Chapter II

ELEMENTS OF DIFFRACTION THEORY AND INTERPRETATION OF X-RAY DIFFRACTION PHOTOGRAPHS

2.1 Diffraction from a three - dimensional lattice

A crystal consists of a three dimensional array of atoms. x-rays are scattered from these atoms in a manner similar to that in which light waves are scattered from the ruled lines of a diffraction grating. The conditions for additive interference between the x-rays scattered from corresponding points along any line in the lattice may be seen from Fig. 1

The incident rays travelling in the direction PA make an angle μ with the line AB passing through a row of lattice points. The diffracted rays travelling in the direction AQ make a corresponding angle ν with AB. Contrasting the rays PAQ and RBS, we see that the path difference amounts to

$$AD - BC = AB\cos\nu - AB\cos\mu. \qquad (1)$$

The condition for additive interference is that the path difference evaluated in (1) shall be equal to a whole multiple of the wave length λ :

$$H\lambda = AB(\cos\nu - \cos\mu) \qquad (2)$$

where H = integer.

Let $\bar{i}$ and $\bar{s}$ be unit vectors of the incident and scattered x-rays respectively and let the repeated translation along AB be given by $\bar{a}$; (2) becomes

$$H\lambda = a(\cos\nu - \cos\mu) \qquad (3)$$

$$H\lambda = \bar{a} \cdot (\bar{s} - \bar{i}) \qquad (4)$$

If $\bar{a}$ and $\bar{i}$ remain fixed, $\bar{s}$ can be in any direction making an angle ν

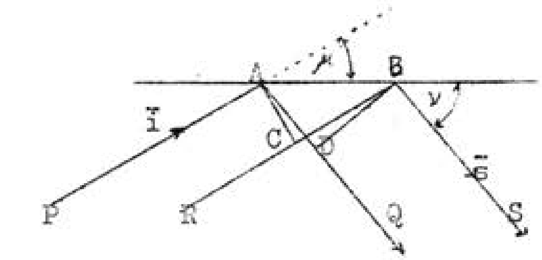


Fig.1 Geometry of X-ray scattering from two points A, B.

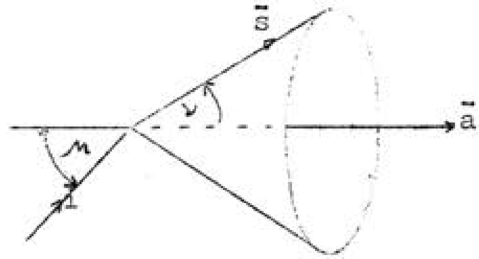


Fig.2a

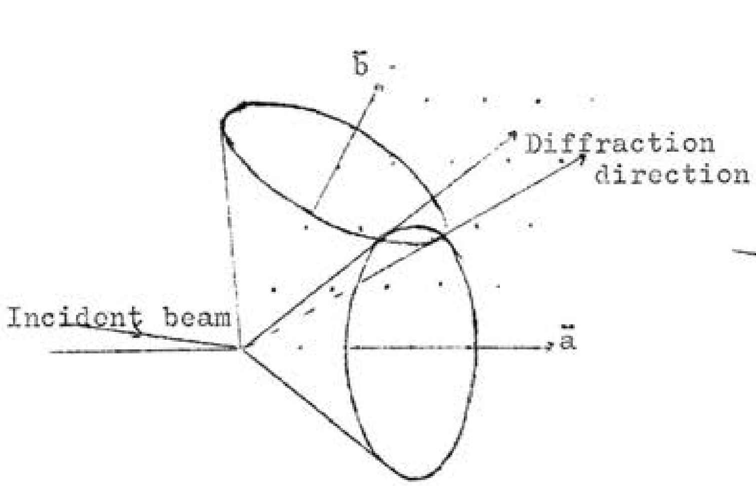


Fig.2b

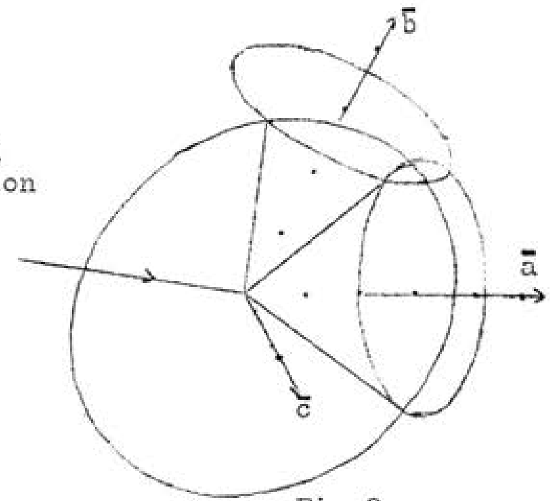


Fig.2c

Fig.2 Intersecting cones defining possible scattering.

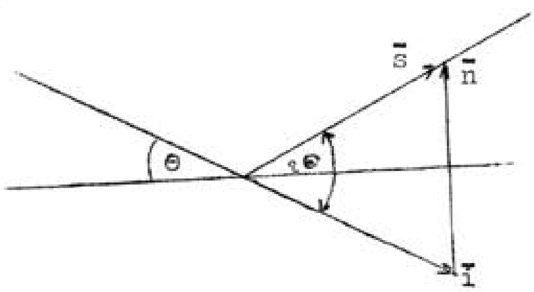


Fig.3 Incident and scattering rays denoted by the unit vectors ī and s̄ relative to lattice plane.

with $\bar{a}$. The diffracted beams will therefore lie in the surfaces of cones, whose common axis is the line of points and whose semivertical angles are ν (Fig. 2a).

For scattering from a 2 - dimensional lattice net with $\bar{b}$ as the second vector defining the net, a second condition

$$K\lambda = \bar{b}.(\bar{s} - \bar{i}),\ K = \text{integer} \qquad (5)$$

is imposed and diffracted beams will only occur along the lines of intersection of the two sets of cones having directions $\bar{a}$ and $\bar{b}$ as axes (Fig. 2b).

