text{pm} \text{ so that } d_{123} = 50 \text{pm}\,/\sqrt{3} = 29 \text{ pm}$$

Example 13. The density of Li metal is 0.53 g cm^{-3} and the separation of the (100) planes of the metal is 350 pm. Determine whether the lattice is f.c.c. or b.c.c. $M(\text{Li})=6.941$ g mol^{-1}.

Solution : Density, $\rho = 0.53$ g cm^{-3} = 530 kg m^{-3}

For the cubic system, $d_{hkl} = a/[h^2 + k^2 + l^2]^{1/2}$

$$\therefore \quad d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = 350 \text{ pm} = 350 \times 10^{-12} \text{ m}$$

We know from Eq. 1, that

$$\rho = nM/(N_A V) = nM/(N_A a^3) \qquad (\because V = a^3)$$

$$\therefore \quad n = \frac{\rho N_A a^3}{M} = \frac{(530 \text{ kg m}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})(350 \times 10^{-12} \text{ m})^3}{6.941 \times 10^{-3} \text{ kg mol}^{-1}} = 1.97 \approx 2$$

As shown in Example 3, for an f.c.c. lattice, n=4 and for a b.c.c. lattice, n=2. Hence, lithium has a *b.c.c. lattice*.

X-RAY DIFFRACTION

The German physicist M. von Laue (1879–1960), in 1913, suggested the possibility of diffraction of X-rays by crystals. The reason for this suggestion was that the wave length of X-rays was of about the same order as the interatomic distances in a crystal. von Laue was awarded the 1914 Physics Nobel Prize for his discovery of diffraction of X-rays by crystals. In fact, W.H. Bragg succeeded in diffracting X-rays from sodium chloride crystal. This observation has proved to be highly useful in determining structures and dimensions of crystals as well as in the study of a number of properties of X-ray themselves.

The Bragg Equation. Bragg pointed out that unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles which are determined by the wave length of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wave length of the X-rays, the interplanar distance in the crystal and the angle of reflection, is known as the Bragg equation.

Derivation of the Bragg Equation. Consider Fig. 10. The horizontal lines in this figure represent parallel planes in the crystal structure separated from one another by the distance d. Suppose a beam of X-rays falls on the crystal at **glancing angle** θ, as shown. Some of these rays will be reflected from the upper plane at the same angle θ while some others will be absorbed and get reflected from the successive layers, as shown. Let the planes ABC and DEF be drawn perpendicular to the incident and reflected beams, respectively. The waves

Fig. 10. X-ray reflections from a crystal.

reflected by different layer planes will be in phase with one another (i.e., will coincide with one another in the plane DEF) only if the difference in the path lengths of the waves reflected from the successive planes is equal to an integral number of wave lengths. Drawing OL and OM perpendicular to the incident and reflected beams, it will be seen that the difference in the path lengths (say, δ) of the waves reflected from the first two planes is given by
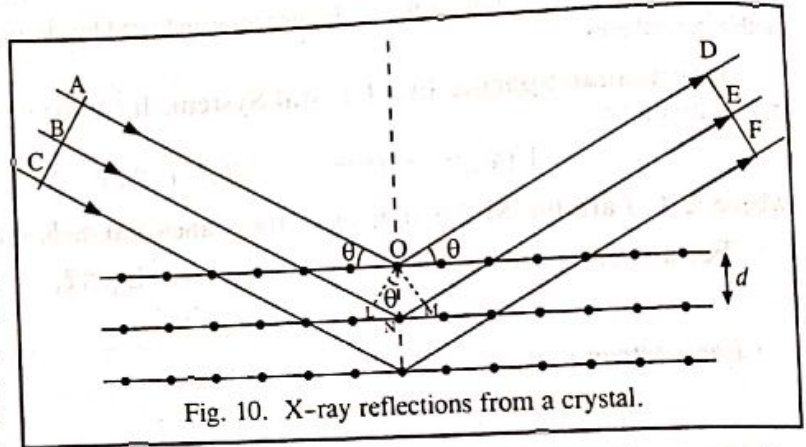
$$\delta = LN + NM \qquad \qquad \text{...(16)}$$

This should be equal to a whole number multiple of wave length λ, i.e.,

$$LN + NM = n\lambda \qquad \qquad \text{...(17)}$$

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

$$\therefore \qquad 2LN = n\lambda \quad \text{or} \quad 2d \sin\theta = n\lambda \qquad \qquad \text{...(18)}$$

This is the **Bragg equation.** Knowing θ, n and λ, d can be calculated.

For a given set of lattice planes, d has a fixed value. Therefore, the possibility of getting maximum reflection (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be found at which the reflections will be maximum. At these positions, n will have values equal to 1, 2, 3, 4, 5, etc. Generally, in experiments on X-ray reflections, n is set as equal to 1. If λ is known, it is possible to determine d, the distance between atomic planes in the crystal by determining θ experimentally. On the other hand, if d is known, λ can be evaluated.

Experimental Methods. The X-ray diffraction techniques used in the study of crystals are of two types known as the rotating crystal technique and the powder technique. Both the techniques make use of the X-ray spectrometer, the setting of which for the former technique is shown in Fig. 11.

