Chapter 3 X-ray Diffractometry

Learning outcomes :

By the end of this topic, student will be able to do the following:

- Identify and list down type of diffraction using X-ray.
- Describe and illustrate Ewald construction
- Describe and illustrate Diffractometer geometries
- Explain and illustrate Moving-crystal methods, Laue method and powder method

3.1 Introduction

- There are three classes of technique which are commonly used :
  - Moving-crystal technique

    →Single-crystal specimen which moving it into a appropriate orientation
  - Laue technique

    →Utilizes polychromatic radiation and a stationary crystal
  - Powder method

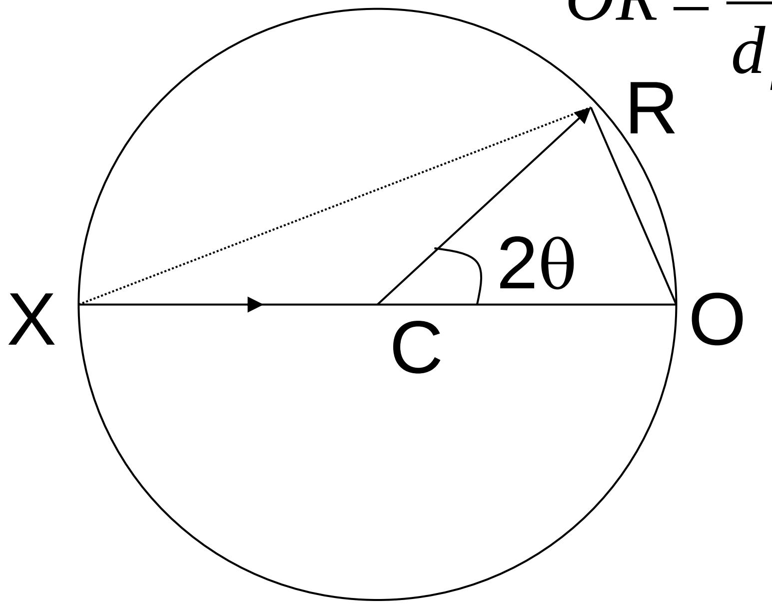
    →Polycrystalline specimen rather than single-crystal specimen is used.

3.2 The Ewald Construction

- The Ewald construction is a very convenient method for representing the geometrical conditions for diffraction.

O is the origin of the reciprocal lattice
XC is the unit vector in the direction of the incident radiation
R is a point any where on the surface of the sphere
C is the centre of the sphere

$$OR = \frac{\lambda}{d_{hkl}}$$



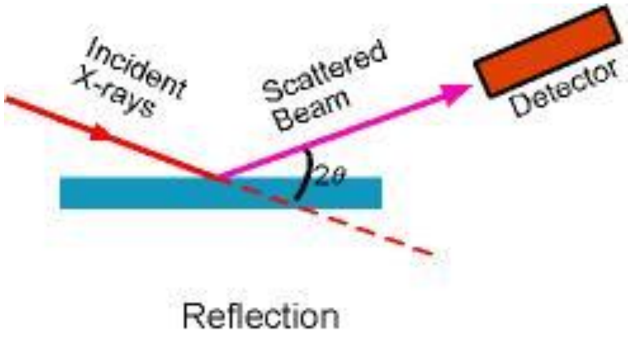
$$OR = 2OC\ Sin\frac{O\hat{C}R}{2}$$

so

$$\lambda = 2d\ Sin\theta$$

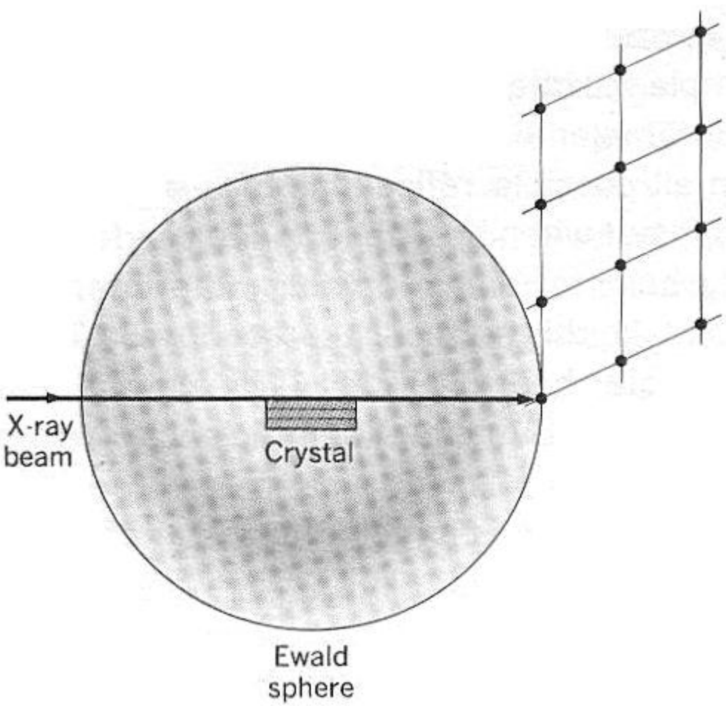
3.3 Diffractometer geometry

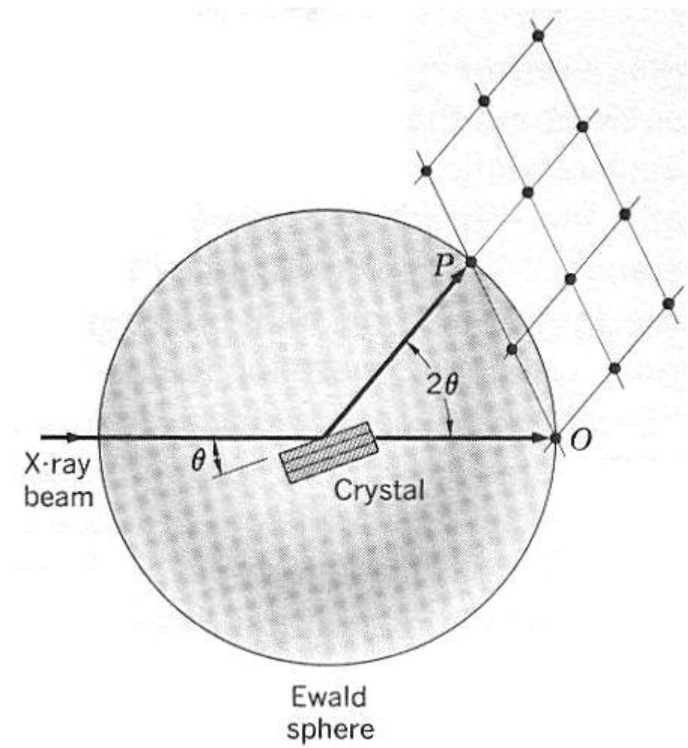
- A diffractometer measures the intensity of X-ray reflected from one stack of planes.
- Therefore, the essential parts of such an instrument are a collimating system for the incoming radiation, orienting crystal and the detector which can be rotated so as to point at the correct angle to accept the diffracted beam.
- A few thing are needed to be consider :
  - Reciprocal-lattice construction
  - Parafocusing
  - Goniometry
  - X-ray optic (for powder method)