If $\bar{c}$ is the third vector defining the lattice, then the third condition

$$L\lambda = \bar{c}.(\bar{s} - \bar{i}),\ L = \text{integer} \qquad (6)$$

must also be satisfied. Diffracted beams can only occur when cones pointed along $\bar{a}$, $\bar{b}$, $\bar{c}$ all intersect in one line (Fig 2c). In general, there is no such direction and if a beam of monochromatic x-rays impinges on a perfect crystal it is unlikely that it will give rise to a diffracted beam.

There are two ways in which the angles of the cones, can be altered so that the three cones intersect in one line, and all three diffraction conditions are satisfied,

a) Varying λ, ν_1 constant (Stationary crystal).

White radiation with a continuous range of wavelengths is used and the crystal picks out the wavelengths which satisfy the three "Laue conditions" Eqs. (4),(5),(6) for various values of the integers H,K and L. But because the wavelengths of the diffracted beams are all different this method has only a restricted use.

b) Varying μ_j, λ constant (Moving crystal).

Varying the directions of $\bar{a}$, $\bar{b}$, $\bar{c}$, relative to $\bar{i}$ is most simply achieved by rotating the crystal. The angles of the cones will vary continuously and when three of them intersect, the diffraction conditions will be satisfied for the monochromatic radiation employed and a diffracted beam will flash out.

<u>The development of the Laue conditions in terms of lattice planes</u>

Since $\bar{s}-\bar{i} = \bar{n}\ 2 \sin\theta$, as shown Fig. 3, where $\bar{n}$ = unit vector in the direction of $\bar{s} - \bar{i}$, the Laue conditions can be written as :

$$\begin{aligned} \bar{a} \cdot \bar{n}\ 2 \sin\theta &= H\lambda = p\,h\,\lambda \\ \bar{b} \cdot \bar{n}\ 2 \sin\theta &= K\lambda = p\,k\,\lambda \qquad (7) \\ \bar{c} \cdot \bar{n}\ 2 \sin\theta &= L\lambda = p\,l\,\lambda \end{aligned}$$

where h,k,l contain no common factor. These equations can be written

$$\frac{\bar{a}.\bar{n}}{h} = \frac{\bar{b}.\bar{n}}{k} = \frac{\bar{c}.\bar{n}}{l} = \frac{p\lambda}{2\sin\theta} \qquad (8)$$

These are the equations of a plane cutting the axes at a/h, b/k, c/l (i.e. the nearest plane to the origin of the set hkl) whose normal is $\bar{n}$ and whose distance from the origin is $p\lambda/2\sin\theta$. Since the next plane of the set passes through the origin, $p\lambda/2\sin\theta = d_{hkl}$ the interplanar spacing. The incident and diffracted beams make equal angles, $90^\circ - \theta$, with the normal $\bar{n}$ to the set of planes, and $\bar{n}$ is necessarily in the same plane as $\bar{s}$ and $\bar{i}$. The incident and diffracted beams obey the ordinary laws of reflection from the set of planes hkl., but in addition, reflection only occurs when the condition $p\lambda = 2d \sin\theta$ is satisfied.

2.2 Laue photograph and the reciprocal lattice concept

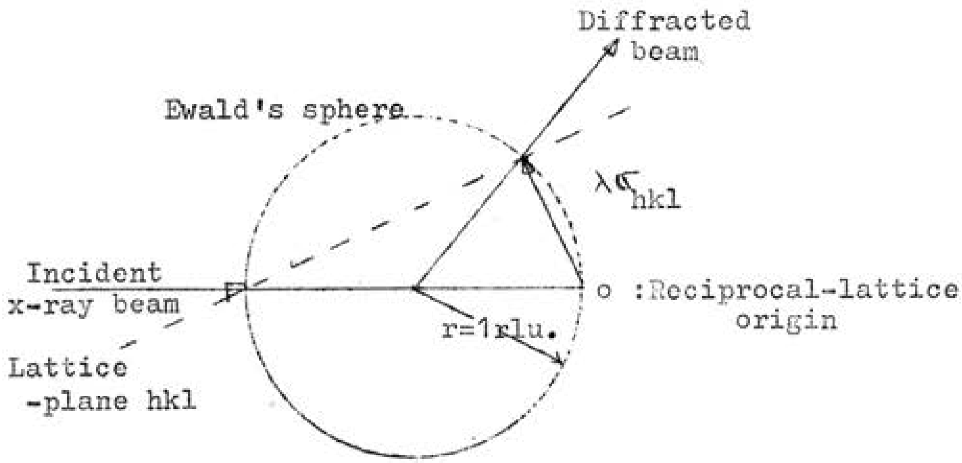
In the discussions of x-ray diffraction it is convenient to construct the reciprocal lattice and the sphere of reflection (James 1962, p.7) illustrated in Fig 4.1. The diffraction condition is satisfied whenever a reciprocal point lying, lies on the sphere of reflection this can be used to determine directly which planes in the crystal are in reflecting position.

If we consider the reciprocal lattice plane cutting the sphere of reflection along some circle, the diffracted beams passing through the reciprocal lattice points along this circle (Fig. 5.1) form a cone, the Laue cone. This axis of the cone is normal to the reciprocal lattice plane. The reciprocal lattice points belonging to this Laue cone are said to have a common zone axis, each reciprocal lattice point represents a lattice plane that is parallel to this zone axis.

When a symmetry element in a stationary crystal is parallel to the incident white x-ray beam, the diffractions surrounding the beam are symmetric. The diffracted beams are recorded on the photographic plate in the front or in the back reflection region perpendicular to the direct beam. The resultant photograph, called Laue photograph, is used to determine the symmetry of a crystal and its orientation relative to the x-ray beam.