Fig. 11. An X-ray spectrometer.
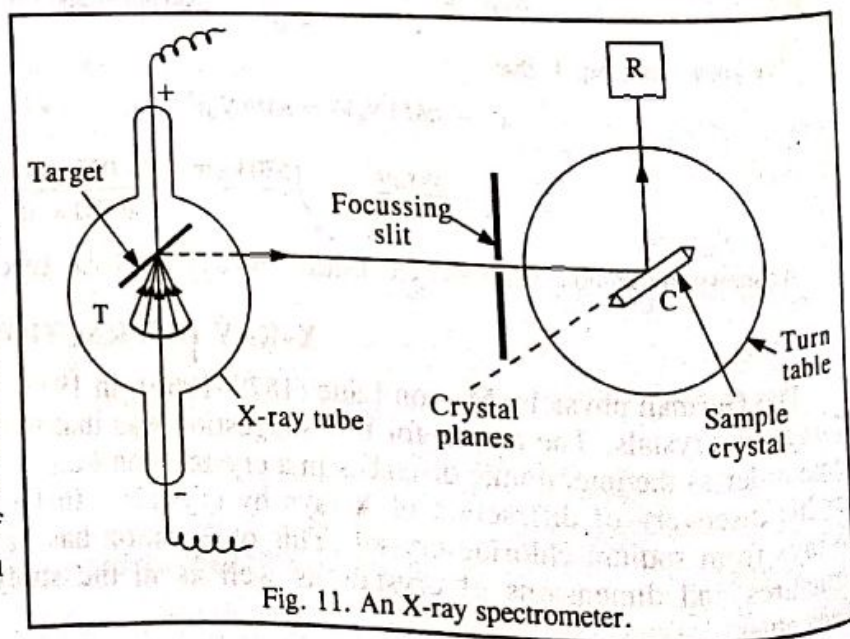
X-rays generated in the tube T are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal C mounted on the turn-table. The crystal is rotated gradually by means of the turn-table so as to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recording device R, such as a photographic plate or an ionisation chamber. The angles for which reflections are maximum give the value of θ. The process is carried out for each plane of the crystal. The lowest angle at which the maximum reflection occurs corresponds to $n=1$. This is called the first order reflection. The next higher angle at which the maximum reflection occurs again, corresponds to $n=2$. This is the second order reflection, and so on.

The values of θ for the first order reflection from the three faces of sodium chloride crystal are found to be 5·9°, 8·4° and 5·2°, respectively. Applying the Bragg equation and knowing that n and λ are the same in each case, the distance d between successive planes in the three faces will be in the ratio of

$$1/\sin 5·9° : 1/\sin 8·4° : 1/\sin 5·2° = 9·61 : 6·84 : 11·04 = 1·00 : 0·70 : 1·14$$

This ratio is very close to that expected to exist between spacings along the three planes of a face-centred cube. Thus, *sodium chloride has face-centred cubic structure.*

Powder Method : The Debye-Scherrer Method.
The powder method is more widely used particularly for crystals with simple structures. The powder, in fact, consists of many small crystals which are oriented in all possible directions. As a result of this, X-rays are scattered from all sets of planes (*e.g.*, 100, 110, etc.). The scattered rays are detected by using an X-ray-sensitive film. The principle of the method is illustrated in Fig. 12. The substance to be examined is finely powdered and is kept in the form of a cylinder inside a thin glass tube. A narrow beam of X-rays is allowed to fall on the powder. The diffracted X-rays strike a strip of photographic film arranged in the form of a circular arc, as shown in the figure.
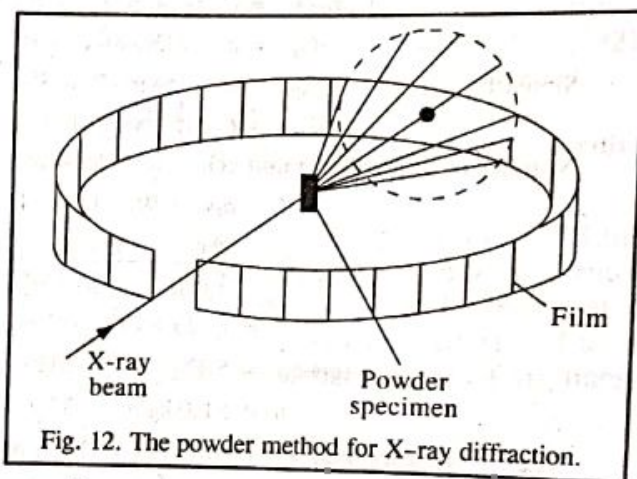

Fig. 12. The powder method for X-ray diffraction.

In this method, no rotation is necessary since the powder sample already contains microcrystals arranged in all possible orientations. Hence, a large number of them will have their lattice planes in correct positions for maximum X-ray reflection to occur. As a result of this we get lighted areas in the form of arcs of lines at different distances from the incident beam, as shown. These distances can be converted into scattering angles to be used in the Bragg equation for different planes of the crystal.

The British physicists W.H. Bragg (1862–1942) and his son W.L. Bragg (1890–1971) shared the 1915 Physics Nobel Prize for the analysis of crystal structure with X-rays. W.L. Bragg became at 25 the youngest Nobel Laureate in history. The Bragg equation is named after both the father and the son.

Example 14. KNO_3 crystallizes in orthorhombic system with the unit cell dimensions $a=542$ pm, $b=917$ pm and $c=645$ pm. Calculate the diffraction angles for first order X-ray reflections from (100), (010) and (111) planes using radiation with wave length $=154·1$ pm.

