Chapter two: X-ray diffraction in crystallography

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2.1 Introduction about the Crystallography

Crystallography is the experimental science of determining the arrangement of atoms in the crystalline solids. Before the development of x-ray diffraction in crystallography, the study of crystals was based on physical measurements of their geometry. This involved measuring the angles of crystal faces, crystallographic axes and establishing the symmetry of the crystal. Crystallographic methods now depend on analysis of the diffraction patterns of a sample targeted by a beam of some type. X-rays are most commonly used, i.e., other beams used include electrons or neutrons.

2.1.1 **Basic definitions**

There are some basic definitions to understand x-ray diffraction in crystallography:

*A **crystal** is defined as atoms arranged in a pattern periodic in three dimensions* As such, crystals differ in a fundamental way from gases and liquids because the atomic arrangements in the latter do not possess the essential requirement of periodicity. Not all solids are crystalline, however; some are amorphous, like glass, and do not have any regular interior arrangement of atoms.

***Crystal structure** is a set of atoms in space arranged in the crystal lattice.* Crystals are composed of three-dimensional patterns. These patterns consist of atoms or groups of atoms which are arranged and repeated at regular intervals. By replacing each group of atoms by a representative point *a **crystal lattice** is obtained*. Thus, ***a crystal lattice** is defined as an array of points in space so arranged that each point has identical surroundings*. By "identical surroundings" we mean that the lattice of points, when viewed in a particular direction from one lattice point, would have exactly the same appearance when viewed in the same direction from any other lattice point. *The crystal lattice can be thought of as an array of 'small boxes' infinitely repeating in all three directions.*
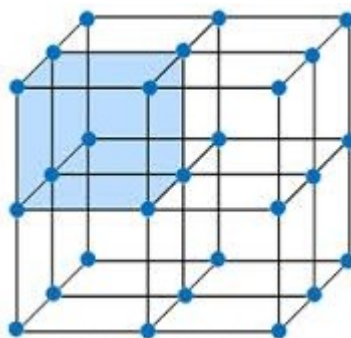

Fig. 1.

Unit cell is the smallest unit of volume (*smallest box*) *that contains all the structural and symmetry information to build-up the structure of the lattice.* The size and shape of the unit cell can be described by the three vectors **x**, **y**, and **z** drawn from one corner of the cell taken as origin. These vectors define the cell and are called the crystallographic axes of the cell. They may also be described in terms of their lengths (*a, b, c*) and the angles between them (α, β, γ). These lengths and angles are the lattice constants or lattice parameters of the unit cell. The whole set of points in the lattice can be produced by repeated action of the vectors **a**, **b**, **c** on one lattice point located at the origin.
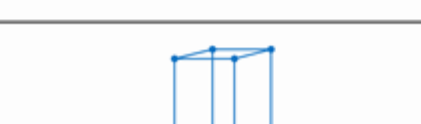
Fig.2.

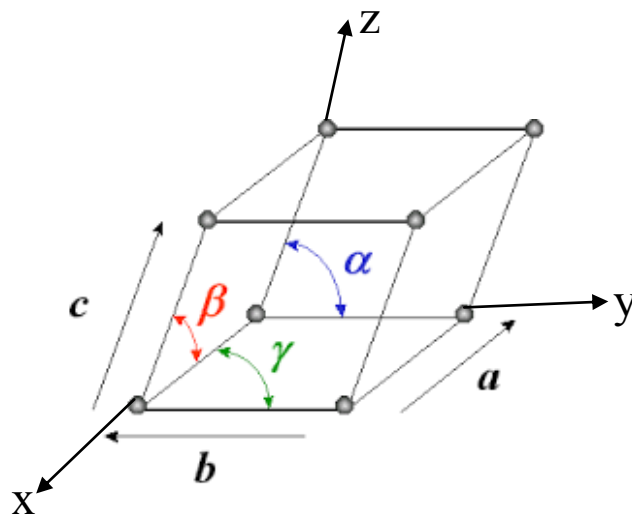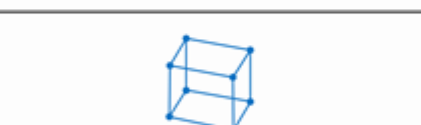## 2.1.2 Crystal system and Bravias lattices