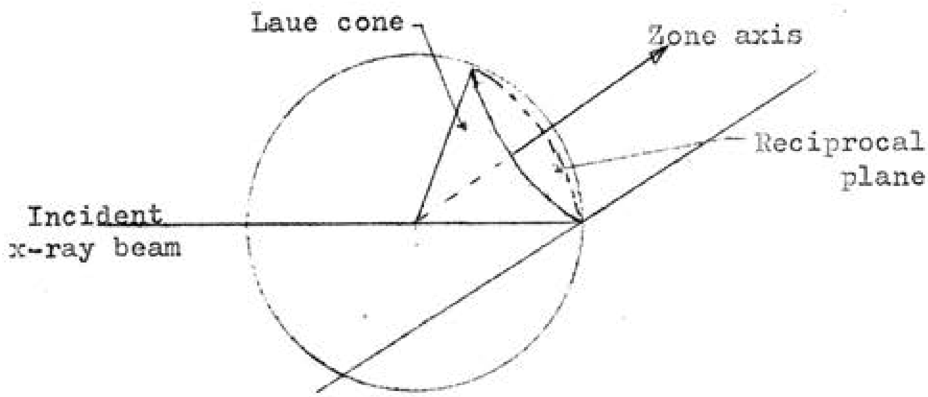
Symmetry of Laue photograph.

When a Laue photograph (transmission or back reflection) is taken the symmetry of the diffraction pattern thus recorded is related to the symmetry of the crystal structure about the direction of transmission of the original x-ray beam. If the incident x-ray beam is directed



Diffracted
beam
Ewald's sphere
$\lambda\sigma_{hkl}$
Incident
x-ray beam
o :Reciprocal-lattice
origin
r=1 rlu.
Lattice
-plane hkl

Fig. 4.1



Laue cone
Zone axis
Reciprocal
plane
Incident
x-ray beam

Fig. 5.1

along a zone axis the symmetry of the diffracted beam is that of the zone axis. If, for example, the direction is the principal axis of a tetragonal crystal, the photograph would display four fold symmetry.

This method, however, has an important limitation. It is impossible to tell whether the crystal is centro symmetrical or not. For this reason, the 32 classes of symmetry give only eleven different groups distinguishable by means of Laue photographs (Phillips 1963, p. 155)

Triclinic	:	$\bar{1}$
Monoclinic	:	2/m
Orthorhombic	:	mmm
Trigonal	:	$\bar{3}$, $\bar{3}$ m
Tetragonal	:	4/m, 4/mmm
Hexagonal	:	6/m, 6/mmm
Cubic	:	m3, m3m

2.3 Rotation photograph

In this method the crystal is rotated about an axis perpendicular to the incident x-ray beam. This allows lattice planes to come into the appropriate positions for reflecting the radiation.

When a crystal is rotated about a principal axis of the crystal, the plane of reciprocal lattice perpendicular to this axis will cut the reflecting sphere in a small circle, producing a cone of reflection as in Fig. 4. The cones of reflected rays are recorded on a cylindrical film (co-axial with the rotation axis) in a series of circles which form straight lines when the film is laid flat. These lines are called the layer lines.

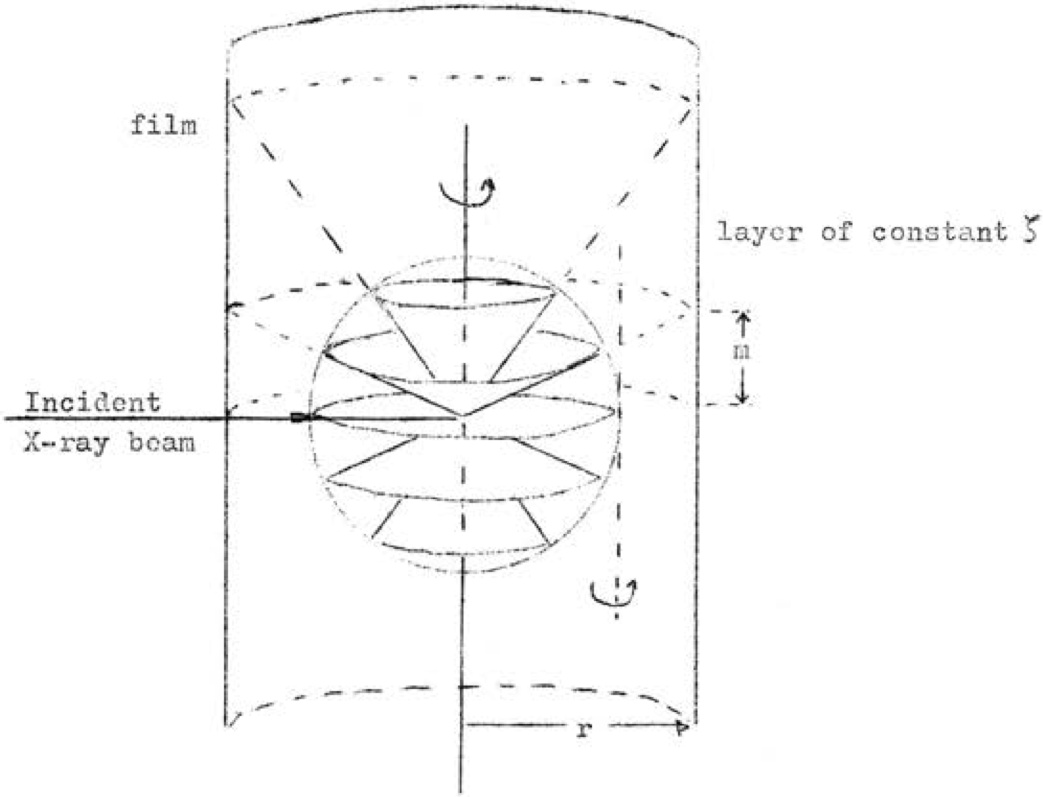


Fig.4 Diagram illustrating the formation of layer lines

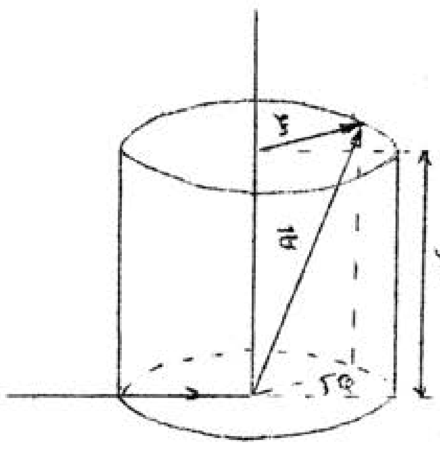


Fig.5 Reciprocal lattice coordinates (Cylindrical coordinates)

