

SOLID STATE

LECTURE-4

Lattice Planes in a Cubic System

Some of the lattice planes in the cubic crystals are shown in Fig. 3.9.3.

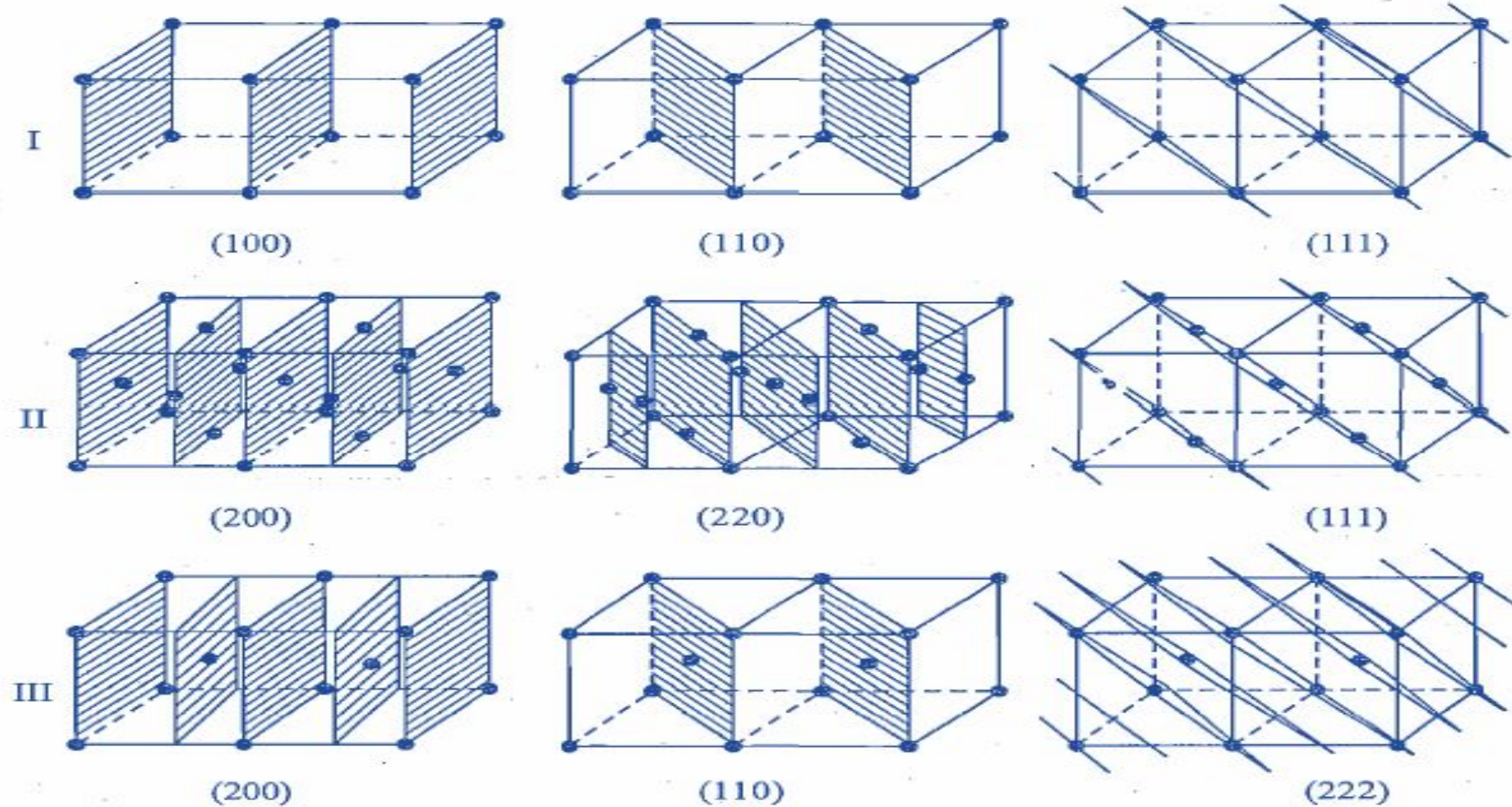


Fig. 3.9.3 Some of the lattice planes of cubic lattice: (I) Primitive cubic lattice, (II) Face-centred cubic lattice, (III) Body-centred cubic lattice

The distances between planes of a crystal can be determined with the help of X-ray diffraction measurements. These can, in turn, be used to determine the system to which the crystal belongs.