By giving special values to the axial lengths (a, b, and c) and angles (α, β, γ), we can produce unit cells of various shapes and therefore various kinds of point lattices, since the points of the lattice are located at the cell corners. It turns out that only seven different kinds of cells are necessary to include all the possible point lattices. These correspond to the seven crystal systems into which all crystals can be classified. These systems are listed in the following Table

Table 1: Crystal system and Bravias lattices

Cubic P Cubic I Cubic F	Three axes at right angles; all equal: $a=b=c$; $\alpha=\beta=\gamma=90°$
Tetragonal P Tetragonal I	Three axes at right angles; two equal: $a=b\neq c$; $\alpha=\beta=\gamma=90°$
P C I F Orthorhombic	Three axes at right angles; all unequal: $a\neq b\neq c$; $\alpha=\beta=\gamma=90°$
Monoclinic P Monoclinic C	Three axes, one pair not at right angles, all unequal: $a\neq b\neq c$; $\alpha=\gamma=90°\neq\beta$
Triclinic P	Three axes not at right angles; all unequal: $a\neq b\neq c$; $\alpha\neq\beta\neq\gamma\neq90°$
Rhombohedral	Three axes equally inclined, not at right angles; all equal: $a=b=c$; $\alpha=\beta=\gamma\neq90°$
Hexagonal	Three axes coplanar at 120°, fourth axis at right angles to these: $a_1=a_2=a_3\neq c$; $\alpha=\beta=90°$, $\gamma=120°$

Seven different point lattices can be obtained simply by putting points at the corners of the unit cells of the seven crystal systems. However, there are other arrangements of points which fulfill the requirements of a point lattice. The French crystallographer *Bravais* worked on this problem and in 1848 demonstrated that there are fourteen possible point lattices and no more; this important result is commemorated by our use of the terms *Bravais lattice and point*

lattice as synonymous. In addition to Primitive lattice (P), i.e., lattice points on the cell corners only. There are three additional Bravais lattice:

- Body-Centered (I): lattice points on the cell corners with one additional point at the center of the cell

- Face-Centered (F): lattice points on the cell corners with one additional point at the center of each of the faces of the cell

- Base-Centered (C): lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered).

2.1.3 Lattice directions and planes

The direction of any line in a lattice may be described by first drawing a line through the origin parallel to the given line and then giving the coordinates of any point on the line through the origin.

uvw are numbers that are related to coordinate systems, no commas between them and written in square brackets like [*uvw*], which are the *indices of the direction of the line. u* represents the vector parallel to the *x*-axis; *v* represents the vector parallel to the *y*-axis; *w* represents the vector parallel to the *z*-axis. Negative indices are written with a bar over the number, e.g., [$\bar{u}vw$].
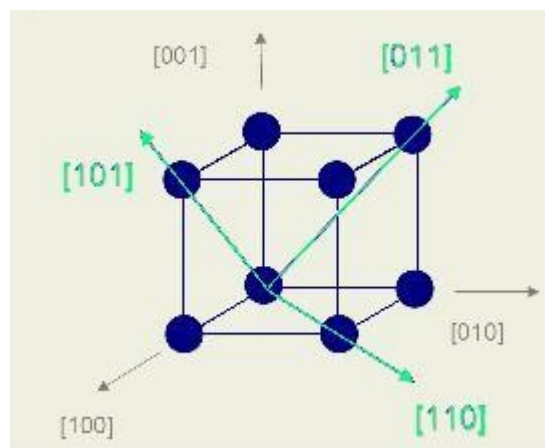

Fig.3.

H.W.: In a cubic unit cell, draw correctly a vector with indices [146].

Miller indices are the orientation of a plane in a lattice and which are defined as *the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.*

(*hkl*) is the *Miller indices of a plane*, where *h* represents the plane perpendicular to the x-axis; *k* represents the plane perpendicular to the y-axis; *l* represents the plane perpendicular to the z-axis.

For example: from Fig.4, what are the Miller indices?

Solution: the intercepts are x = $3a$, y = $2b$ and z = $1c$

Therefore, $\frac{x}{a} = 3$, $\frac{y}{b} = 2$ and $\frac{z}{c} = 1$

The reciprocals of above numbers are $\frac{1}{3}$, $\frac{1}{2}$ and 1

Multiply by 6, we get the following numbers: 2, 3, 6

So that, the above numbers are the Miller indices of

the plane, where *h*=2, *k*=3, and *l*=6,

which can be written as (2,3,6)

Fig. 4.