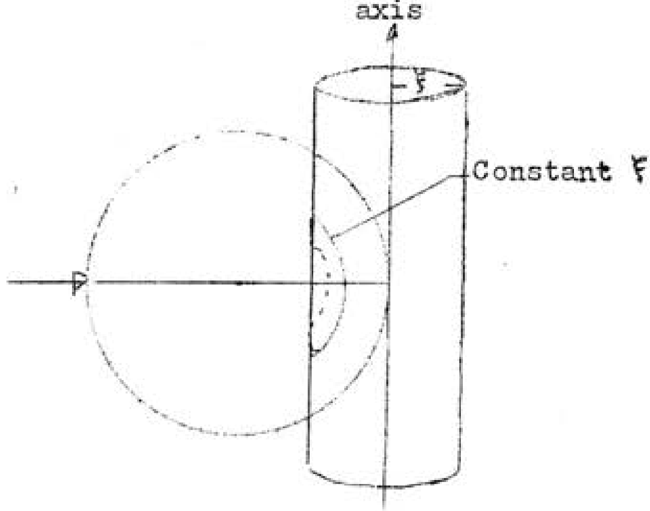


Fig.6 Intersection of cylinder having constant ξ with the Ewald sphere

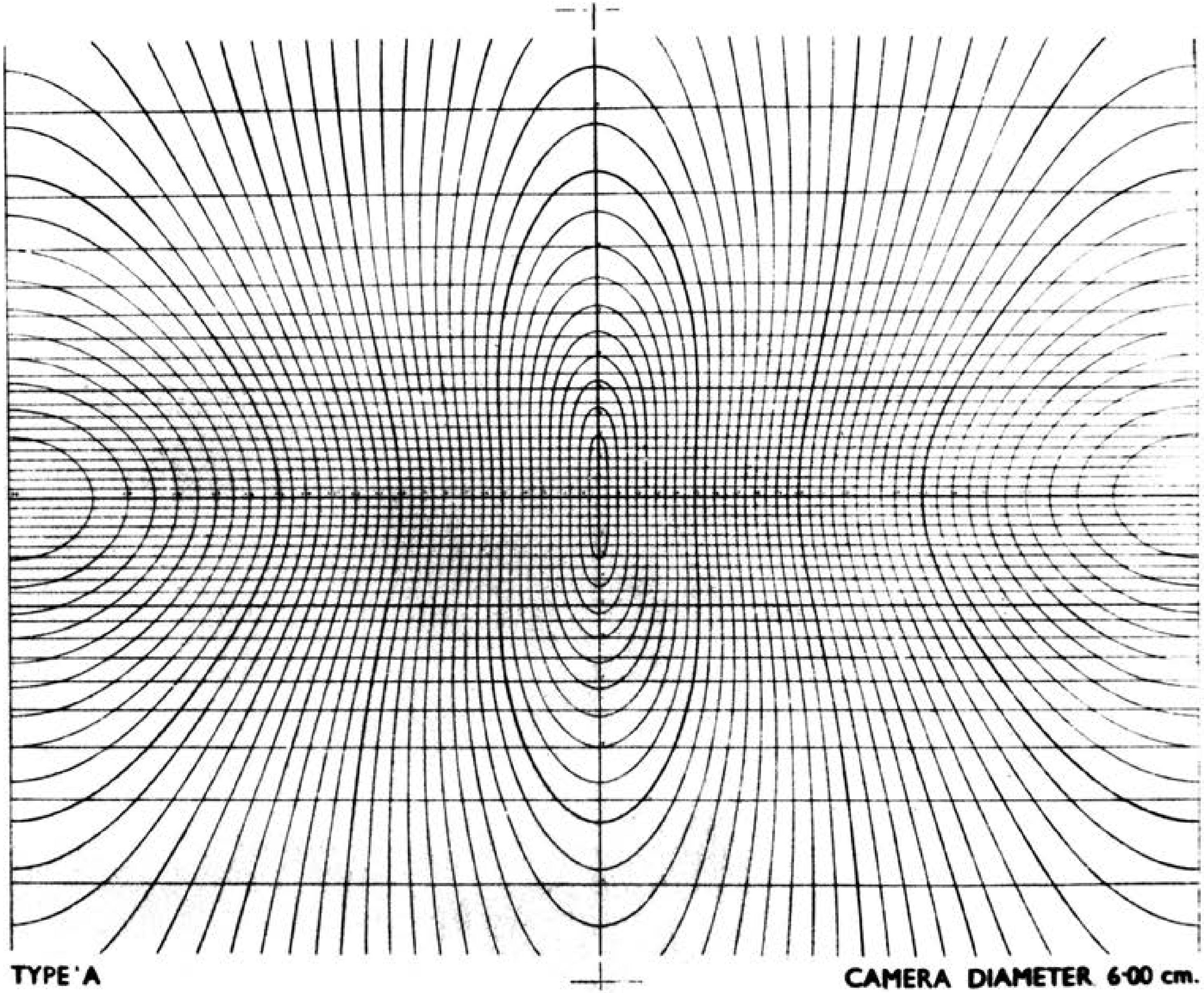


Fig.7 Bernal Chart.

Since cylindrical film is used, it is convenient to use cylindrical co-ordinates to specify the reciprocal lattice, Thus the orientation of the reciprocal lattice vector σ_{hkl} is specified by two mutually orthogonal vectors: $\bar{\zeta}$ along the rotation axis and $\bar{\xi}$ in a plane normal to the rotation axis. The angle φ is formed by the direct beam and the plane containing $\bar{\zeta}$ and $\bar{\xi}$ (Fig. 5)

When the crystal is rotated, the reciprocal lattice planes cut the sphere of reflection at a constant ζ above the equator. Similarly, points having a constant ξ value lie in a cylinder about the rotation axis and cut the Ewald sphere along curves (Fig. 6.) These curves appear on a cylindrical film as shown in Fig. 7. From this we can prepare a chart, for a series of constant ζ and ξ, also taking into account the radius of cylindrical film, known as Bernal chart, Fig. 7. Such a chart can be superimposed directly over the film and the ζ and ξ co-ordinates of each spot of reflection can be read directly off the chart.