INTERPLANAR DISTANCES FOR CUBIC SYSTEMS

A Few Typical Examples

(1) (100) planes Distance between these planes is equal to the length a of the side of a cube, i.e. $d_{100} = a$.

(2) (200) planes Distance between these planes is equal to the half length $a/2$ of the side of a cube, i.e. $d_{200} = a/2$.

(3) (110) planes Spacing between these planes is one-half of the diagonal of the square base of the cube, i.e. $d_{110} = (\sqrt{a^2 + a^2})/2 = a/\sqrt{2}$

(4) (111) planes The entire cross diagonal d of a cube spans three (111) planes. Thus, the distance between the two of each of these planes is $d/3$. Now,

$$d = \sqrt{a^2 + a^2 + a^2} = \sqrt{3}a$$

$$\text{Therefore } d_{111} = \frac{\sqrt{3}a}{3} = \frac{a}{\sqrt{3}}$$

(5) (222) planes These planes are in between (111) planes. Thus, the distance between any two such planes is

$$d_{222} = \frac{d_{111}}{2} = \frac{a}{2\sqrt{3}}$$

General Formula

General formula for the interplanar spacing in the cubic system (orthogonal axes) is

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.10.1)$$

where hkl are Miller indices of the planes and a is edge length of the cube.

Utility of Interplanar Distances

It is obvious that if one had a method for determining d_{hkl} experimentally, the constancy of the quantity $d_{hkl}\sqrt{h^2 + k^2 + l^2}$ will not only determine the value of a but will also indicate to what cubic system the given crystal belongs.

The ratios of interplanar distances of different faces in the three cubic lattices (Fig. 3.9.3) are:

$$\text{Simple cubic lattice} \quad d_{100}:d_{110}:d_{111} = 1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}, \quad \text{i.e.} \quad 1:0.707:0.577$$

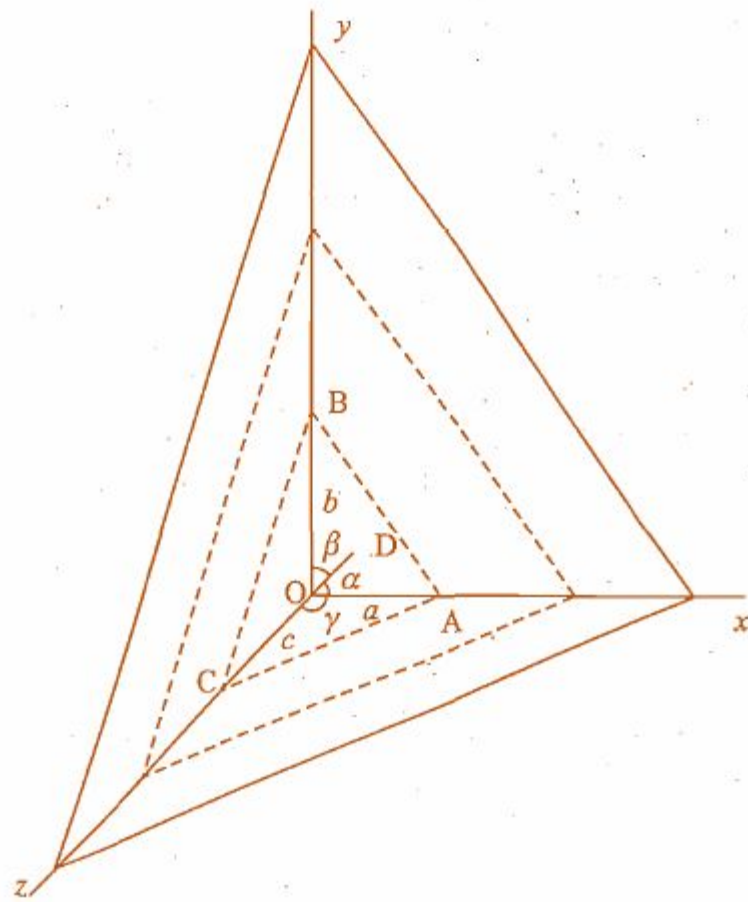
$$\text{Face-centred cubic lattice} \quad d_{200}:d_{220}:d_{111} = \frac{1}{2}:\frac{1}{2\sqrt{2}}:\frac{1}{\sqrt{3}}, \quad \text{i.e.} \quad 1:0.707:1.154$$

$$\text{Body-centred cubic lattice} \quad d_{200}:d_{110}:d_{222} = \frac{1}{2}:\frac{1}{\sqrt{2}}:\frac{1}{2\sqrt{3}}, \quad \text{i.e.} \quad 1:1.414:0.577$$

Geometrical Method

The general formula for the interplanar spacing in a system of orthogonal axes can be derived geometrically.[†] As stated earlier, the Miller indices define the set of parallel planes, one of which passes through the origin. Thus, if a perpendicular is drawn from the origin to the nearest plane of Miller indices (hkl), then this perpendicular distance, represented as d_{hkl} , will be equal to the interplanar spacing between planes of Miller indices (hkl) as shown by OD in Fig. 3.10.1.