Solution :
$$2d_{hkl} \sin \theta = n\lambda$$
For an orthorhombic system, we have
$$1/(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2 \qquad \qquad ...(Eq. 15)$$

∴
$$1/(d_{100})^2 = (1/542 \text{ pm})^2 + (0/917 \text{ pm})^2 + (0/645 \text{ pm})^2 = (1/542 \text{ pm})^2$$
∴
$$d_{100} = a = 542 \text{ pm}$$

Similarly,
$$d_{010} = b = 917 \text{ pm} \quad \text{and} \quad d_{111} = c = 378 \text{ pm}$$

For first order reflection, $n=1$. Also $\lambda = 154·1$ pm

$$\therefore \quad \sin \theta_{100} = \frac{\lambda}{2d_{100}} = \frac{154 \cdot 1 \text{ pm}}{2 \times 542 \text{ pm}} = 0 \cdot 142 \quad \text{whence} \quad \theta_{100} = 8°10'$$

$$\sin \theta_{010} = \frac{\lambda}{2d_{010}} = \frac{154 \cdot 1 \text{ pm}}{2 \times 917 \text{ pm}} = 0 \cdot 084 \quad \text{whence} \quad \theta_{010} = 4° 49'$$

$$\sin \theta_{111} = \frac{\lambda}{2d_{111}} = \frac{154 \cdot 1 \text{ pm}}{2 \times 378 \text{ pm}} = 0 \cdot 204 \quad \text{whence} \quad \theta_{111} = 11° 46'$$

Example 15. $HgCl_2$ crystallizes in orthorhombic system. Using radiation with $\lambda = 154$ pm, the (100), (010) and (001) reflections (first order) from $HgCl_2$ in an X-ray diffractometer occur at 7° 25', 3° 28' and 10° 23', respectively. If the density of the crystal is 5·42 g cm^{-3}, calculate the dimensions of the unit cell and the number of $HgCl_2$ molecules in the unit cell. $M(HgCl_2) = 271 \cdot 5$ g mol^{-1}.

Solution : Dimensions of the unit cell : For first order reflections, $n = 1$. Hence,

$$2\, d_{hkl} \sin \theta_{hkl} = \lambda \quad \text{so that } d_{hkl} = \lambda/2 \sin \theta_{hkl}$$

For the orthorhombic system,

$$1/(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2$$
$$1/(d_{100})^2 = (1/a)^2 + (0/b)^2 + (0/c)^2 = 1/a^2$$

$$\therefore \quad d_{100} = a = \lambda/2\sin \theta_{100} = 154 \text{ pm}/2\sin (7° 25') = \mathbf{597 \text{ pm}}$$

Similarly, $d_{010} = b = 154$ pm/2 sin 3° 28' = **1270 pm**

$$d_{001} = c = 154 \text{ pm}/2 \sin 10°13' = \mathbf{434 \text{ pm}}$$

Number of molecules in unit cell : The volume of the unit cell,

$$V = abc = 597 \times 1270 \times 434 \text{ pm}^3 = 3 \cdot 29 \times 10^{-28} \text{ m}^3$$

$$\therefore \quad \rho = \frac{nM}{VN_A} = \frac{(n)(271 \cdot 5 \text{ g mol}^{-1})}{(3 \cdot 29 \times 10^{-28} \text{ m}^3)(6 \cdot 022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 1 \cdot 37\, n \times 10^6 \text{ g m}^{-3} = 1 \cdot 37\, n \times 10^3 \text{ kg m}^{-3}$$

$$\rho \text{ (given)} = 5 \cdot 42 \text{ g cm}^{-3} = 5420 \text{ kg m}^{-3}$$

$$\therefore \quad n = 5420 \text{ kg m}^{-3}/1 \cdot 37 \times 10^3 \text{ kg m}^{-3} = \mathbf{3 \cdot 97 \approx 4}$$

Since n = 4, hence there are **4 molecules of $HgCl_2$ per unit cell.**

Example 16. Calculate the angle at which (a) first order reflection and (b) second order reflection will occur in an X-ray spectrometer when X-rays of wave length 1·54 Å are diffracted by the atoms of a crystal, given that the interplanar distance is 4·04 Å.

Solution : (a) For first order reflection ($n = 1$), the Bragg equation is $2d \sin \theta = \lambda$

$$\therefore \quad \theta = \sin^{-1}(\lambda/2d) = \sin^{-1}(1 \cdot 54 \text{ Å}/8 \cdot 08 \text{ Å}) = \sin^{-1}(0 \cdot 191) = \mathbf{10° 59'}$$

(b) For second order reflection ($n = 2$), the Bragg equation is $2d \sin \theta = 2\lambda$

$$\therefore \quad \theta = \sin^{-1}(\lambda/d) = \sin^{-1}(1 \cdot 54/4 \cdot 04) = \sin^{-1}(0 \cdot 381) = \mathbf{22° 24'}$$

Example 17. The density of LiF is 2·601 g cm^{-3}. The (111) first order reflection in the X-ray diffraction from LiF occurs at 8°44' when X-rays of wave length 70·8 pm are used. If there are four LiF molecules per unit cell, calculate Avogadro's number. LiF crystallizes in the cubic system. Li = 6·939, F = 18·998.