<u>Measurument of unit cell dimensions</u> (Henry, Lipson, Wooster 1961,p.51)

We have seen that straight layer lines are produced only when a zone axis of the crystal is taken as the rotation axis. The spacing between layer lines in a rotation photograph is directly proportional to ζ (Fig. 4), the spacing between reciprocal lattice planes normal to rotation axis.

From the ζ values of the layer lines on the film we can obtain a dimension of the Bravais lattice along the direction of the rotating zone axis. Fig 8 shows a unit cell of triclinic Bravais lattice with the three reciprocal axes. By definition, the directions of x^*, y^* and z^* are normal to the plane yz,zx and xy respectively.

Hence the set of planes of reciprocal points paralled to x* and y* perpendicular to the zone axis $[001]$ (z axis). The perpendicular distance between these planes of reciprocal points is denoted by $\zeta_{[001]}$ and where $\rho_{[001]}$ is the angle between the z axis and the z* axis.

$$\zeta_{[001]} = c^* \cos \rho_{[001]} \quad \text{(a)}$$

By definition

$$c^* = \frac{\lambda}{d_{001}} \quad (10)$$

But it is clear that

$$d_{001} = c \cos \rho_{[001]} \quad (11)$$

Hence

$$\zeta_{[001]} = \lambda / c \;. \quad (12)$$

Since a set of parallel planes through the reciprocal points exists perpendicular to each zone axis, this result is general and we can write

$$d = n\lambda / \zeta_n \quad (13)$$

where d is the repeat distance along a zone axis and ζ_n is the value of ζ for the nth layer line in photograph taken with the zone axis as the axis of rotation.

If a Bernal Chart is not available, the value of ζ can be obtained from a measurement of the distance of any layer line from the zeroth layer line. In Fig 4, it is clear that $\zeta/1 = \sin \nu$ (reflecting sphere radius = 1 reciprocal lattice unit (r l u.) and for cylindrical camera of radius r ,

$$m/r = \tan \nu$$

where m is the height of the layer line above the zeroth layer line

Thus by taking rotation photographs with each of the three crystallographic axes as rotation axis we can determine the dimensions a,b,c, of the unit cell.

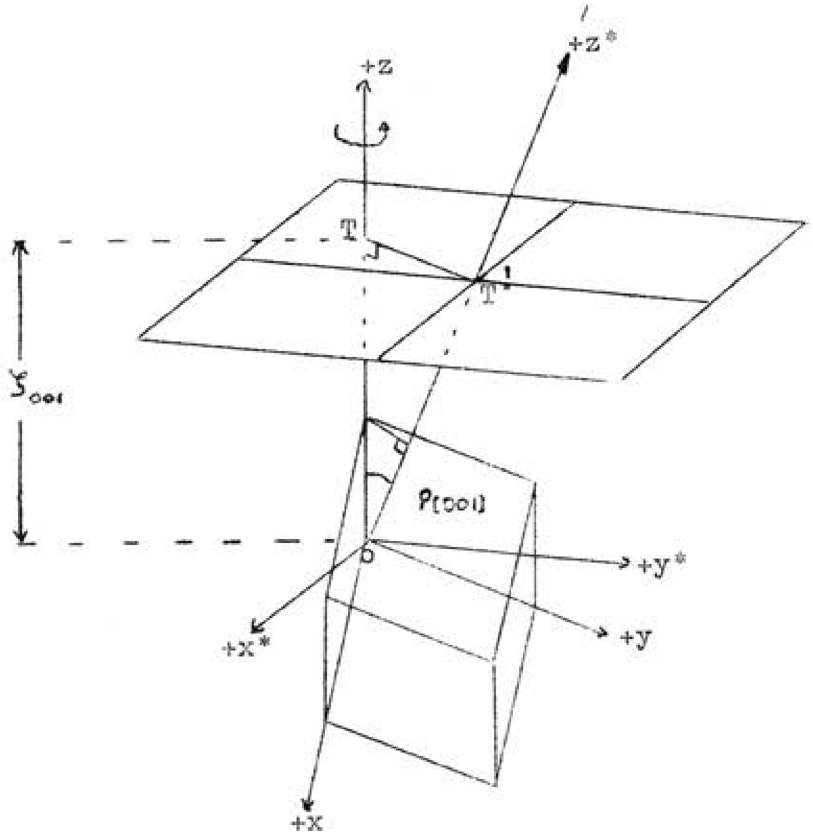


Fig. 8 Diagram showing the relation between the z axis of the Bravais lattice and of the reciprocal lattice.

2.4 Weissenberg Photograph

The rotation photograph method is an attempt at recording the reflection corresponding to the three co-ordinates of a reciprocal lattice point with two film co-ordinates. Thus it is difficult to identify the spot of reflection exactly. To resolve this problem, K. Weissenberg in 1924, proposed a moving film method in which only a reflection from one layer of a reciprocal lattice plane (which is two dimensional) is allowed to be recorded on the film. Each layer line was singled out by a layer line screen (Fig9). The film cassette was translated parallel to the rotation axis and being synchronised to the rotation of the crystal. While the irradiated crystal rotates, causing successive reciprocal lattice points to intersect the sphere of reflection, the film is continuously moving, so that, as successive reflections emanate from the crystal, the film is displaced by a finite amount. Each Weissenberg photograph records the reflection for one layer of the reciprocal lattice plane, the different reflections being clearly resolved on different portions of the film.

Normal beam photograph of zero layer.