Reciprocal-lattice construction

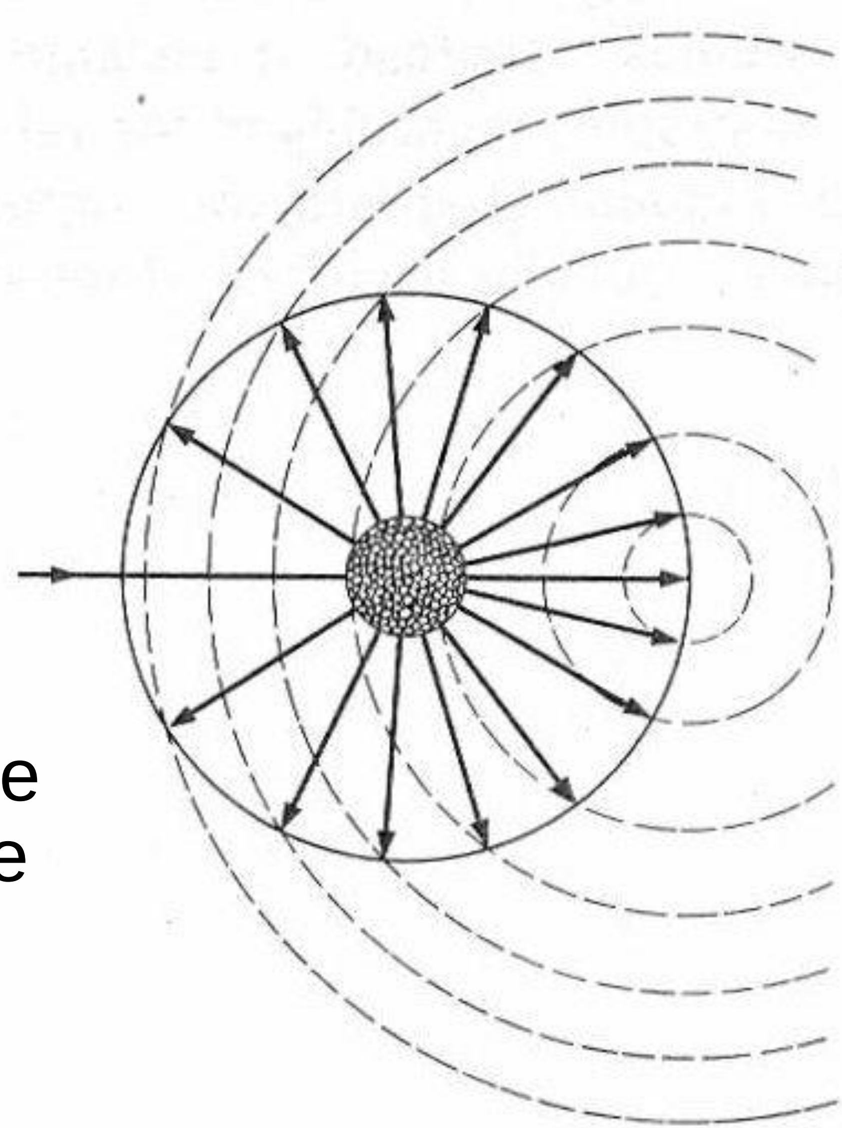
- If a single crystal is set parallel to the incident X-ray beam the reciprocal-lattice construction appears.
- If the crystal rotated by θ, now the new reciprocal-lattice construction appear.





- When a polycrystalline is place at the center of the Ewald sphere, the reciprocal-lattice construction has the appearance.

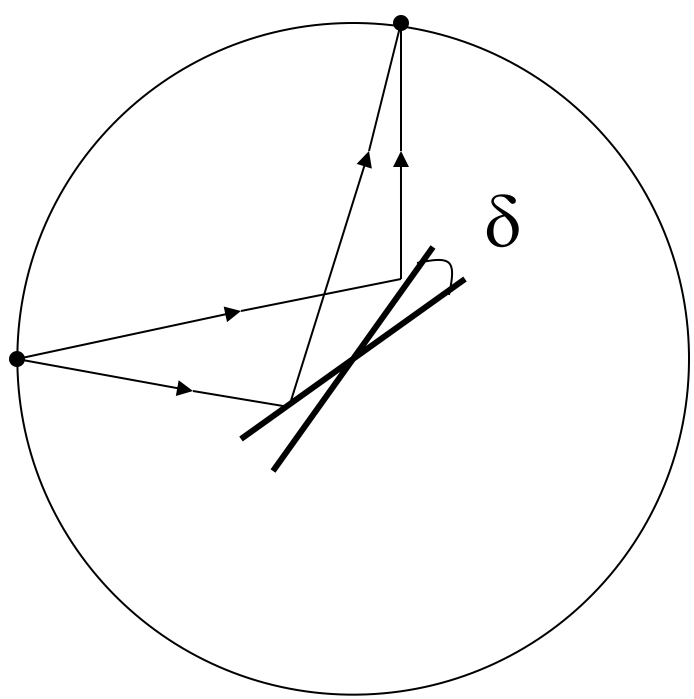
- The concentric reciprocal-lattice spheres intersect the Ewald sphere and give rise to diffraction cones.



Parafocusing

- When a large single crystal is irradiated by a diverging beam of X-ray, small angular displacements δ cause it to reflect slightly different wavelength components to the same point on a circle.

Point X-ray source

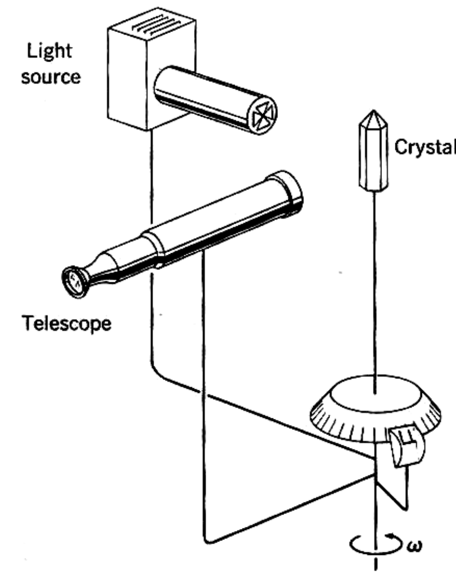


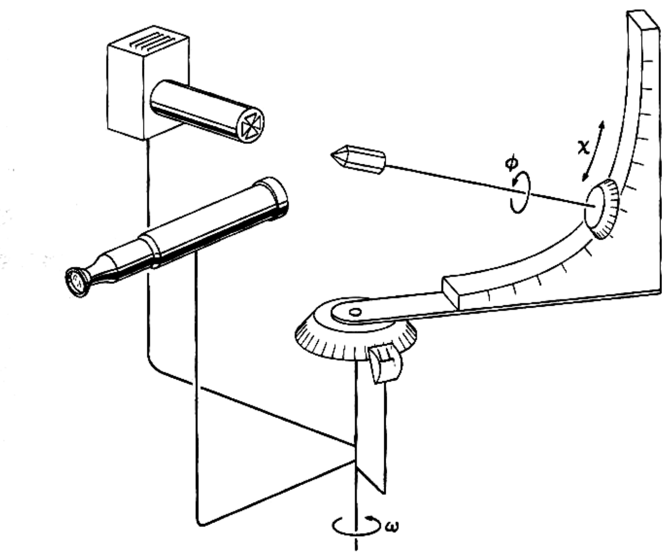
- However, when a slightly diverging and imperfectly monochromatic X-ray beam is used, this has the effect of “focusing” the reflected rays.
- This is a consequence of the finite spectral widths of X-ray sources.
- So it should be distinguished from true optical focusing by employing the term “***parafocusing***”.