Fig. 3.10.1 Interplanar distance of the planes



If α , β , and γ are the angles which this perpendicular makes with the three axes, then

$$d_{hkl} = OA \cos \alpha = \left(\frac{a}{h} \right) \cos \alpha, \quad d_{hkl} = OB \cos \beta = \left(\frac{b}{k} \right) \cos \beta$$

and
$$d_{hkl} = OC \cos \gamma = \left(\frac{l}{c} \right) \cos \gamma$$

or
$$\cos \alpha = \left(\frac{h}{a} \right) d_{hkl}, \quad \cos \beta = \left(\frac{k}{b} \right) d_{hkl}, \quad \text{and} \quad \cos \gamma = \left(\frac{l}{c} \right) d_{hkl}$$

Now since $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ are the direction cosines of the perpendicular line, therefore

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

Substituting their values in terms of d_{hkl} , we have

$$\left(\frac{h}{a}\right)^2 d_{hkl}^2 + \left(\frac{k}{b}\right)^2 d_{hkl}^2 + \left(\frac{l}{c}\right)^2 d_{hkl}^2 = 1$$

or
$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

For a cubic system $a = b = c$, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{or} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For a tetragonal system, $a = b \neq c$, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

For an orthorhombic system $a \neq b \neq c$, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

DIFFRACTION OF ELECTROMAGNETIC RADIATION

Characteristics of Waves

Electromagnetic radiation consists of waves that are propagated through space with the velocity of light. It can be characterized by either frequency or wavelength. The former gives the number of cycles through which the wave moves in one second and the latter gives the distance between two points on the wave which have gone through a complete cycle. These two, i.e. frequency and wavelength, are related by the expression

$$v = \frac{c}{\lambda}$$

Associated with the wave is the amplitude which is the displacement of the wave in a direction perpendicular to the direction of its propagation. The wave nature can be represented by either a sine wave or a cosine wave as shown in Fig. 3.11.1.

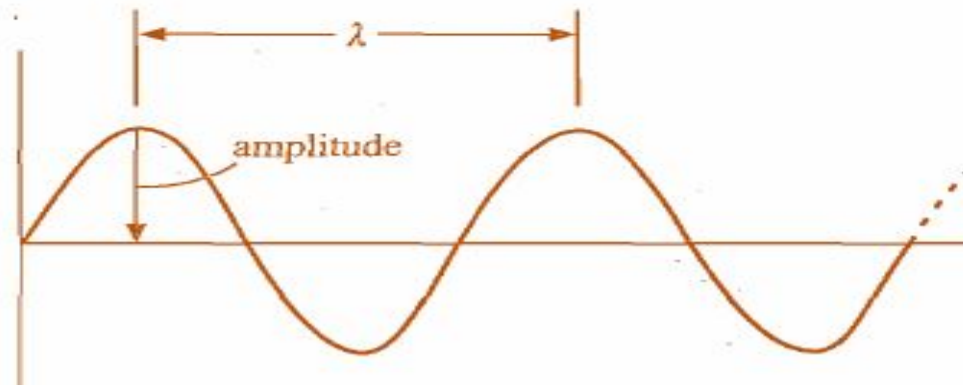


Fig. 3.11.1 Wave propagation

Constructive and Destructive Interferences

Two waves coming from two different sources having the same wavelength and same amplitude reinforce each other when their maxima and minima coincide. On the other hand, they will interfere and exactly cancel each other when their maxima and minima do not coincide. The former is known as *constructive interference* and the latter as *destructive interference*. The amplitude of the resultant wave at any point is obtained by the algebraic sum of the amplitudes of the two individual waves at the point.