In order to see the relationship between the reciprocal lattice construction and the appearance of individual reflections on a film, consider Fig. 10. Suppose that at an initial position a central row in the reciprocal lattice is oriented at right angles to the direct beam. If the points row rotates from this initial position through and angle ϕ , the reflected beam is deviated with respect to incident beam by an angle 2ϕ. Hence the distance of the spot

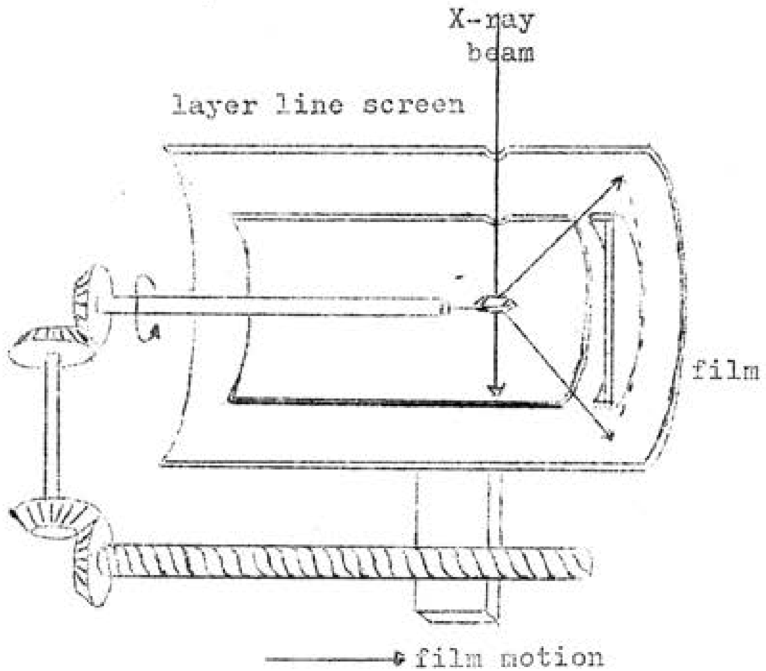


Fig.9 Component parts of Weissenberg goniometer.

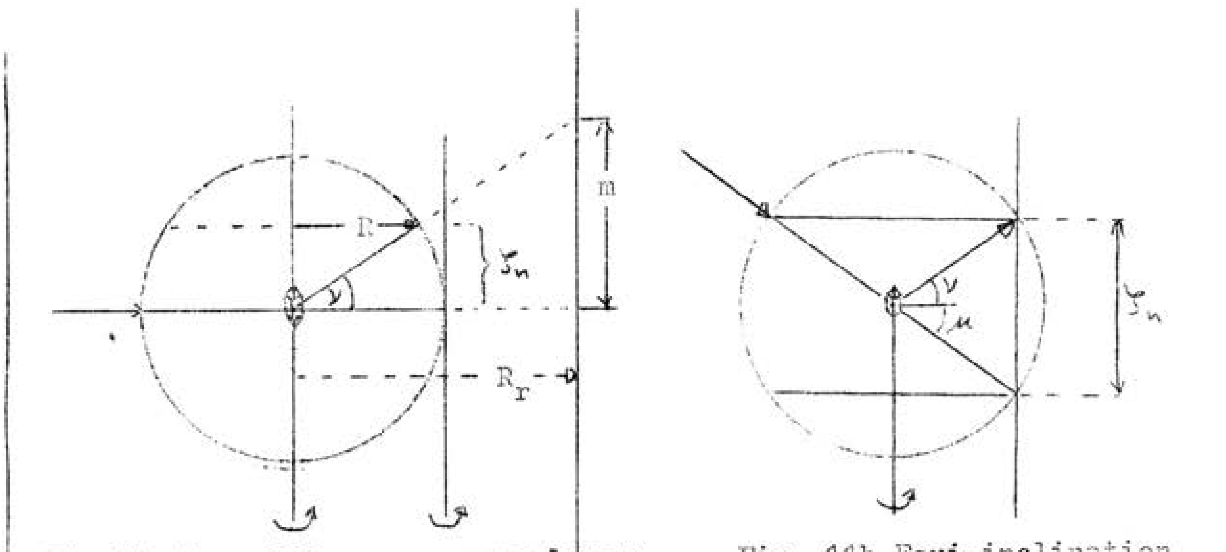


Fig.11a Normal beam non-zero layer   Fig. 11b Equi-inclination non-zero layer only

Fig.11 Geometric arrangement for the Weissenberg method.