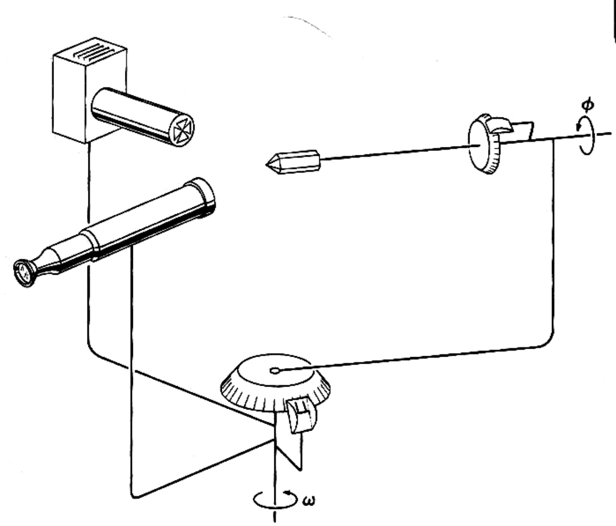
- Beside focusing, it is also necessary to provide a reorienting crystal so that many different planes can be positioned to reflect the incident beam.
- This can be done by mounting the crystal on a device, called “***goniometer***”

Goniometer

- Three type of goniometer can be constructed :
  - One-circle goniometer
  - Two-circle goniometer
  - Three-circle goniometer

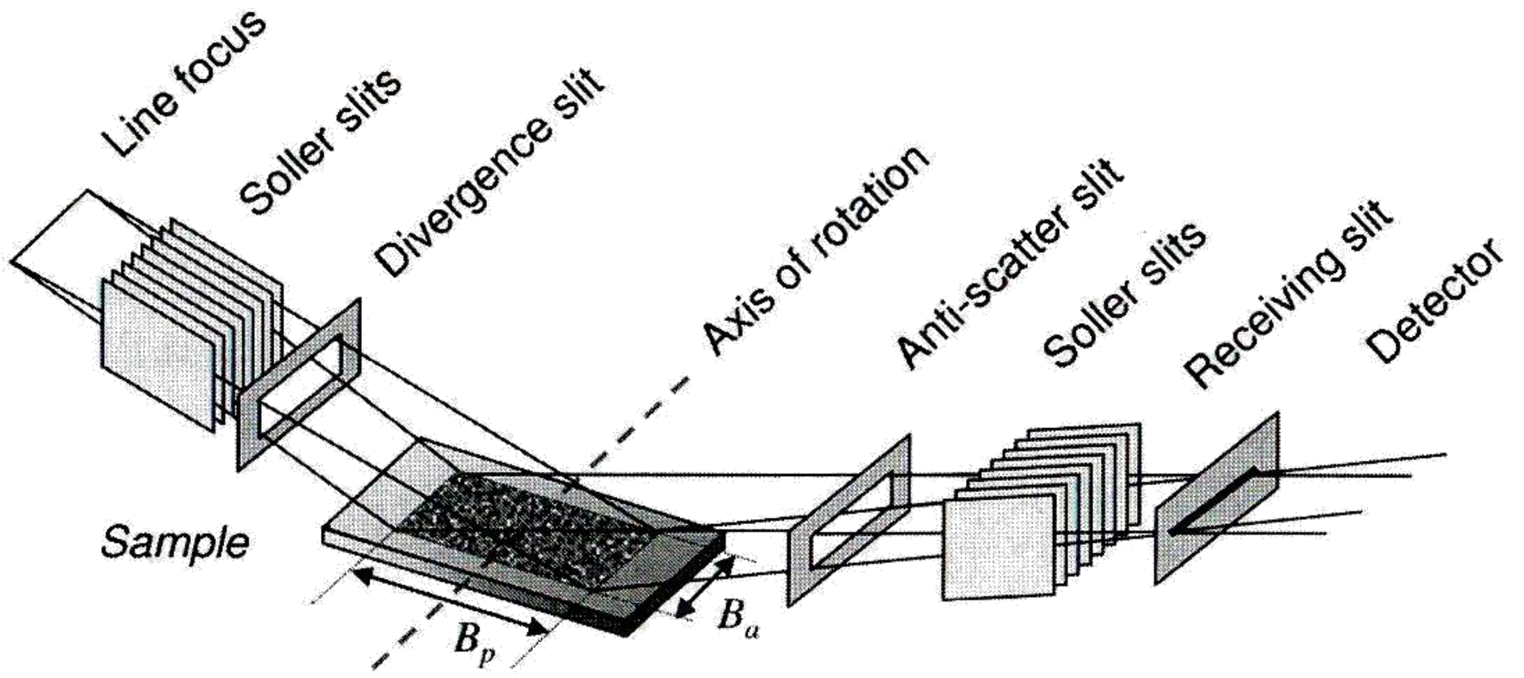






X-ray optics

- Figure shows a typical X-ray system.
- It consist of :
  - Soller slit (a stack of parallel metal foils).
  - Divergence slit
  - Receiving slit
  - Anti-Scattering slit



- Function of the parallel metal foils is to limit the angular divergence of the X-ray beam at right angles to focusing plane.

- The focusing plane is in horizontal, so soller slit limit the vertical divergence.