This interference phenomenon forms the basis of the diffraction of light by a diffraction grating. A typical diffraction grating consists of a transparent medium (such as glass) on which are ruled a large number of very fine, equidistant, parallel, opaque lines. When light from a monochromatic source is incident perpendicular on the grating, all the clear spaces will act as secondary sources of light and, therefore, will emit light waves in all directions radially outward. The wavelengths and frequencies of the diffracted light waves are the same as that of the incident light waves. The waves from two apertures will cross at some point beyond the grating. If a screen is placed at this point, a series of bright and dark spots will be observed on the screen. A bright spot is obtained where the waves from adjacent apertures in the grating reinforce one another. A dark spot arises from the destructive interference of waves at the point. Figure 3.11.2 shows the interference of waves from two adjacent apertures of a grating.

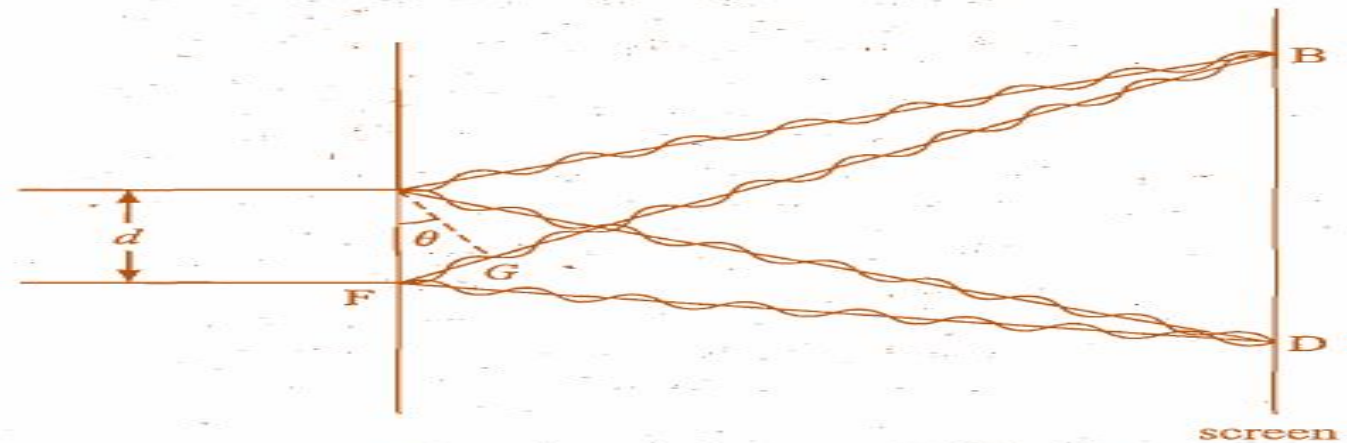


Fig. 3.11.2 Diffraction of light by a diffraction grating (waves from only two adjacent apertures are shown). B—Bright spot. D—Dark spot

Condition for Bright Spot

A bright spot is observed when both the waves are in phase. The essential condition for this to be observed is that the extra distance travelled by one of the waves is an integral multiple of wavelength.

$$\text{Thus } FG = n\lambda \quad n = 0, 1, 2, \dots$$

From Fig. 3.11.2, it follows that

$$FG = d \sin \theta$$

Equating these two, we get

$$n\lambda = d \sin \theta \quad n = 0, 1, 2, \dots$$

A grating with $4,000 \text{ lines cm}^{-1}$ is illuminated with Hg green line having a wavelength equal to 546 nm . At what angle will the first and second order diffraction maxima occur?

The grating spacing, $d = \frac{1}{4000 \text{ cm}^{-1}} = 2.5 \times 10^{-4} \text{ cm} = 2.5 \times 10^{-6} \text{ m}$

Therefore, angle of first order diffraction maxima is

$$\sin \theta_1 = \frac{n\lambda}{d} = \frac{(1) (546 \times 10^{-9} \text{ m})}{2.5 \times 10^{-6} \text{ m}} = 0.2184$$

or $\theta_1 = 12.62^\circ$

Angle of second order diffraction maxima is

$$\sin \theta_2 = \frac{(2) (546 \times 10^{-9} \text{ m})}{2.5 \times 10^{-6} \text{ m}} = 0.4368$$

or $\theta_2 = 25.9^\circ$

Calculate the angle at which the first order maxima occurs if an electromagnetic wave of 10 nm is exposed to the above grating.