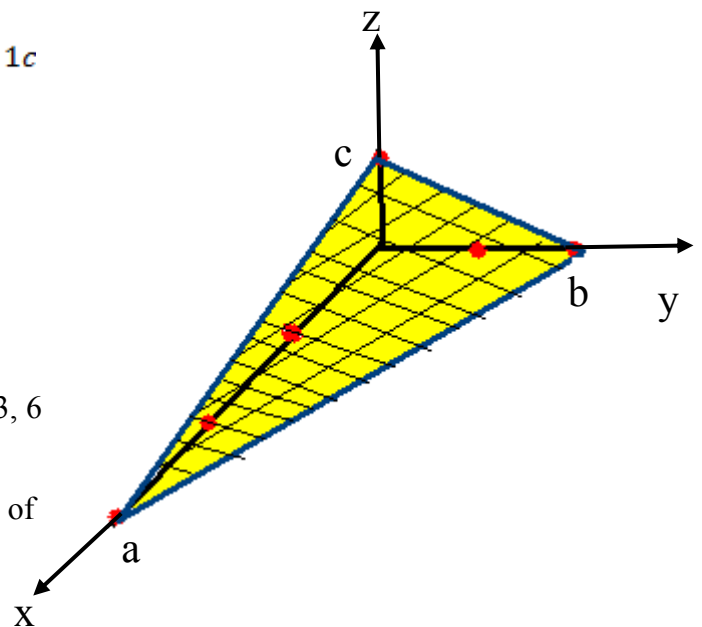**H.W.: Draw correctly the lattice planes from the following Miller indices (110), (220), (020) and (321).**

The directions of cubic system have the same indices are equivalent regardless of their order or sign, i.e., [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001] and [00$\bar{1}$], which are called the family of direction of cubic system and can be written between angular brackets ⟨100⟩

6

In non-cubic systems such as orthorhombic ($a \neq b \neq c$) and tetragonal ($a = b \neq c$), directions that have the same indices are not necessarily equivalent.

The various sets of planes in a lattice have various values of interplanar spacing (d_{hkl}), i.e., interplanar spacing is the distance between the plane in the lattice. The interplanar spacing measured at right angles to the planes, is a function both of the Miller indices (hkl) and the lattice constants (*a, b, c*). The exact relation depends on the crystal system involved and for the cubic system takes on the relatively simple form:

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \text{ for cubic system; } d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2(a^2/c^2)}} \text{ for tetragonal system}$$

H.W.: If the crystal system is cubic, calculate interplanar spacing for the plane (211).

2.2 X-ray diffraction and Bragg's law

Two geometrical facts are worth remembering:

(1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar.

(2) The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally.

Diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This requirement follows from the Bragg law. Since $\sin \theta$ cannot exceed unity, which mean:

$$\frac{n\lambda}{2d} = \sin \theta \leq 1$$

Therefore, $n\lambda$ must be less than $2d$. For diffraction, the smallest value of n is 1. Therefore the condition for diffraction at any observable angle 2θ is:

$\lambda < 2d$

For most crystals d ~ 3 Å this lead to λ ≤ 6 Å. For UV radiation λ ≈ 500 Å, whereas Cu Kα λ = 1.542 Å.

The Bragg law may be written in the form:

$\lambda = 2d \sin \theta$

If the path AB + CD is a multiple of the x-ray wavelength λ, then two waves will give a constructive interference: $n\lambda = AB + CD = 2d \sin \theta$
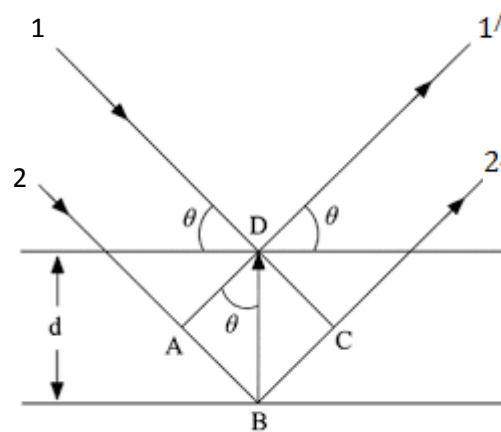

Fig.5.