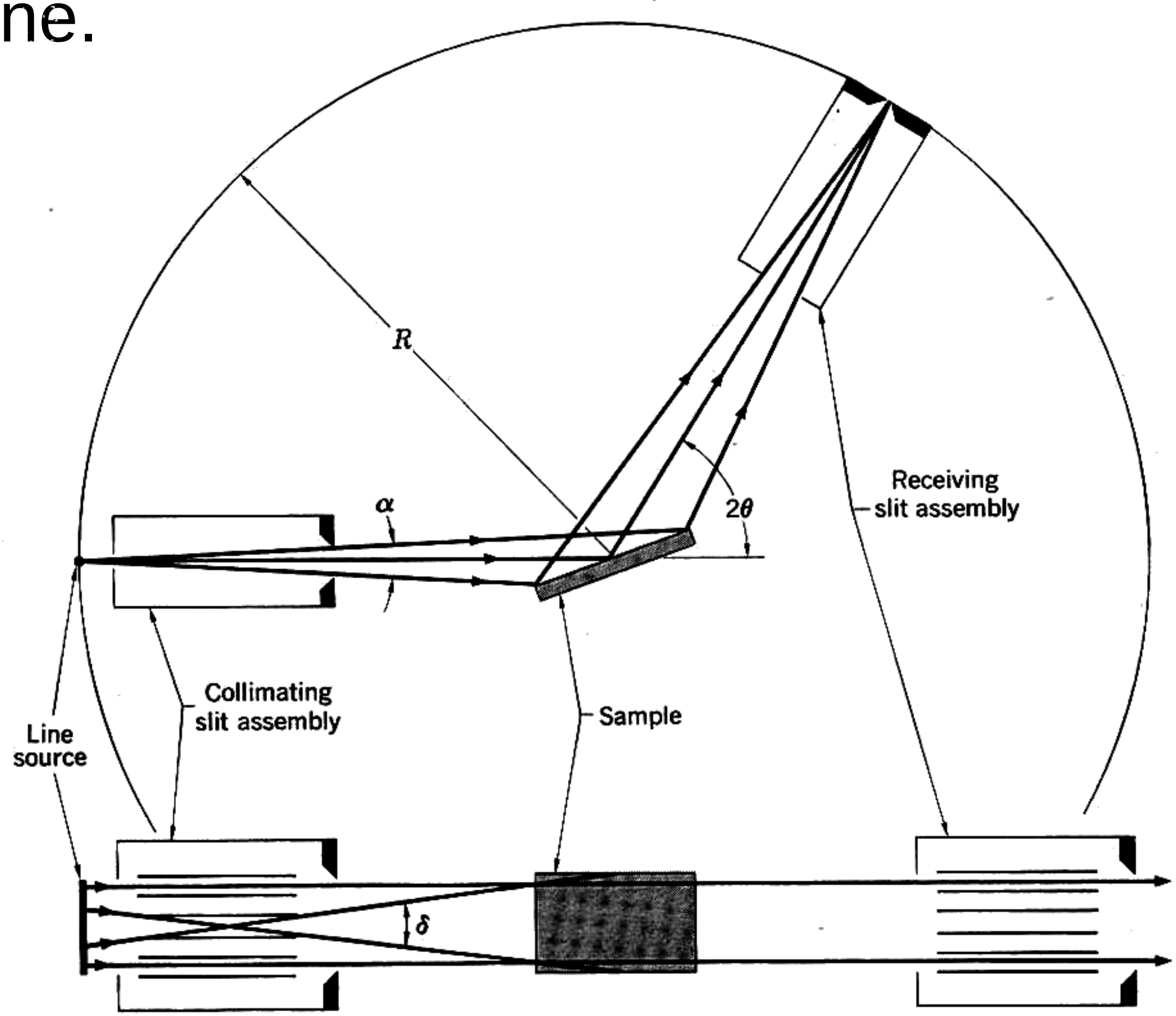
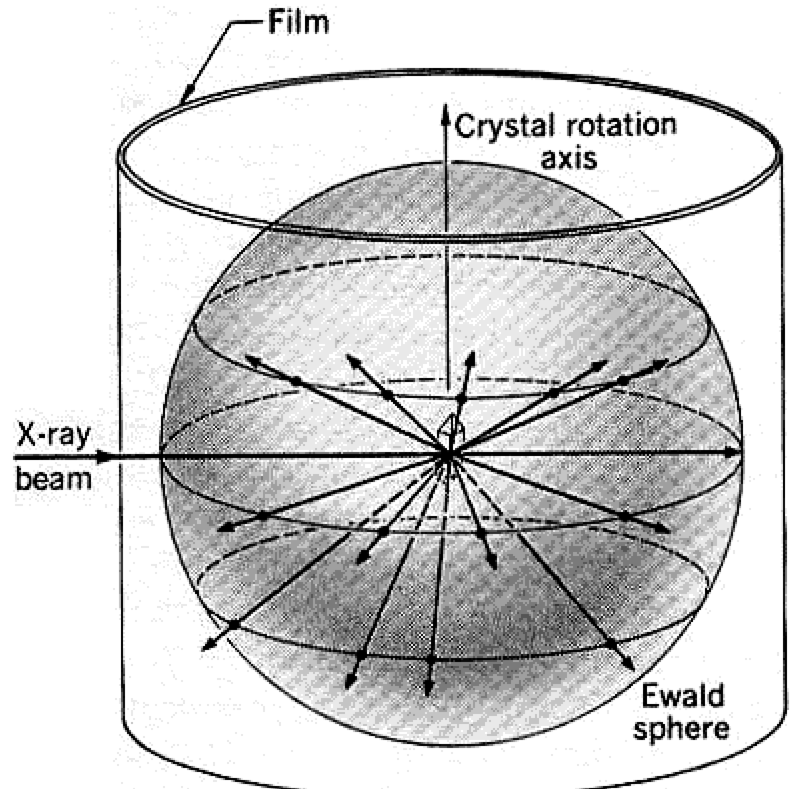


Fig. 13-11

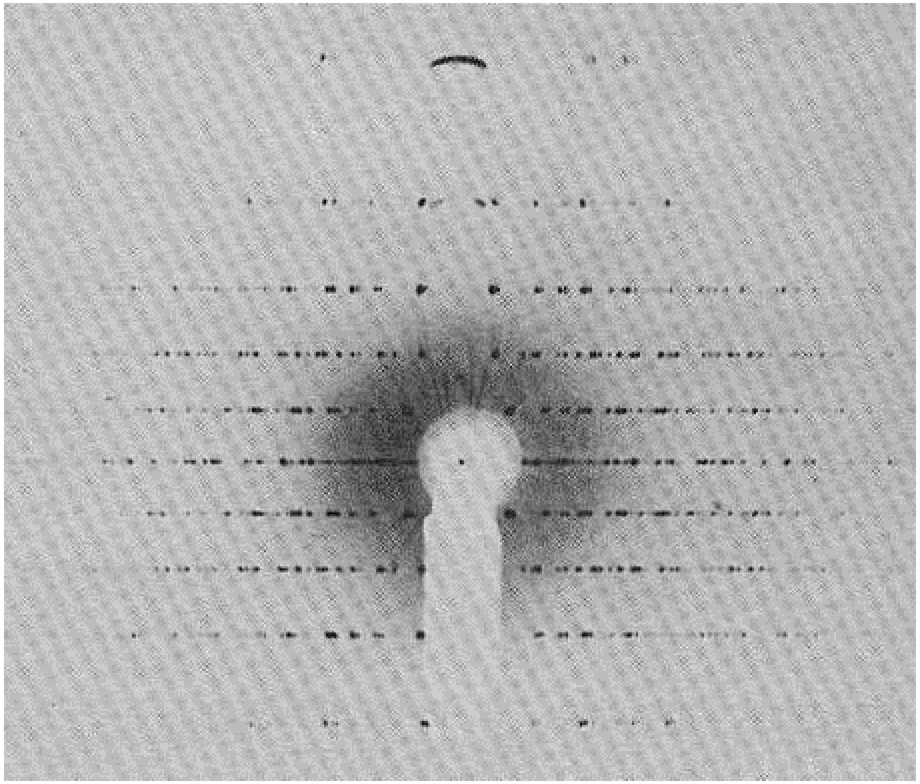
3.4 Rotating-crystal Method

- When a crystal is rotated about an axis oriented normal to the incident-beam direction, usually called the ***normal-beam method***, the individual layer of the reciprocal lattice cut the Ewald sphere.

- Each time a reciprocal-lattice point hkl intersects the sphere of reflection, point on the sphere is produced.