The angle at which first order maxima is observed is given by

$$\sin \theta = \frac{(1) (10 \times 10^{-9} \text{ m})}{2.5 \times 10^{-6} \text{ m}} = 4.0 \times 10^{-3}$$

or $\theta = 0.23^\circ$

Comment

The calculated angle of first order maxima in Example 3.11.2 is too close to the intense beam which occurs at $\theta = 0$ and thus cannot be determined accurately. In order to obtain measurable separation of maxima, it is essential that the spacing between lines of grating should be approximately equal to the wavelength of the employed electromagnetic radiation.

DIFFRACTION OF X-RAYS BY CRYSTALS

Laue Method

In 1912, Max von Laue predicted that since the distances between particles in a crystal are of the same order of magnitude ($\approx 10^{-8}$ cm) as the wave length of X-rays, the former could be used as a *3-dimensional diffraction grating* and thus if a beam of non-homogeneous X-rays were passed through a crystal, a diffraction pattern would be observed. The experiments carried out on various substances verified Laue's prediction. The diffraction pattern can be recorded by placing a photographic plate behind the crystal as shown in Fig. 3.12.1. On developing the film, one observes a series of spots arranged in some symmetrical way around the intense central undiffracted beam. The arrangement of these spots (known as Laue spots) is highly characteristic of the structural arrangement of the crystal. From the position of Laue spots, it is possible to calculate the size and shape of the unit cell. However, the actual analysis of the Laue diffraction pattern is highly complicated and difficult.

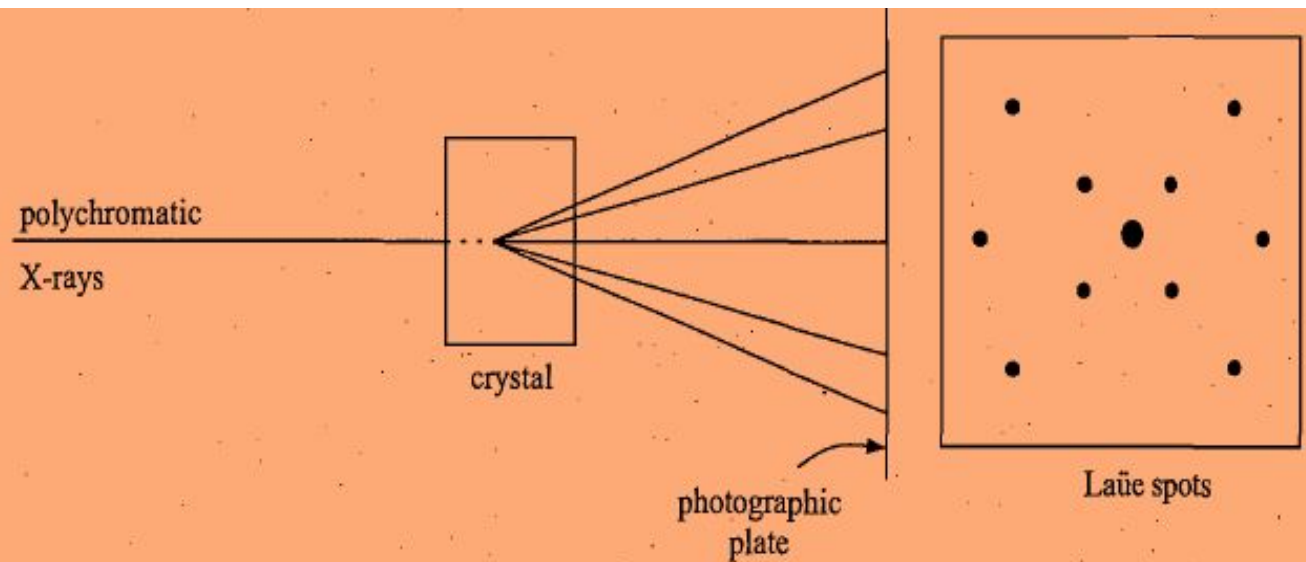


Fig. 3.12.1 Laue diffraction pattern

Crystal as a Reflection Grating

B.H. Bragg and W.L. Bragg were of the opinion that since a crystal is composed of a series of equally spaced atomic planes, it may be employed not only as a transmission grating as in the Laue method, but also as a *reflection grating*. When X-rays are incident on a crystal face, they penetrate into the crystal and suffer reflections on striking the atoms in successive planes as shown in Fig. 3.13.1. If the reflected waves from successive layers are out of phase, then due to the destructive interference, no diffraction will be observed. If, however, the reflected waves are in phase, then due to the constructive interference, a diffraction spot will be observed. The condition for a reflection to give constructive interference can be derived from Fig. 3.13.1 as follows.