Solution : $2d_{hkl} \sin \theta_{hkl} = n\lambda$; $n = 1$ for first order reflection

$$\therefore \quad d_{111} = \frac{\lambda}{2 \sin \theta_{111}} = \frac{70 \cdot 8 \text{ pm}}{2 \sin (8° 44')} = \mathbf{233 \text{ pm}}$$

Also, for the cubic system,

$$d_{hkl} = a/[h^2 + k^2 + l^2]^{1/2}$$

$$\therefore \quad d_{111} = a/[1^2 + 1^2 + 1^2]^{1/2} = a/\sqrt{3} \quad \text{so that } a = \sqrt{3}\, d_{111}$$

Thus, $a = \sqrt{3} \times 233$ pm = 40·356 pm = 403·56 × 10^{-12} m

Density, $\rho = M/V = 2 \cdot 601$ g cm^{-3} (given) = 2,601 kg m^{-3}

Since there are four LiF molecules in the unit cell, hence,

$$M = 4 (25 \cdot 937 \text{ g mol}^{-1}) = 103 \cdot 748 \text{ g mol}^{-1} = 103 \cdot 748 \times 10^{-3} \text{ kg mol}^{-1}$$

$$V = N_A a^3 = M/\rho$$

$$\therefore \quad N_A = \frac{M}{\rho a^3} = \frac{103 \cdot 748 \times 10^{-3} \text{ kg mol}^{-1}}{(2,601 \text{ kg m}^{-3})(403 \cdot 56 \times 10^{-12} \text{ m})^3} = 6 \cdot 49 \times 10^{23} \text{ mol}^{-1}$$

This value compares very well with the accepted value of $6 \cdot 022 \times 10^{23} \text{ mol}^{-1}$.

X–Ray Diffraction Patterns of a Cubic System

It is of particular importance to discuss the X-ray diffraction patterns of a cubic system. We know that for a cubic system, the interplanar distance d_{hkl} is given by

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2} \qquad \qquad ...(19)$$

Combining this result with the Bragg equation, viz., $\lambda = 2d_{hkl} \sin \theta_{hkl}$, we get

$$\lambda = \frac{2a \sin \theta_{hkl}}{(h^2 + k^2 + l^2)^{1/2}} \qquad \qquad ...(20)$$

$$\therefore \quad \sin^2 \theta_{hkl} = (\lambda^2/4a^2)(h^2 + k^2 + l^2) = K(h^2 + k^2 + l^2) \qquad ...(21)$$

where $K = \lambda^2/4a^2$. K has a constant value for a given cubic crystal and a given wave length λ.

We can use Eq. 21 for predicting the diffraction patterns of the three types of lattices of the cubic system, as illustrated below.

1. Primitive Cubic Lattice. Using Eqs. 19 and 21 and integral values (0, 1, 2,...) for the Miller indices h, k, and l, we construct Table 3. It may be noted that since the integer 7 cannot be written in the form $h^2 + k^2 + l^2$, hence, $\sin^2 \theta$ cannot be equal to $7K$. The diffraction lines will be observed at angles shown in Table 3. The diffraction pattern for a primitive cubic lattice will thus consist of a set of equally spaced six lines followed by an extinction (i.e., a gap) and then another series of six lines.

TABLE 3
Interplanar distances and angles ($\sin^2 \theta_{hkl}$ values) for which diffraction lines are observed for a primitive cubic lattice

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

2. Body–Centered Cubic Lattice. Using Eqs. 19 and 20 and integral values (0, 1, 2,....) for h, k and l, we construct Table 4. We see that all diffraction lines for which $(h+k+l)$ is an odd integer, are absent. We observe lines at angles shown in Table 4.

TABLE 4
Interplanar distances and angles ($\sin^2 \theta_{hkl}$ values) for which diffraction lines are observed for a body-centred cubic lattice

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

3. Face-Centred Cubic Lattice. Proceeding as above, we construct Table 5. We see that the diffraction lines are observed only from those planes for which the values of h, k and l are either all odd or all even. We observe diffraction lines at angles shown in Table 5.

TABLE 5
Interplanar distances and angles ($\sin^2 \theta_{hkl}$ values) for which diffraction lines are observed for a face-centred cubic lattice

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

The X-ray diffraction patterns for the three types of cubic lattices are collectively shown in Fig. 13.
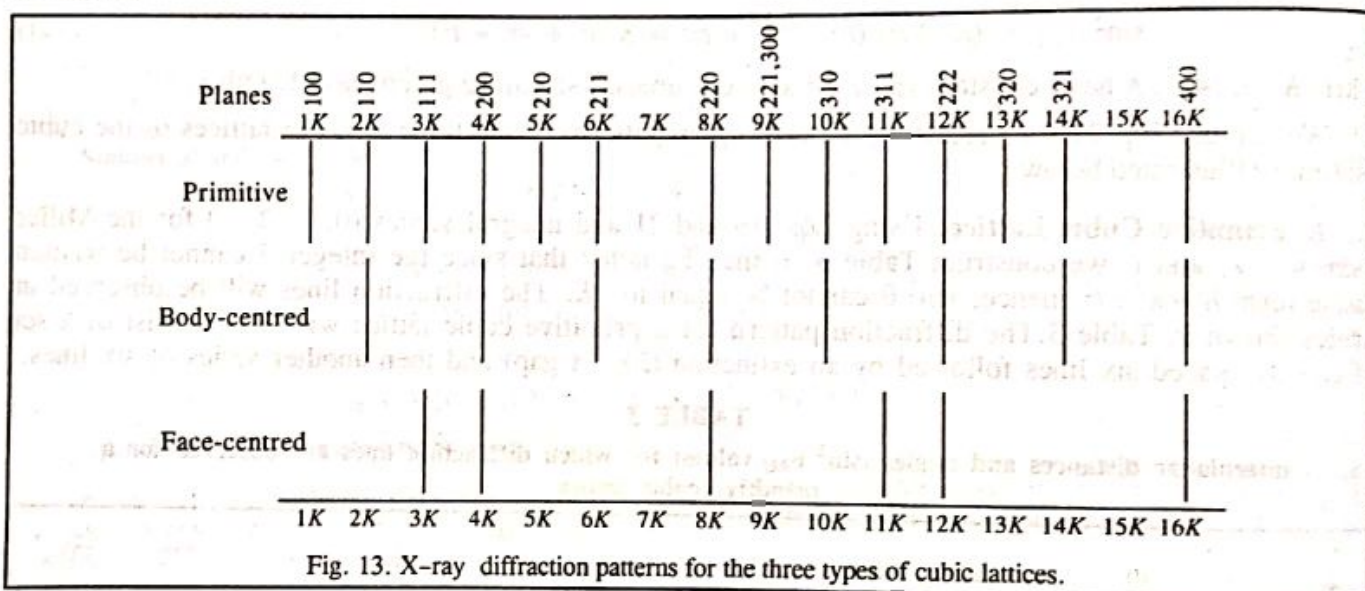