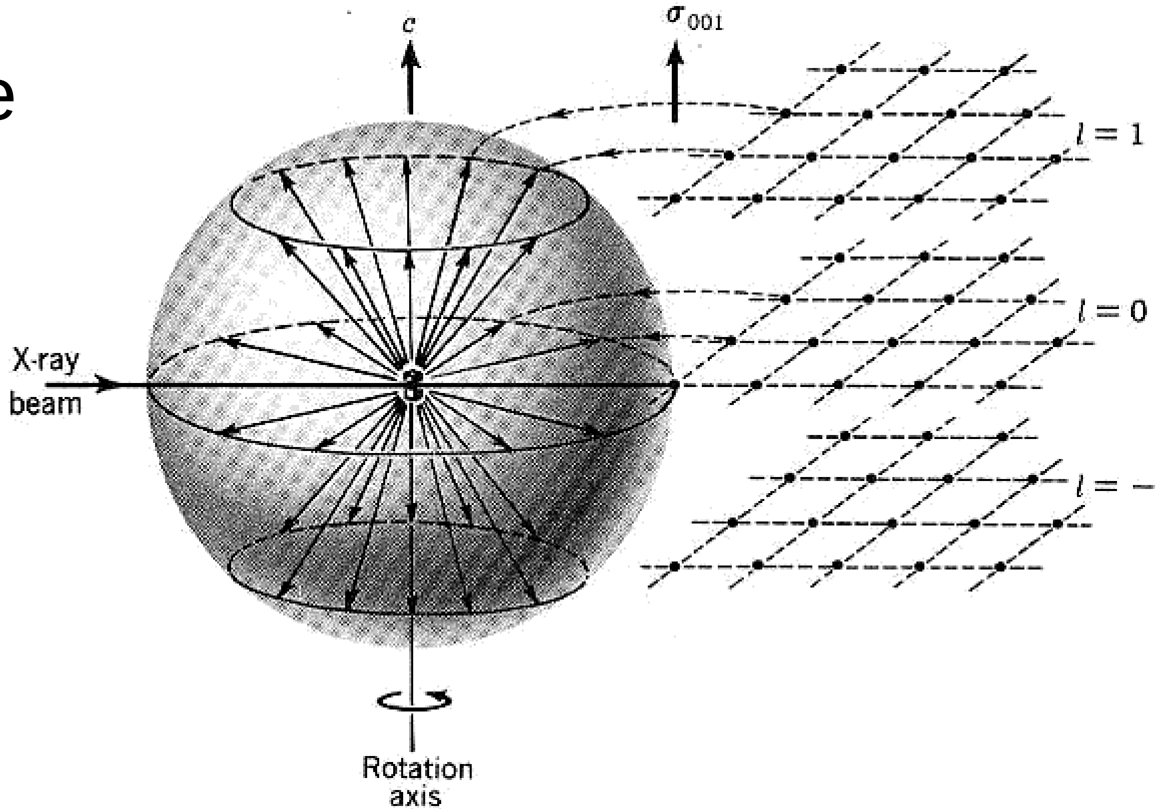
- During a complete rotation of the crystal, the individual diffracted beams form cones that are coaxial about the rotation axis of the crystal.
- Inorder to record the maximum number of the reflections produced, therefore, a film is placed cylindrically about the crystal’s rotation axis.
- The individual reflections thus are recorded as spots lying along horizontal rows on the film, called ***layer lines***.



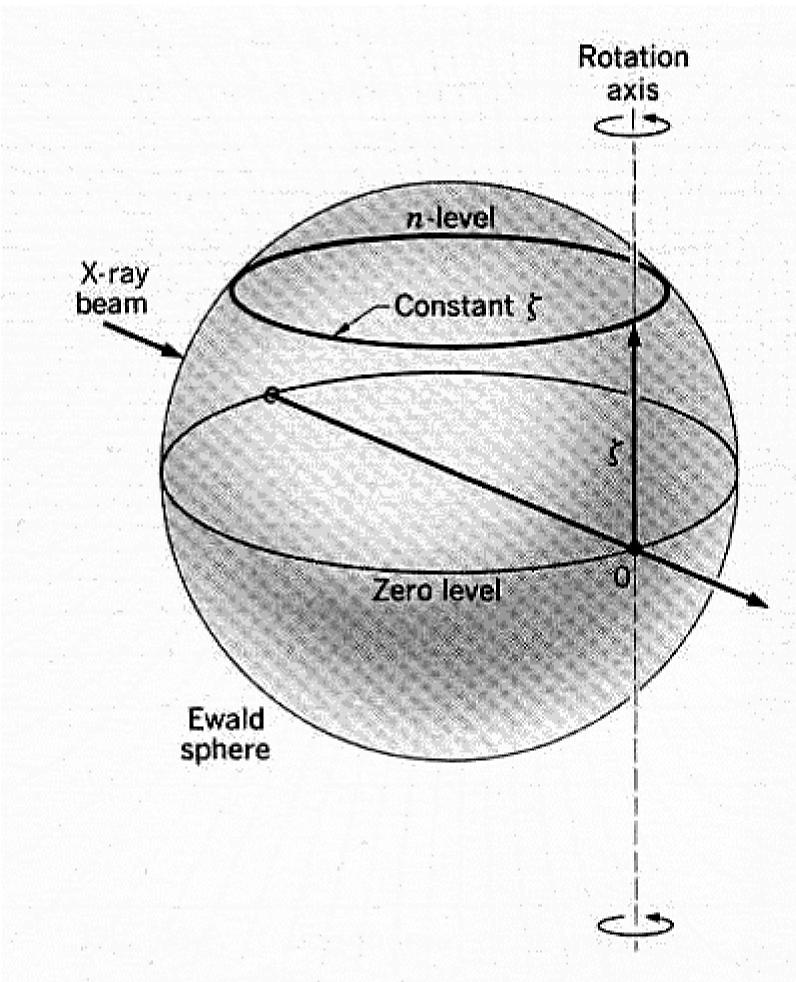
Example

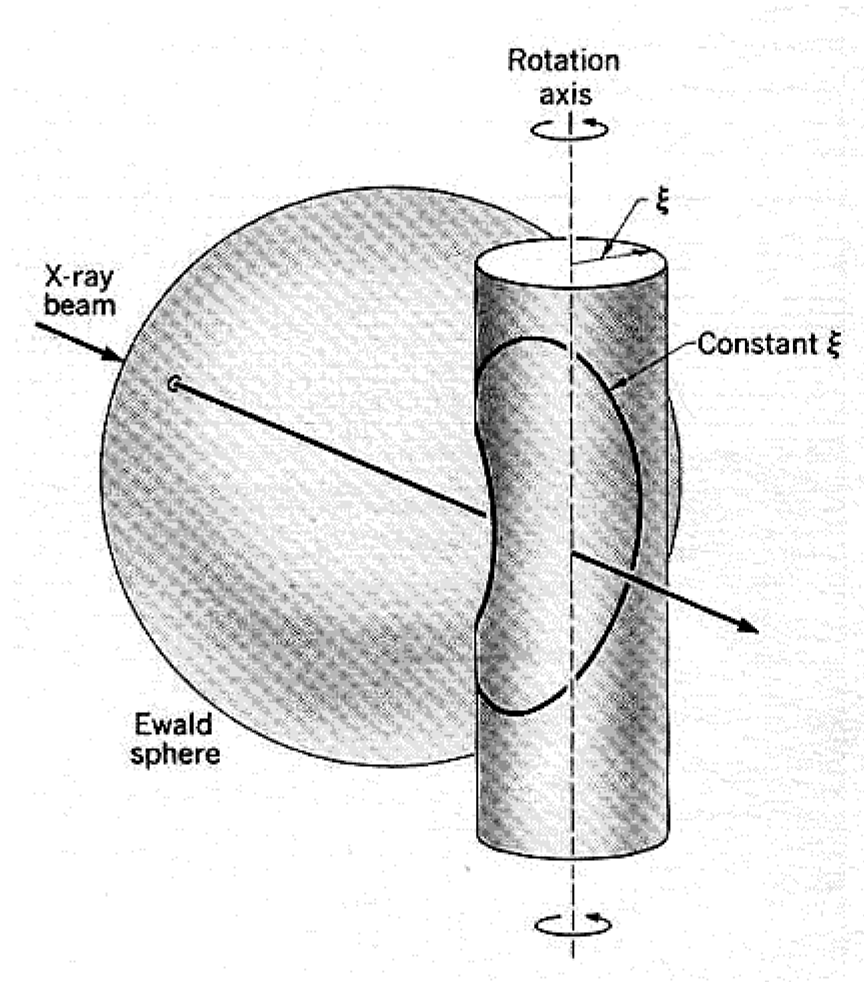
- A tetragonal crystal at the center of the sphere of reflection

- A portion of the reciprocal lattice is shown.
- The crystal rotates about c axis.
- A couple of point in the l=0 and l=1 level.