2.3 X-ray spectroscopy

Experimentally, the Bragg law can be utilized in two ways. By using x-rays of known wavelength λ and measuring θ, we can determine the spacing d_{hkl} of various planes in a crystal: this is *structure analysis*. Alternatively, we can use a crystal with planes of known spacing d_{hkl}, measure θ, and thus determine the wavelength λ of the radiation used: this is x-ray spectroscopy. The essential features of an x-ray spectrometer are shown in the following Figure:
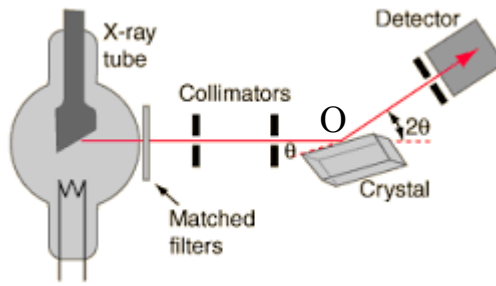
Fig.5.

X-rays from the tube are incident on a crystal which may be set at any desired angle to the incident beam by rotation about an axis through O, the center of the spectrometer circle. Detector is a form of counter which measures the intensity of the diffracted x-rays; it can also be rotated about and set at any desired angular position. The crystal is usually cut or cleaved so that a particular set of reflecting planes of known spacing is parallel to its surface. In use, the crystal is positioned so that its reflecting planes make some particular angle θ with the incident beam, and the detector is set at the corresponding angle 2θ. The intensity of the diffracted beam is then measured and its wavelength calculated from the Bragg law, this procedure being repeated for various angles θ. It is in this way that curves such as in below Figure
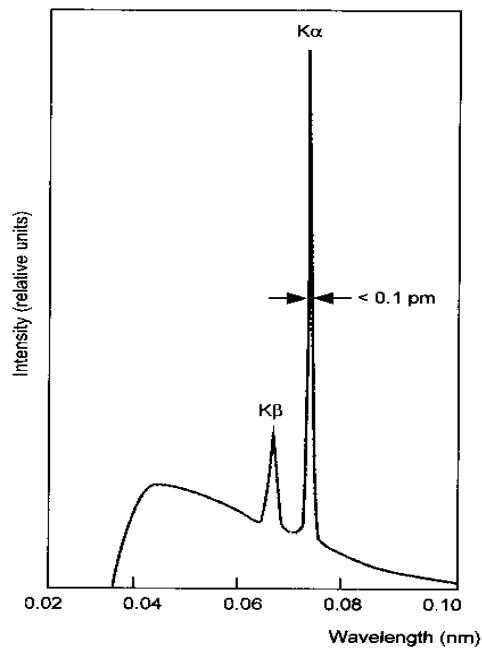

Fig.6.

W. H. Bragg designed and used the first x-ray spectrometer, and the Swedish physicist Siegbahn developed it into an instrument of very high precision.

2.4 Diffraction directions

Referring to Fig.5, we see that various diffraction angles $2\theta_1$, $2\theta_2$, $2\theta_3$, ... can be obtained from the (100) planes by using a beam incident at the correct angle θ_1, θ_2 , θ_3, and producing first-, second-, third-, . . . order reflections. But diffraction can also be produced by the (110) planes, the (111) planes, the (213) planes, and so on. We obviously need a general relation which will predict the diffraction angle for any set of planes. This relation is obtained by combining the Bragg law and the plane-spacing equation applicable to the particular crystal involved.

For example, if the crystal is cubic, then

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

and

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$

Combining these equations, we have

$$sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

This equation predicts, for a particular incident wavelength λ and a particular cubic crystal of unit cell size a, all the possible Bragg angles at which diffraction can occur from the planes (*hkl*). For (110) planes, for example, the above equation becomes

$$sin^2\theta_{110} = \frac{\lambda^2}{2a^2}$$

If the crystal is tetragonal, with axes a and c, then the corresponding general equation is:

$$sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right)$$

and similar equations can readily be obtained for the other crystal systems. In short, *diffraction directions are determined solely by the shape and size of the unit cell.*

2.5 Diffraction methods

Diffraction can occur whenever the Bragg law, $\lambda = 2d\sin\theta$, is satisfied. This equation puts very stringent conditions on λ and θ for any given crystal. With monochromatic radiation, an arbitrary setting of a single crystal in a beam of x-rays will not in general produce any diffracted beams. Some way of satisfying the Bragg law must be devised, and this can be done by continuously varying either λ or θ during the experiment. The ways in which these quantities are varied distinguish the three main diffraction methods:

Diffraction methods	λ	θ
Laue method	Variable	Fixed
Rotating-crystal method	Fixed	Variable (in part)
Powder method	Fixed	Variable

2.5.1 Laue method

A beam of white radiation, the continuous spectrum from an x-ray tube, is allowed to fall on a fixed single crystal. The Bragg angle θ is therefore fixed for every set of planes in the crystal, and each set picks out and diffracts that particular wavelength which satisfies the Bragg law for the particular values of d and involved. Each diffracted beam thus has a different wavelength.