Fig. 13. X-ray diffraction patterns for the three types of cubic lattices.

From the above discussion we see that extinctions (*i.e.*, missing reflections) in the diffraction patterns can help in distinguishing between the three types of cubic lattices. In the X-ray diffraction studies, the crystallographer searches for the missing reflections. It should be noted that whereas the spacing between the lines of a primitive cubic system is equal to K (with a gap after the 6th, 14th and 22nd, etc., lines) the spacing between lines of a body-centred cubic system is equal to $2K$. Thus, the number of lines obtained in the diffraction pattern can help in distinguishing between these two systems. After the identification of the diffraction pattern, it is possible to assign each line with the correct values of the Miller indices h, k and l. From the measurement of any one of these lines, we can determine the value of a, the length of the edge of the cube, by using the equation

$$a = (\lambda / 2 \sin \theta_{hkl}) (h^2 + k^2 + l^2)^{1/2} \qquad \ldots(22)$$

If the lines are indexed correctly, the same value of a is obtained from all the values of $\sin \theta_{hkl}$.

X-ray Diffraction Pattern for Tungsten Crystal. The X-ray diffraction pattern for tungsten crystal is shown in Fig. 14.

We notice that there is variation in intensity of the diffracted X-ray beam for different sets of *hkl* planes. This is presumably due to the variation of density of atoms in these planes. The planes having high atomic density give rise to a better X-ray diffraction thereby producing a more intense diffracted beam.
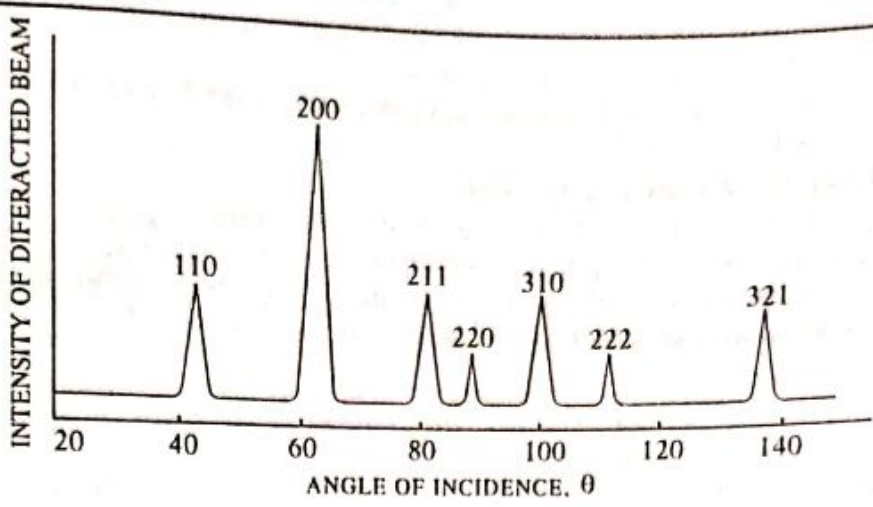

Fig. 14. X-ray diffraction pattern for tungsten crystal.

If the crystal contains more than one kind of atoms, the atom containing greater number of electrons scatters the X-rays to a greater extent. It is found that the *scattering power of an atom is directly proportional to the number of electrons* in the atom. Thus, when the unit cell of a crystal contains hydrogen atoms and other heavier atoms, the scattering effect of hydrogen atoms is overshadowed by that of the other atoms which contain larger number of electrons. Hence, *the positions of hydrogen atoms in the unit cell of a crystal cannot be determined from the X-ray diffraction pattern.* Their positions can be determined by *neutron diffraction.* We shall discuss this aspect a little later in this chapter.

Example 18. The X-ray diffraction pattern of silver, known to crystallize in the cubic system, was obtained using X-rays with wave length 154·1 pm. The first six lines occurred at the following angles : 19·08°, 22·17°, 32·26°, 38·74°, 40·82° and 49·00°. (a) Determine the type of the cubic system, (b) Calculate the length of the edge of the cube, (c) Calculate the interplanar distance of the plane (111).