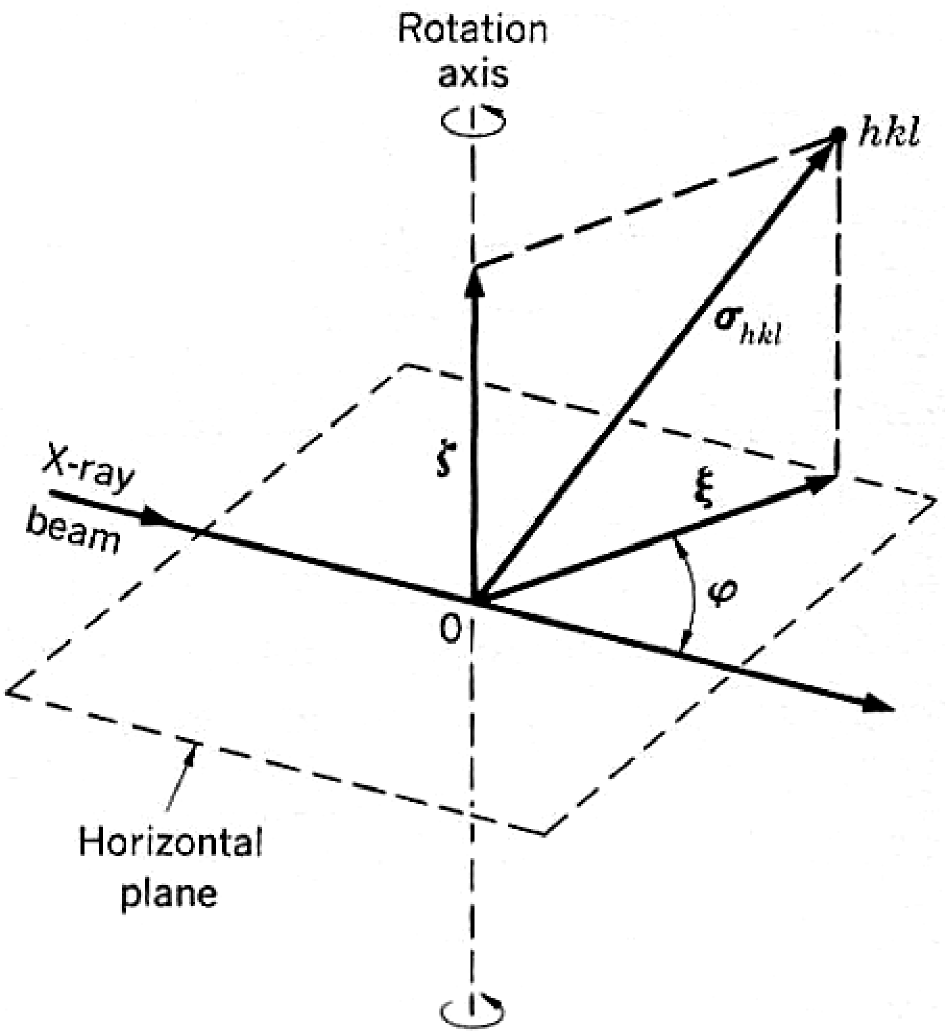


- In this method, the reciprocal lattice of a crystal is recorded directly in diffraction experiments.
- A cylindrical film is used so that it is convenient to select cylindrical coordinates.

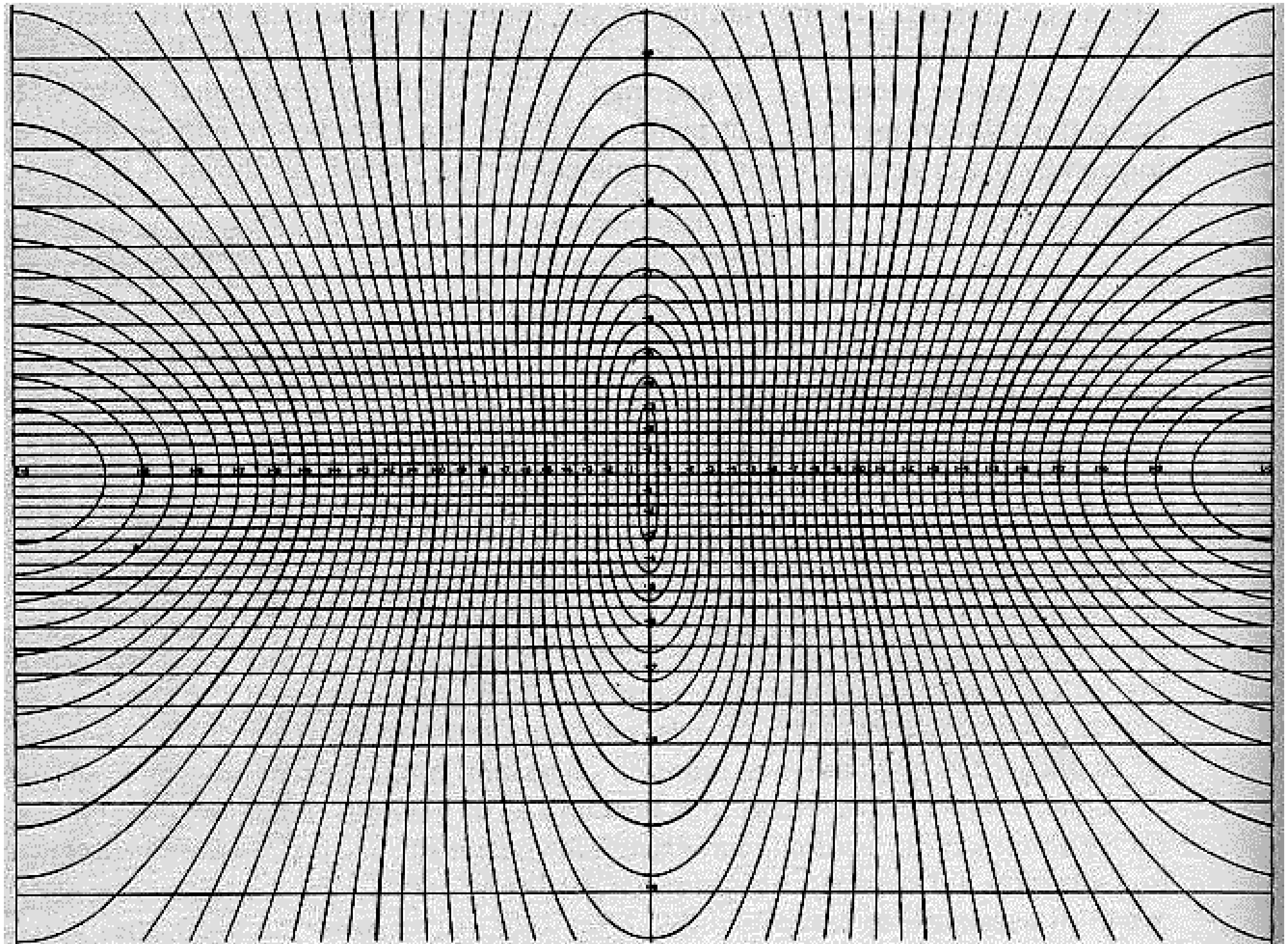




- The orientation of the reciprocal-lattice vector σ_{hkl} is in a special orthogonal vectors, ζ along the rotation axis and ξ in plane containing the x-ray beam.
- An angle φ formed by the direct beam and the plane containing ζ and ξ.