There are two variations of the Laue method, depending on the relative positions of source, crystal, and film. In each, the film is flat and placed perpendicular to the incident beam. The film in *the transmission Laue method* is placed behind the crystal so as to record the beams diffracted in the forward direction. This method is so called because the diffracted beams are partially transmitted through the crystal. In *the back-reflection Laue method* the film is placed between the crystal and the x-ray source, the incident beam passing through a hole in the film, and the beams diffracted in a backward direction are recorded. In either method, the diffracted beams form an array of spots on the film. This array of spots is commonly called a pattern. This method used to determination the symmetry, direction of the crystal and the shape of the unit cell.
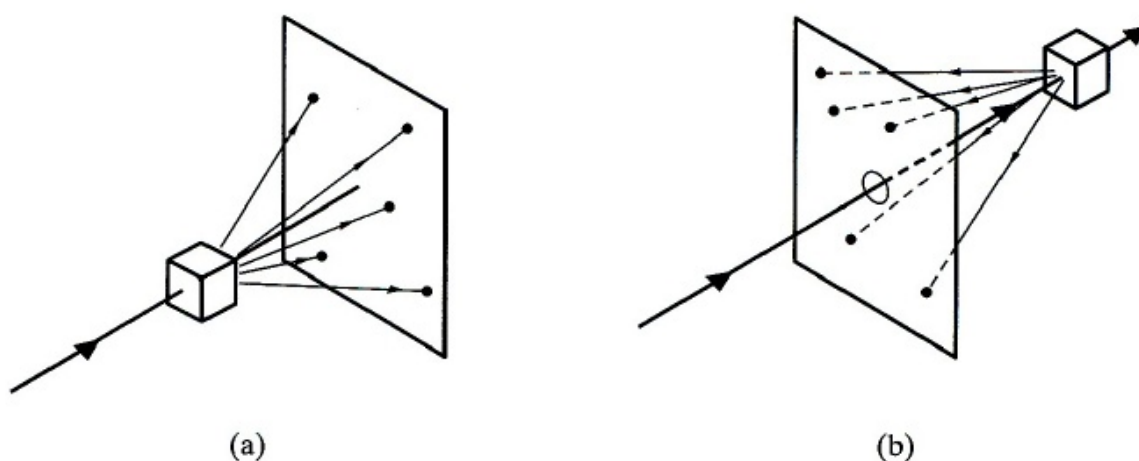

(a)   (b)

Fig. 7 (a) Transmission and (b) back-reflection Laue methods.

2.5.2 Rotating-crystal method

This method used to study the structure of the single crystal (shape, size of unit cell and the arrangement of the atoms inside the unit cell). A single crystal is mounted with one of its axes, or some important crystallographic direction, normal to a monochromatic x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen

direction, the axis of the film coinciding with the axis of rotation of the crystal. As the crystal rotates, a particular set of lattice planes will, for an instant, make the correct Bragg angle for reflection of the monochromatic incident beam, and at that instant a reflected beam will be formed.
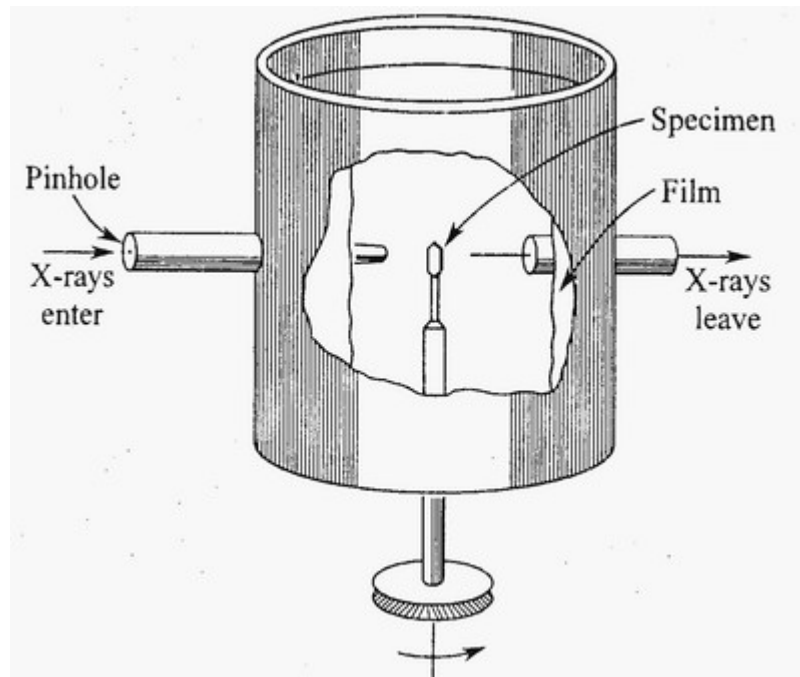