Let θ be the incident angle of monochromatic X-rays of wavelength λ with the parallel equidistant planes of atoms with interplanar spacing equal to d . The waves are in phase before striking the planes. Two such waves labelled as wave 1 and wave 2 are shown in Fig. 3.13.1. After the reflection, the two waves will be in phase provided the extra distance travelled by wave 2 is an integral multiple of wavelength λ . This extra distance can be obtained by dropping perpendiculars BG and BH from B on to wave 2. It is obvious from Fig. 3.13.1 that

$$AB = DG; \quad BC = HF; \quad GE = EH = d \sin \theta$$

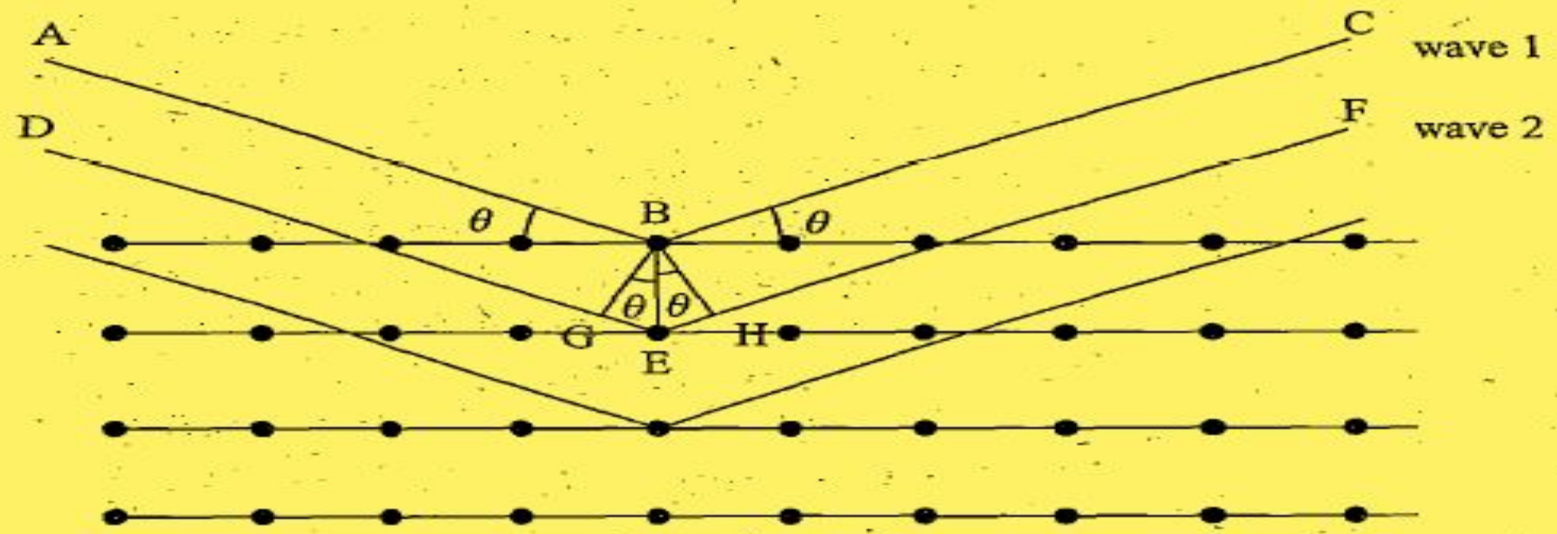
Now the extra distance travelled by wave 2 is given as

$$\begin{aligned} DEF - ABC &= (DG + GE + EH + HF) - (AB + BC) \\ &= GE + EH \\ &= 2d \sin \theta \end{aligned}$$

Thus, in order to have wave 1 and wave 2 in phase, we must have

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots \quad (3.13.1)$$

Fig. 3.13.1 Reflection of X-rays from the planes of a crystal



Equation (3.13.1) is known as the Bragg's equation. The constant n gives the order of reflection and is equal to the number of wavelengths in the path difference between waves reflected by adjacent planes. Thus, n can take only integral values subject to the limitation that $\sin \theta$ cannot be greater than one. For fixed values of λ and d , we can have more than one reflection at angles $\theta_1, \theta_2, \dots$ corresponding to the values of n equal to 1, 2, 3, ..., respectively. From Eq. (3.13.1), it can be concluded that the higher order reflections will occur at larger values of $\sin \theta$ and hence at larger angles. Experimentally, it is found that the lower order reflections are the most intense and the intensities of higher order reflections decreases rapidly.