Solution : (a) From Eq. 21, $\sin^2 \theta_{hkl} = K (h^2 + k^2 + l^2)$ where $K = \lambda^2/4a^2$,

We construct the following table with $K = 0·0356$:

θ	19·08°	22·17°	32·26°	38·74°	40·82°	49·00°
$\sin \theta$	0·3268	0·3773	0·5338	0·6257	0·6536	0·7547
$\sin^2 \theta$	0·1067	0·1424	0·2848	0·3915	0·4272	0·5696
	3K	4K	8K	11K	12K	16K

Comparing this pattern with that given in Fig. 13, we see that silver crystallizes in face-centred cubic system.

(b) From Eq. 22, $\qquad a = \dfrac{\lambda}{2 \sin \theta_{hkl}} (h^2 + k^2 + l^2)^{1/2}$

The reflection at 19·08° is due to the (111) plane.

∴ $\qquad a = \dfrac{154·1 \text{ pm}}{2 \times 0·3268} (1^2 + 1^2 + 1^2)^{1/2} = 408·6 \text{ pm}$

(c) From Eq. 13, $\qquad d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$

∴ $\qquad d_{111} = 408·6 \text{ pm}/(1^2 + 1^2 + 1^2)^{1/2} = 408·6 \text{ pm}/\sqrt{3} = 235·9 \text{ pm}$

Example 19. AgCl has a face-centred cubic unit cell whereas CsCl has a body-centred unit cell. Determine which of the following Miller indices are permitted in the X-ray diffraction pattern of (a) AgCl and (b) CsCl : 100, 010, 001, 200, 020, 002, 110, 101, 011, 120, 102, 012, 210, 201, 021, 220, 202, 022, 111, 222, 221, 212, 122, 211, 121, 112.

Solution : (a) AgCl has a f.c.c. unit cell. So, the only allowed reflections are those in which all indices are even or all are odd, giving Miller indices 200, 020, 002, 220, 202, 022, 111 and 222. Since $a=b=c$, 200=020=002 and 220=202=022 so that only four peaks will be observed corresponding to 200, 220, 111 and 222.

(b) CsCl has a b.c.c. unit cell. So, the only allowed reflections are those in which $h+k+l=$ even, giving 200=020=002 ; 110=101=011 ; 220=202=022 and 211=121=112.

Fourier Synthesis of Electron Density in a Crystal

Since X-rays are scattered by the electrons in a crystal, the ultimate goal of X-ray crystallography is to determine the electron density $\rho(xyz)$ as a function of the coordinates x, y, z. Since the number of electrons and the size of the atomic orbitals both vary from atom to atom, different atoms have different scattering efficiencies. The *scattering factor f* of an atom is defined as

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin kr}{kr} r^2 dr \qquad \qquad ...(23)$$

where $\rho(r)$ is the spherically symmetric electron density (number of electrons per unit volume) of the atom and $k = (4\pi/\lambda) \sin \theta$ where λ is the wave length of the X-rays and θ is the scattering angle. Since the wave length of the X-rays used for recording the X-ray diffraction pattern is of the size of an atom, the scattered waves from different regions of an atom interfere constructively. The integral in Eq. 23 takes this interference into account through the factor $(\sin kr)/kr$. Before proceeding further we shall prove an important result that the scattering factor of an atom in the direction $\theta \to 0$ is equal to the number of electrons (N_e) in the atom, *i.e.*,

$$\underset{\theta \to 0}{\text{Limit}} f = N_e \qquad \qquad ...(24)$$

Here $\theta \to 0$ implies that the X-rays pass straight through the atom. If $\theta = 0$, then $k = 0$ and the term $(\sin kr)/kr$ in Eq. 23 is indeterminate. Hence, to evaluate the integrand, we evaluate the limit $(\sin kr)/kr$.
$$kr \to 0$$

We know from the result of the power series that

$$\underset{\theta \to 0}{\text{limit}} \frac{\sin \theta}{\theta} = \underset{\theta \to 0}{\text{limit}} \frac{\theta - \dfrac{\theta^3}{3!} + \dfrac{\theta^5}{5!} - ....}{\theta} \qquad \qquad ...(25)$$

$$\approx 1 - \frac{\theta^3}{3!} + \frac{\theta^4}{4!} - ..... \approx 1 \qquad \qquad ...(26)$$

Hence, $\underset{kr \to 0}{\text{limit}} (\sin kr)/kr = 1$ so that

$$f = 4\pi \int_0^\infty \rho(r) r^2 dr = N_e \qquad \qquad ...(27)$$

since the integrand is the product of the electron density and the spherical volume element $4\pi r^2 dr$, which upon integration yields the total number of electrons in the atom.

Let us now return to the electron density $\rho(xyz)$ which is so defined that $\rho(xyz)dxdydz$ is the number of electrons in the volume element $dxdydz$. Since the electron density is a periodic function, it can be expanded by a Fourier series :

$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) \exp\left[-2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right)\right] \qquad ...(28)$$

where V is the volume of the unit cell ; x, y, z are the coordinates of a point in the unit cell ; a, b, c are the unit cell dimensions ; (hkl) are the Miller indices and $F(hkl)$ are the Fourier coefficients which are

also referred to as the **structure factors**. Each structure factor is associated with a particular reflection from the (*hkl*) planes. Though the triple summation in Eq. 28 is over all the values ($-\infty$ to $+\infty$) of h, k, l, in practice all the terms need not be included in the summation although the more the terms included, the higher is the resolution of $\rho(xyz)$. The structure factors contain all the information about all the atoms in a unit cell. The structure factor $F(hkl)$ is defined as

$$F(hkl) = \sum_j f_j \exp\left[2\pi i\left(\frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c}\right)\right] \qquad ...(29)$$