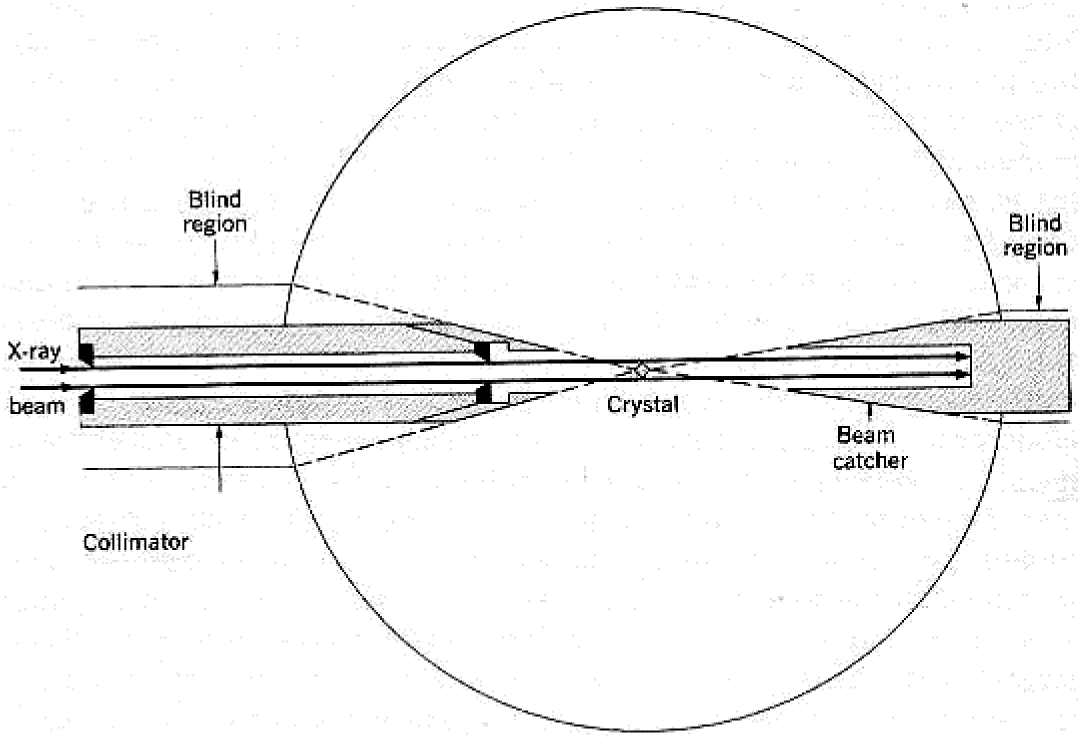


- The spots is recorded using the Bernal chart as shown here.
- However, due to its limited recording range, a flat-plat camera can be utilized in place of a cylindrical film.



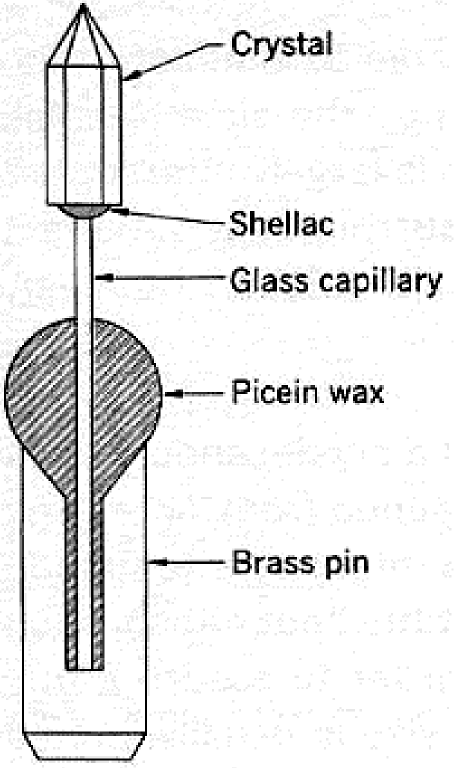
Collimation system

- Collimation system is used to limit the shadow or blind region.
- The reason for using a deep cone-shaped receptor than a flat disk is to prevent the direct beam striking the beam stopper and the scattered backward beam will causes the film to become fogged.



Mounting and adjustment of crystal

- The optimum size that a crystal should have in a diffraction experiment is proportional to the reciprocal of the linear absorption coefficient for the radiation selected.
- In order to ensure a uniformly exposed diffraction photograph, the crystal size is usually limited to below a half millimeter in diameter.
- This limitation is to assures that the crystal will be surrounded completely by the incident beam during the exposure.
- Then the sample is mount in such a way that it can be proper adjusted in the X-ray beam.