Alternative Way of Writing Bragg's Equation

While dealing with X-ray diffraction, it is more convenient to express higher order reflections in terms of the first order reflection from planes of higher Miller indices (hkl). For example, a second order reflection from (111) planes may be considered equivalent to the first order reflection from (222) planes. Similarly a third order reflection from (111) planes may be considered as the first order reflection from (333) planes. This fact can be introduced into the Bragg equation $n\lambda = 2d \sin \theta$ by rewriting it as

$$\lambda = 2 \left(\frac{d}{n} \right) \sin \theta = 2 d_{hkl} \sin \theta$$

where d_{hkl} is the perpendicular distance between adjacent planes having the indices (hkl).

Experimental Set-up

The reflection angles and the intensities of the reflected beams corresponding to these angles can be determined with the help of Bragg X-ray spectrometer, a schematic diagram of which is shown in Fig. 3.13.2. This method consists of the following steps.

(1) The X-rays are generated in tube A by bombarding cathode rays on a suitable target B. The most commonly used target metals and their characteristic wavelengths are *copper* 154.1 pm, *molybdenum* 70.9 pm and *chromium* 229.0 pm.

(2) The generated X-rays are passed through a series of slits and filters (C, D, etc.) in order to get a sharp monochromatic beam. It is then directed to strike the face of a crystal placed on a *graduated turntable* F. The latter may be rotated to any desired angle of incidence.

(3) The reflected beam is passed into an *ionization chamber* G containing SO_2 . The reflected X-rays ionize the SO_2 gas in proportion to their intensity. The extent of ionization and hence the intensity of reflection can be determined with the help of an electrometer.

(4) The experiment is repeated at various incident angles of X-rays and the angle at which maximum reflection occurs is determined.