where f_j is the scattering factor of the jth atom in the unit cell and the summation is over all the atoms in the unit cell. To account for the above expression for $F(hkl)$, we recall that when the Bragg law is satisfied for a given reflection, the amplitude of the wavelet scattered from an atom in one unit cell of the crystal is in phase with the amplitudes of the scattered wavelets from the corresponding atoms in the millions of the other unit cells of the crystal. However, the wavelet scatterred by one atom may, in general, not be in phase with the wavelet scattered by another atom within the same unit cell with the result that the intensity $I(hkl)$ of reflection will depend upon the extent to which amplitudes of the wavelets reflected from different atoms (denoted by f_j) are in phase with one another. It is known that

$$I(hkl) \propto |F(hkl)|^2 \qquad ...(30)$$

i.e., the intensities of the X-ray diffraction patterns from the (*hkl*) planes of the crystal are proportional to the square of the modulus (absolute value) of $F(hkl)$. $I(hkl)$ can be determined from the densities of spots on the photographic film. From the values of $I(hkl)$, $|F(hkl)|^2$ can be determined. But the crystallographer needs $F(hkl)$ rather than $|F(hkl)|^2$ to calculate $\rho(xyz)$ with the help of Eq. 28. Since $F(hkl)$ is a complex number, we can write

$$F(hkl) = A(hkl) + iB(hkl) \qquad ...(31)$$

Hence,
$$|F(hkl)|^2 = [A(hkl) + iB(hkl)][A(hkl) - iB(hkl)]$$
$$= [A(hkl)]^2 - [B(hkl)]^2 \qquad ...(32)$$

Since the values of $A(hkl)$ and $B(hkl)$ are not obtained directly, indirect methods are employed to determine these quantities for the evaluation of $F(hkl)$. For a centrosymmetric crystal, $F(hkl)$ is of the form

$$F(hkl) = \pm f_{heavy} \pm f_{light} \qquad ...(33)$$

where f_{heavy} are the scattering factors of the heavy atoms and f_{light} are the scattering factors of the light atoms. The f_{light} are much smaller than f_{heavy} and their phases are almost random if the atoms are distributed throughout the unit cell. Thus, the heavy atoms dominate scattering since their scattering factors are of the order of their atomic numbers. Since the net result of f_{light} changes $F(hkl)$ only slightly, it follows that $F(hkl)$ will have the same sign as that calculated from the location of the heavy atoms. This phase is then combined with the observed $|F(hkl)|$ obtained from the observed value of $I(hkl)$ to perform the Fourier synthesis of the entire electron density in the unit cell thereby enabling the location of both the heavy and the light atoms. This is how the **phase problem** in crystallography is solved.

Patterson Synthesis. This technique is employed for determining relative orientations of pairs of atoms in a given crystal structure. The technique makes use of the Patterson equation, viz.,

$$\vec{P(r)} = \frac{1}{V}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}|F(hkl)|^2\exp\left[-2\pi i\left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right)\right] \qquad ...(34)$$

The values of $|F(hkl)|^2$ can be obtained without ambiguity from the value of $I(hkl)$. The Patterson equation is manifested in the form of a map of *vector separation* between the atoms in the unit cell. Thus, if (x_A, y_A, z_A) and (x_B, y_B, z_B) are, respectively, the coordinates of atoms A and B in the unit cell, then there would occur a peak at $(x_A-x_B, y_A-y_B, z_A-z_B)$ and also at $(x_B-x_A, y_B-y_A, z_B-z_A)$ since there is a vector

from B to A as well as a vector from A to B. The height of the peak in the map is proportional to the product $Z_A Z_B$ where Z_is are the atomic numbers. Thus, the relative orientation of each pair of atoms in the original structure can be obtained from the Patterson map. This technique was used extensively by the British crystallographer Dorothy Hodgkin (1910–1994) during 1940–1960 to determine the structures of important biochemical substances. She was awarded the 1964 Chemistry Nobel Prize for her work.

More advanced techniques, known as direct methods, were developed in the 1950s by the American crystallographers H. Hauptman and J. Karle for the determination of crystal structures. The discussion of these methods is, however, beyond the scope of the present volume. Hauptman and Karle were awarded the 1985 Chemistry Nobel Prize for their contributions.

Example 20. Calculate the structure factor $F(hkl)$ values for the three types of cubic lattices, *viz.*, the primitive cubic (P), body centred cubic (I) and face–centred cubic (F) and therefrom determine which reflections would be absent from the diffraction pattern. The fractional coordinates (x_j, y_j, z_j) of the atoms in the three types of lattices are :

P : (0, 0, 0) ; I : (0, 0, 0) and (1/2, 1/2, 1/2) and F : (0, 0, 0), (1/2, (1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2)

Solution : This example illustrates the use of the structure factors to distinguish between the three types of cubic lattices.

For the primitive cubic (P) lattice,

$$F(h, k, l) = \sum_j f_j \exp\left[2\pi i \left(\frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c}\right)\right]$$

$$= \sum_j f_j \qquad \text{(since } x_j, y_j, z_j) \text{ are zero and } e^0 = 1)$$

Thus, $F(hkl)$ has the same value for all h, k and l. Hence there would be reflections in the diffraction pattern for all integral values of h, k and l.