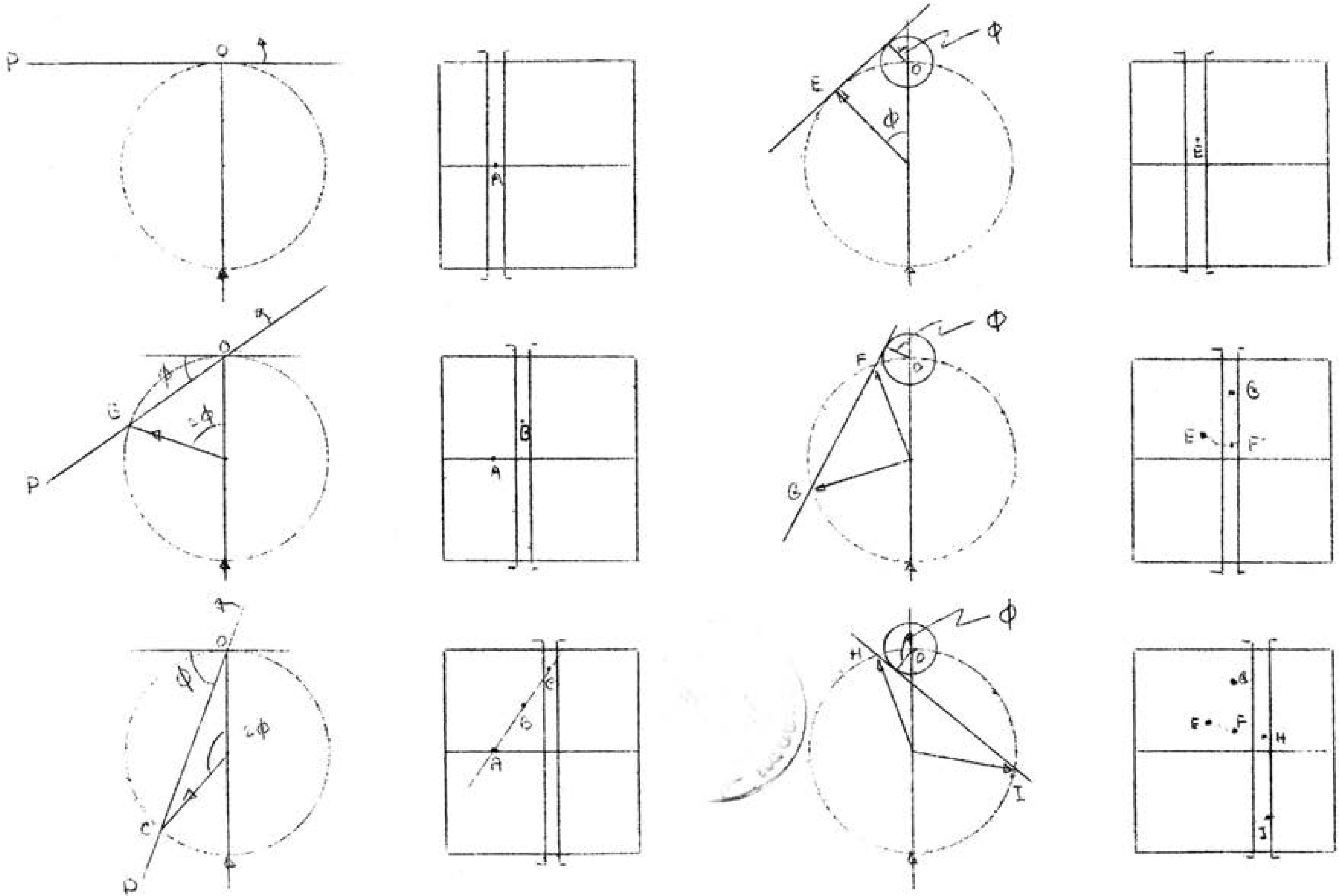


Fig.10 Diagrams showing relation between reciprocal point rows and corresponding lines of spots on Weissenberg photographs.

produced by the reflected x-rays from a line trace of direct beam on the film is $2\phi R_w$ where R_w is the radius of the film.

The translation of the camera during a rotation of the crystal through an angle ϕ is $f\phi$, wher f is the appropriate coefficient, synchronizing translation of the film and the rotation of the crystal.

Since $2Rw\phi$ is proportional to $f\phi$ the reflected spots must lie on a diagonal straight line sloping at an angle $\tan^{-1}(2 R_w/f)$. As the crystal rotates through 180° the points along OP will produce two collinear lines of spots one above the central band on the film and the other below this band. Next consider a reciprocal lattice row that is parallel to those we have just discussed, but which do not pass through the origin, and consequently is not tangent to the sphere at the direct beam trace on the film. In fact as can be seen in Fig. 10, such a row intersects the sphere of reflection at point E, and then proceeds to cut it on both sides of this point as the crystal rotates. (Henry, Lipson. Wooster 1961, p. 84)

A side view of the rotating crystal surrounding by the Ewald sphere is shown in Fig 11a, when the incident beam is perpendicular to the rotation direction, a blind region develops near the center of the any upper level. A Weissenberg photograph of an upper level in the normal beam arrangement therefore fails to record certain reflections lying near the origin of that level. As pointed out by Buerger, it is possible to move the rotating point of any level onto the sphere of reflection. The arrangement shown in Fig. 11b. is called the Buerger equi-inclination method. This is the case when the direct beam is inclined to the normal by an amount μ.

This has the obvious advantage that the central blind region is eliminated and the reciprocal lattice distortion in the n-level photograph is identical with that of a zero-level photograph.

The setting of the instrument to record upper level requires a knowledge of the layer line separations parallel to the rotation axis. This is usually determined by first taking a rotation photograph.

The relationship between the interlayer distance m on the film and the radius of the camera (film radius) is R_r, according to Fig. 11a

$$\tan \nu = m/R_r , \qquad (15)$$

where

$$\sin \nu = \zeta_n/1 . \qquad (16)$$

In Fig. 11 b the equi-inclination angle μ is related to ζ by

$$\sin \mu = \zeta_n/2 . \qquad (17)$$

We can solve for μ (Azaroff 1968, p. 441)

It is also necessary to advance the layer line screen opening by an appropriate amount. The necessary displacement s is determined by the radius of the layer line screen cylinder r

$$s = r\tan\mu . \qquad (18)$$

<u>The Weissenberg chart</u>

As has been seen, a set of parallel point rows produced a family of curves on the photographic film. So a standard of such curves corresponding to point rows at a distance of 0.1 reciprocal lattice unit (rlu) apart has been built on the photograph (Fig 12). It is easy to read off directly the distance apart of the point rows which gives the prominent family of curves on the photographic film by superimposing the standard curve on the film.

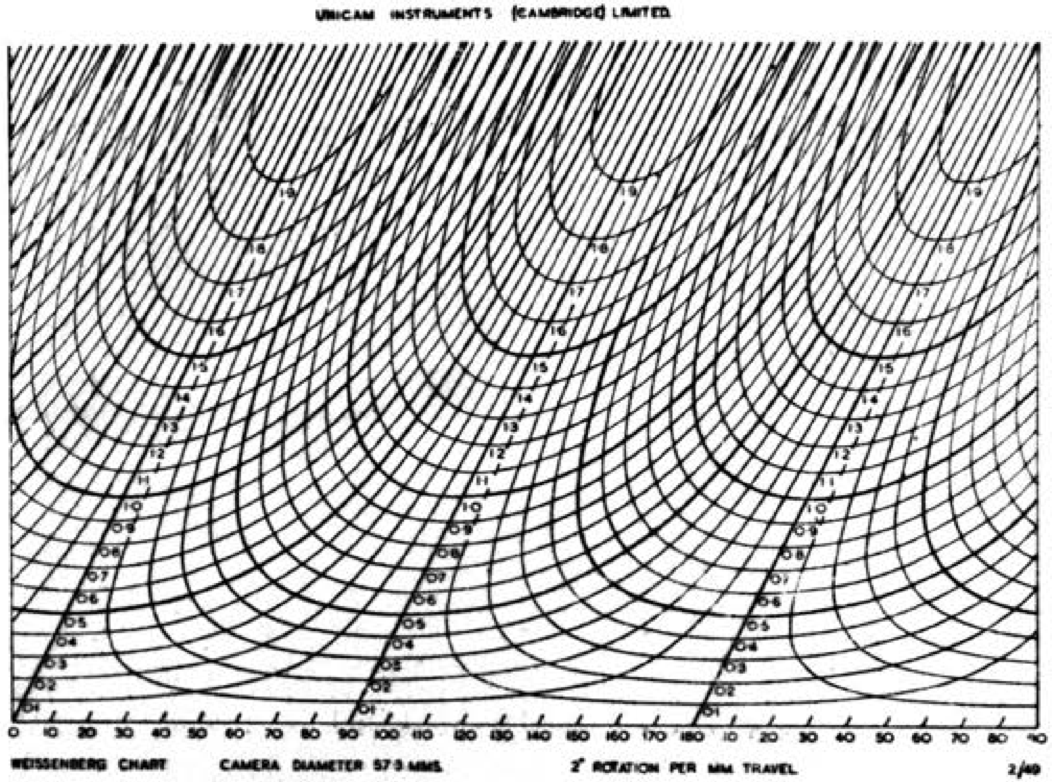


Fig. 12 Weissenberg Chart.