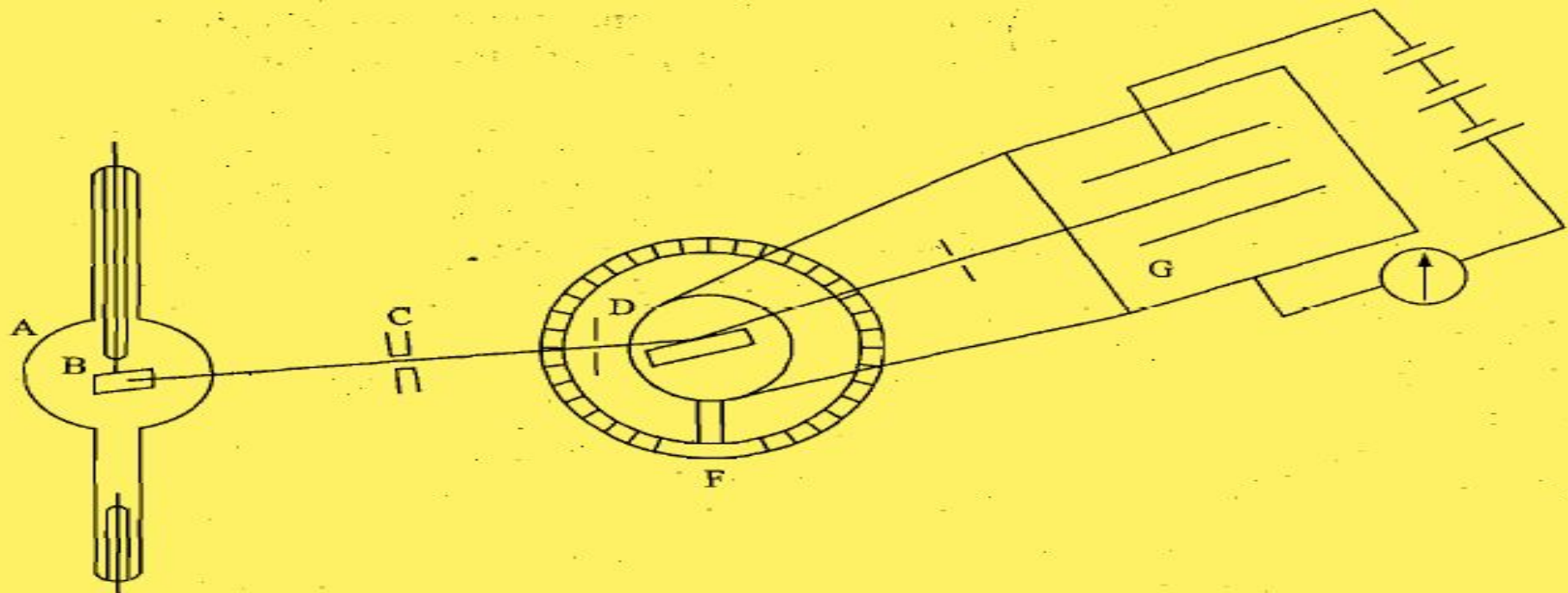
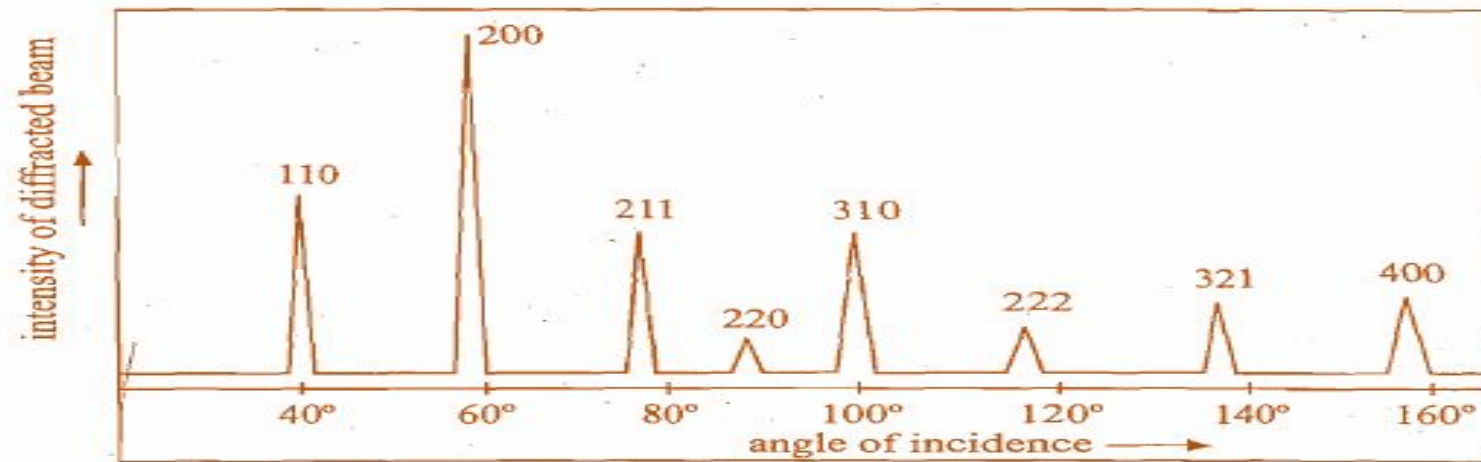


Fig. 3.13.2 Bragg X-ray spectrometer

X-ray Diffraction Pattern

The X-ray diffraction pattern (only schematic) for a crystal of tungsten is shown in Fig. 3.13.3.

Fig. 3.13.3 X-ray diffraction pattern (only schematic) for a crystal of tungsten



The variation in intensity of the diffracted beam for different sets of planes is due to the variation in density of atoms in these planes. The planes of high atomic density produce better scattering of X-rays which gives a more intense beam.

When a certain crystal was studied by the Bragg technique using X-rays of wavelength 229 pm, an X-ray reflection was observed at an angle of $23^{\circ} 20'$. (a) What is the corresponding interplanar spacing? (b) When another X-ray source was used, a reflection was observed at $15^{\circ} 26'$. What was the wavelength of these X-rays?

(a) Given that

$$\lambda = 229 \text{ pm} \quad \text{and} \quad \theta = 23^{\circ} 20'$$

Substituting these in the Bragg equation, we have

$$\begin{aligned} d_{hkl} &= \frac{\lambda}{2 \sin \theta} = \frac{229 \text{ pm}}{2 \times \sin (23^{\circ} 20')} = \frac{229 \text{ pm}}{2 \times 0.396} \\ &= 289.2 \text{ pm} \end{aligned}$$

(b) Now $\theta = 15^{\circ} 26'$, thus

$$\begin{aligned} \lambda &= 2d_{hkl} \sin \theta = 2(289.2 \text{ pm}) \sin (15^{\circ} 26') \\ &= 2(289.2 \text{ pm}) (0.226 2) = 153.9 \text{ pm} \end{aligned}$$