For the body–centred cubic (I) lattice,

$$F(h, k, l) = f \exp[2\pi i (0 + 0 + 0)] + f \exp[2\pi i (h/2 + k/2 + l/2)]$$

$$= f[1 + \exp i\pi (h+k+l)]$$

Recalling that $e^{i\theta} = \cos\theta + i\sin\theta$ (Euler's relation) with $\theta = \pi$, we have

$$e^{i\pi} = \cos\pi + i\sin\pi = -1$$

Thus, $F(h, k, l) = f[1 + (-1)^{h+k+l}]$

If $(h+k+l)$ is even, $F(h,k,l) = 2f$ and if $(h+k+l)$ is odd, $F(hkl) = 0$. Thus, in the X–ray diffraction pattern, reflections such as (110), (200), (211), (310), etc., will be present and reflections such as (100), (111), (210), (300), etc., will be absent.

For the face–centred cubic (F) lattice,

$$F(hkl) = f \exp[2\pi i (0+0+0)] + f \exp[2\pi i (h/2+k/2+0)] + f \exp[2\pi i (h/2 + 0 + h/2)] + f \exp[2\pi i(0 + k/2 + l/2)]$$

$$= f[1 + \exp(i\pi(h+k)) + \exp(i\pi(h+l) + \exp(i\pi(k+l)]$$

$$= f[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]$$

If h, k, l are all even or all odd, $F(hkl) = 4f$ and these reflections will be present. If one is even and the other two are odd, or the reverse, then these reflections will be absent.

ELECTRON DIFFRACTION

The wave–particle duality of matter was proposed by the French physicist Louis de Broglie in 1924. According to de Broglie's hypothesis, the wave length λ of electrons moving with velocity v is given by $\lambda = h/(m_e V)$, where m_e is the mass of the electron. Electrons can be accelerated to precisely controlled energies by applying a known potential difference. When accelerated through 10 keV, they acquire a wave length of 12 pm which makes them suitable for molecular diffraction investigations. Electron diffraction studies generally utilize electrons with energies of the order of 40 keV. Since electrons are charged, they are scattered strongly by their interaction with electrons and nuclei of atoms of the sample. Hence, they

cannot be used for studying the interiors of solid samples. They can, however, be used *for* studying molecules in the gaseous state held on surfaces and in thin films. The most important application involves the study of electron diffraction by substances in their vapour state at low pressures (of the order of 10^{-5} torr). The strong interaction of electrons with molecules of the sample plus a very great effect on the photographic plate combine to require a very short exposure of the order of tenths of a second.

Whereas the diffraction of X-rays by a crystal depends upon the spacing between the layers, *the diffraction of electrons by gaseous molecules depends upon the distances between the atoms in a molecule.* Since the gaseous molecules are randomly oriented relative to the electron beam, the diffraction pattern, like that of an X-ray powder photograph, consists of concentric rings. There is an appreciable amount of background scatter of the electron beam with the result that diffraction bands are only poorly resolved. New experimental techniques have, however, greatly improved the resolution of the bands.

It is possible to calculate the electron scattering from a pair of nuclei separated by a distance R_{ij} and oriented at a definite angle to the incident beam. The overall diffraction pattern is then calculated by allowing for all possible orientations of this pair of atoms. This procedure amounts to integration over all possible orientations. The final expression obtained for the diffraction intensity is

$$I_{ij}(\theta) = 2f_i f_j \{(1 + \sin s\, R_{ij})/s\, R_{ij}\} \qquad \ldots(35)$$

where $s = - (4\pi/\lambda) \sin(\theta/2)$, λ is the wave length of electron beam and θ is the scattering angle. The quantities f_i and f_j are the scattering factors of the ith and jth atoms. They determine the scattering power of the atoms. If a molecule consists of a number of atoms, the total intensity is given by the Wierl equation, *viz.*,

$$I(s) \propto \sum_{i,j} f_i f_j \frac{\sin s\, R_{ij}}{s\, R_{ij}} \qquad \ldots(36)$$

where the summation is over all the atoms i and j of the molecule. The electron diffraction pattern can be interpreted in terms of the distances between all possible pairs of atoms in the molecule (not simply those bonded together). The Wierl equation does not, unfortunately, allow the direct calculation of the internuclear distances R_{ij} from the measurements of $I(s)$ at various values of s.

The electron diffraction studies are useful for evaluating the bond lengths and bond angles in relatively simple gaseous molecules. As the number of atoms in the molecules increases, one soon reaches the situation where the number of pieces of information available (*viz.*, the spacings of the resolved diffraction rings) is not great enough to evaluate all of the necessary structural parameters. The number of electron diffraction rings observed is usually much less than the number of X-ray diffraction spots observed in the X-ray crystal study. This shows that difficulties lie in the path of structure determination by electron diffraction. In spite of these difficulties, however, many molecular structures have been determined by this method. The accuracy of bond length and bond angles obtained from electron diffraction studies is comparable to that obtained from X-ray diffraction studies for simple molecules.

NEUTRON DIFFRACTION

As dissussed above, diffraction patterns can be obtained by means of electron beams when they are scattered by molecules. Because of their negative charge and hence low penetrating power, the electron beams are generally used for the investigation of surfaces and thin films. Neutrons, on the other hand, have a high penetrating power and are particularly useful for structural studies of solids. Neutron diffraction by crystals was demonstrated as early as in 1936 but the method did not become important until the advent of nuclear piles. Fast neutrons produced in a nuclear pile are slowed down by collisions with a moderator (D_2O or graphite) to produce thermal neutrons, *i.e.*, neutrons for which the range of kinetic energies is determined by the temperature of the surroundings.