<u>Transformation from a film position to polar co-ordinates of the reciprocal lattice.</u> (Buerger 1965, p. 254)

The diagram of Fig 11b shows that the n^{th} layer of the reciprocal lattice cuts the reflection sphere in a circle of radius R. And the radius of this circle is evidently given by

$$\cos \nu = R , \qquad (19)$$

and is controlled by the relation:

$$\sin \nu = \xi_n/2 . \qquad (2)$$

Fig. 13, corresponds to a view looking along the rotating axis of the crystal. The reciprocal co-ordinate ξ (in cylindrical co-ordinates) of the corresponding spot on a film may be easily obtained from the relation.

$$\sin \tau/2 = \xi /2 R, \qquad (21)$$

$$\tau = x/R_w, \qquad (22)$$

where R_w is the film radius, x is the distance of the spot from the direct beam trace (Fig. 13), and τ is the angle between direct beam and reflected beam. From these relations we can build a scale of ξ which helps us to read directly the ξ value of each spot from the film, by superimposing this scale on the film (Fig. 14).

Note that, a different layer, corresponding to a different radius of reflecting circle, requires a different scale of ξ value.

The axis of ξ is generally taken along the $O\xi$ (inclined axis having slope = $2R_w/f$), but not along the vertical edge of the film because in cylindrical co-ordinates, the ξ value of each reciprocal lattice point are on line radiated from the origin which each line produced a straight line having slope = $2R_w/f$ on the film as we have discussed. We can read the ξ values of reflecting spots in the same

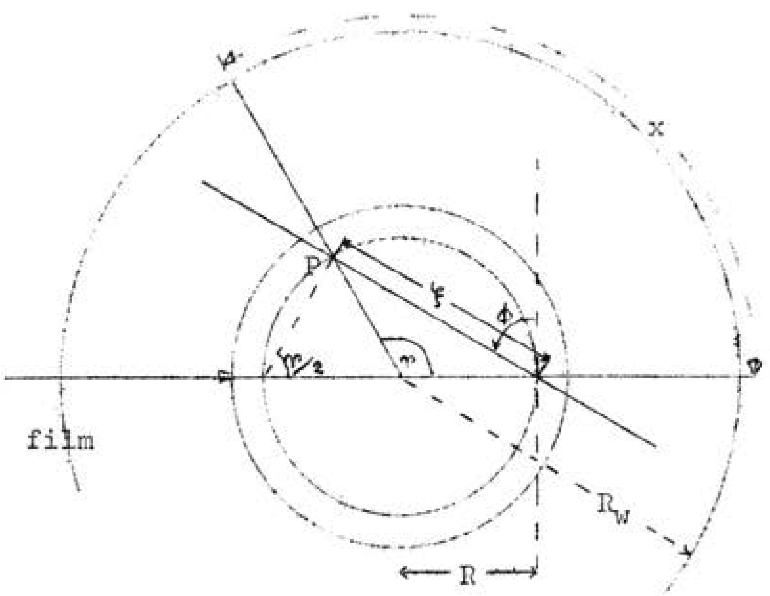


Fig.13 Relation of film position and polar coordinate.

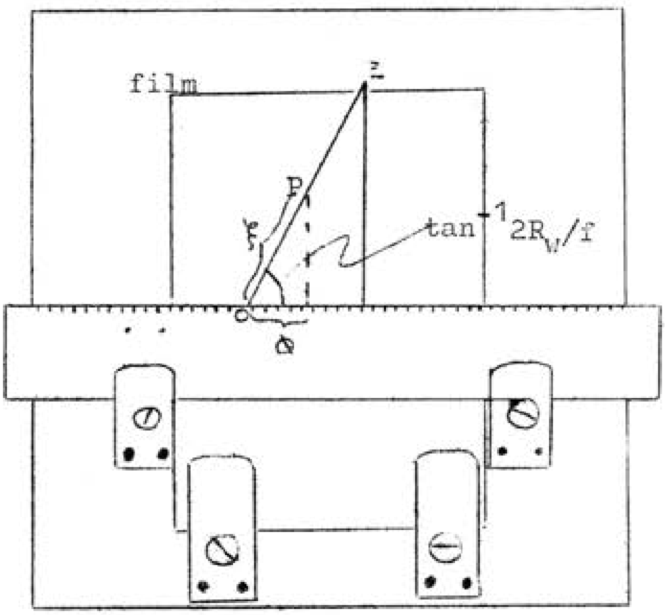


Fig.14 Apparatus for measuring ξ coordinate and angle Ø.

row promptly. Since the rotation of the crystal and the translation of the film are synchronised, an angle ϕ between each row can be measured directly from the film.

Reconstruction of the reciprocal lattice

As in Fig. 14 we construct a ξ value on a side of triangle sliding along a horizontal ruler so the ξ along one side of the triangle and ϕ , rotation angle of the crystal, along the ruler can be measured.

We can choose any spot on the film as an initial position, then the ξ and ϕ values of each reflection related to this position can be plotted. By this method the reciprocal net was reconstructed, and we can choose the axis of the reciprocal net. It is advantageous to choose the axis of reciprocal lattice from the film by first determining the number of densely populated central reciprocal lattice rows recorded in a 180° rotation interval. From these we construct the reciprocal net and then index each spot of reflection.