Fig.8.

2.5.3 Powder method

The crystal to be examined is reduced to a very fine powder and placed in a beam of monochromatic x-rays. Each particle of the powder is a tiny crystal oriented at random with respect to the incident beam. Just by chance, some of the particles will be correctly oriented so that their (100) planes, for example, can reflect the incident beam. Other particles will be correctly oriented for (110) reflections, and so on. The result is that every set of lattice planes will be capable of reflection. The mass of powder is equivalent, in fact, to a single crystal rotated, not about one axis, but about all possible axes. Consider one particular *hkl* reflection.

One or more particles of powder will, by chance, be so oriented that their *(hkl)* planes make the correct Bragg angle for reflection; Fig. 9 shows one plane in this set and the diffracted beam formed. If this plane is now rotated about the incident beam as axis in such a way that θ is kept constant, then the reflected beam will travel over the surface of a cone, the axis of the cone coinciding with the transmitted beam. This method used to study the lattice constant and phase purity.
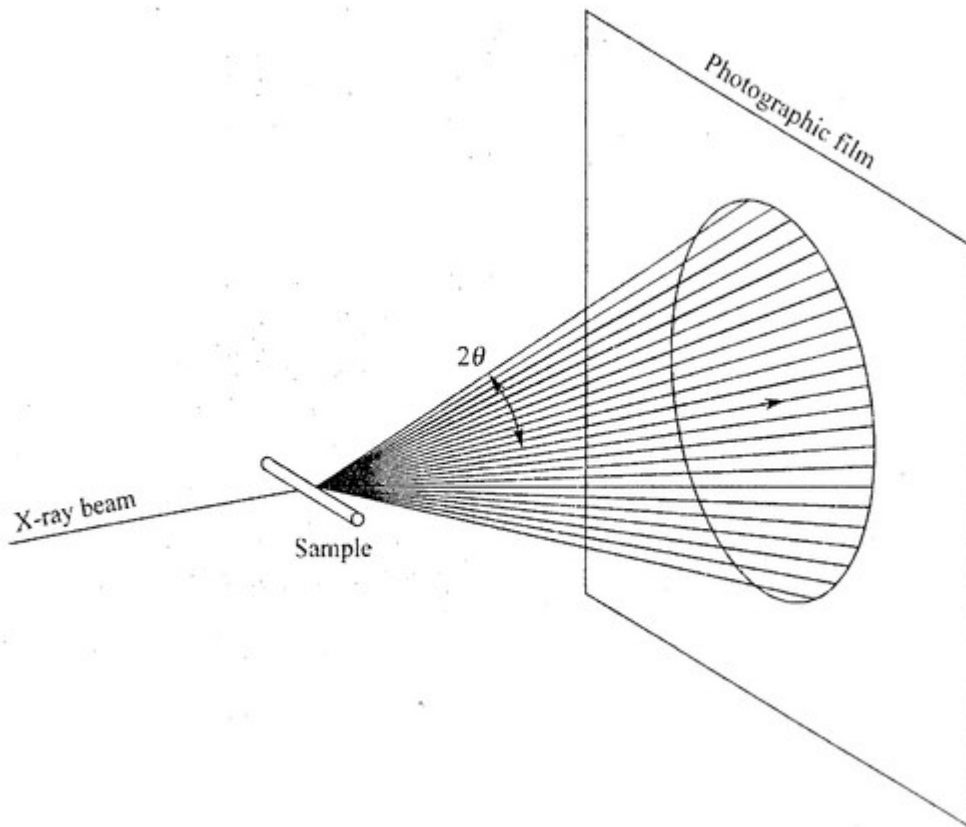

Fig. 9.