Interpretation of photographs

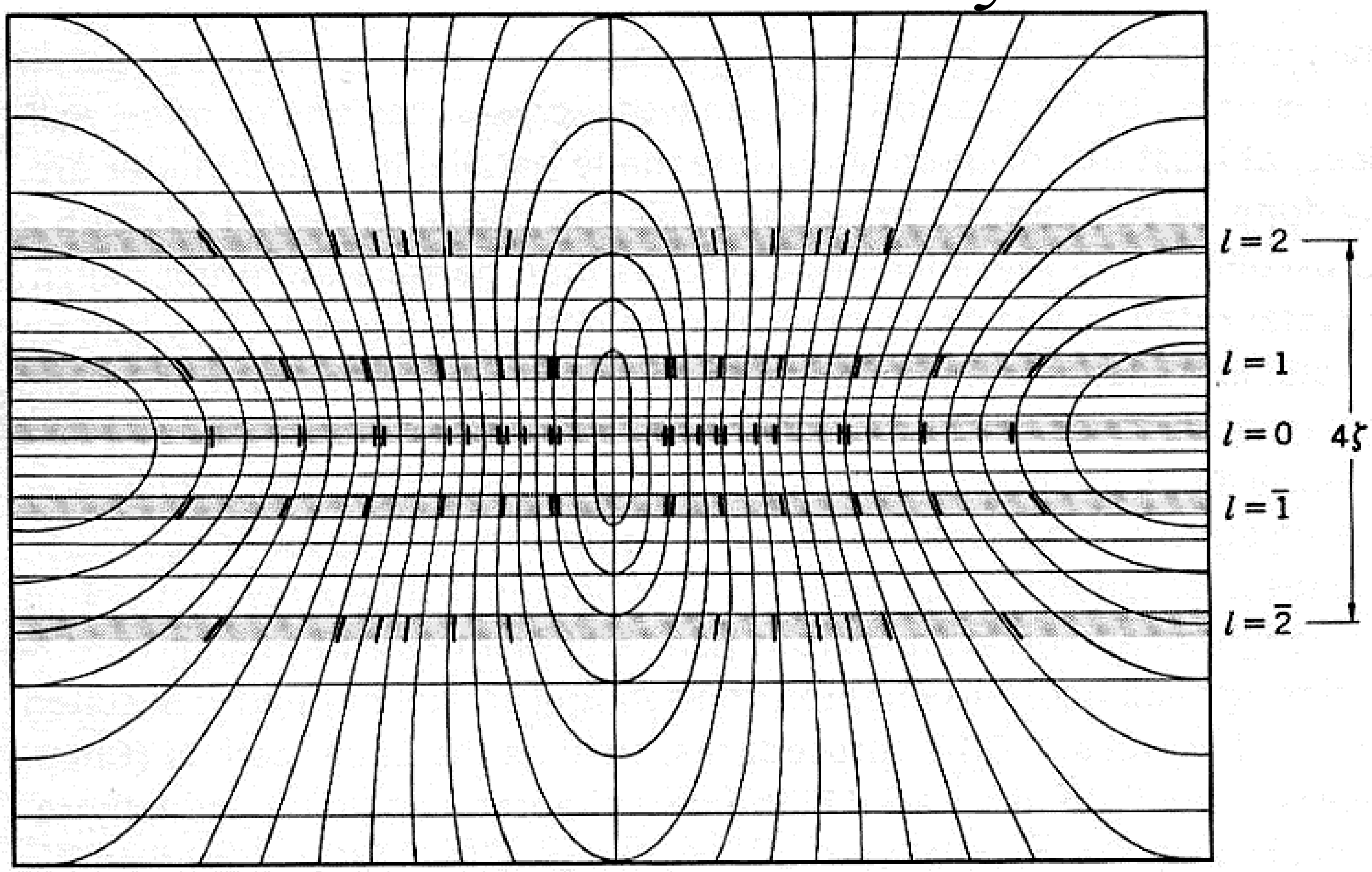
- From privious discussion, the spacing between layer lines in a rotation photograph is directly proportional to ζ, the reciprocal-lattice normal to the rotation axis.

- Superimposing a rotation photograph on an appropretely scalled Bernal chart allows the determination of this value directly.

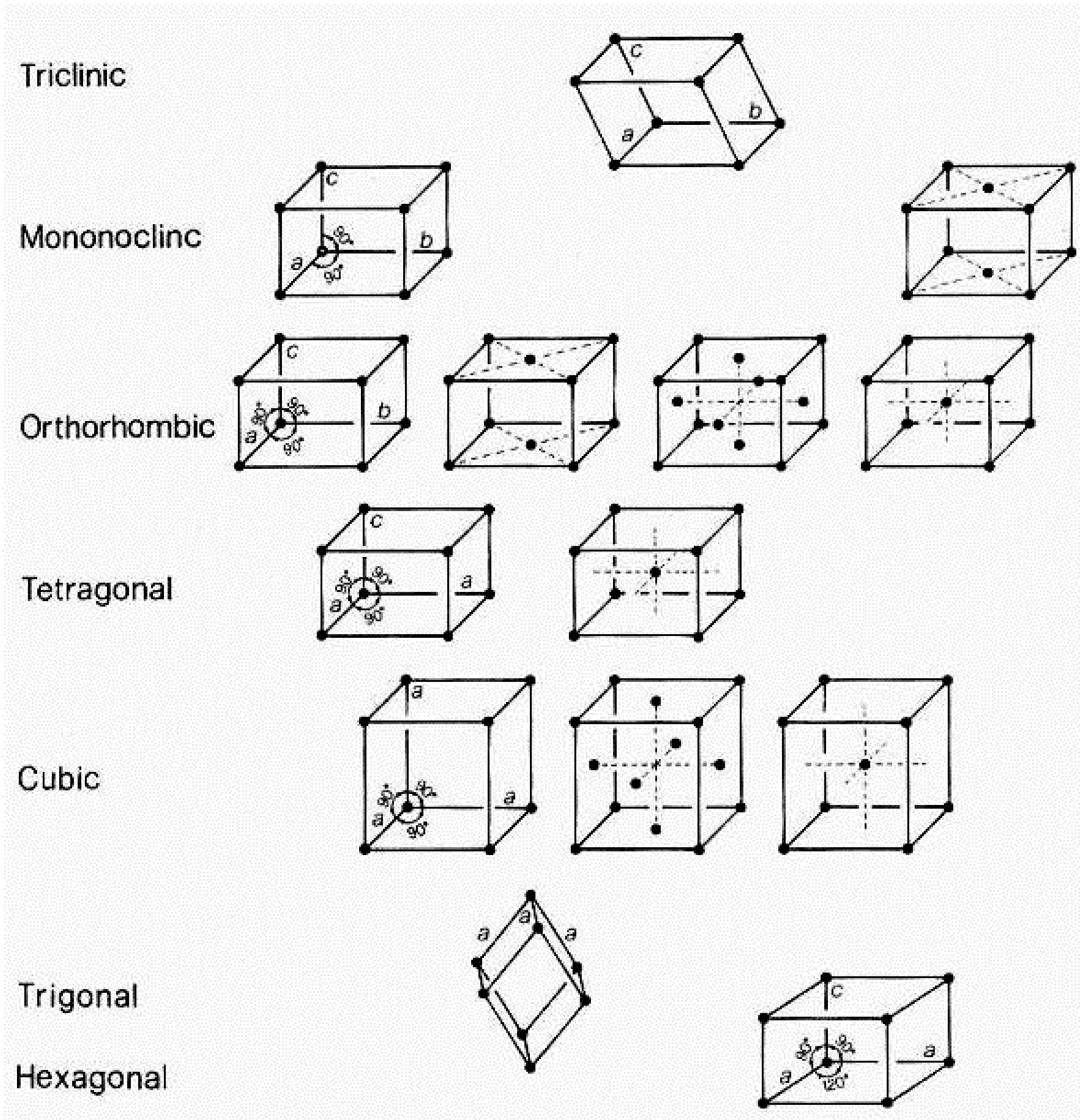
- The distance between the uppermost and lowermost layers is measured and divided by thr number of layers.

- Assuming that the crystal was mounted to rotate about the normal to the (001) planes, the value of d_{001} is then given by

$$d_{001} = \frac{\lambda}{\zeta}$$



- In the cubic system, all three cell edges are the same, so one rotation photograph about a is all that is needed.
- In the tetragonal and hexagonal system, rotations about c and a are necessary.
- In the orthorhombic system, the three cell edges are distinct and mutually orthogonal, so that three rotations are needed to determine their lengths.
- In the monoclinic and triclinic system, rotation photographs can be used to determine the length of the cell, but the presence of arbitrary angles complicates their interpretation, particularly for the triclinic system.
- So, moving-film methods are preferred for such studies.


Triclinic
Mononoclinc
Orthorhombic
Tetragonal
Cubic
Trigonal
Hexagonal

3.5 Laue Method

- In the Laue method, a single crystal is mounted so that a collimated beam of white radiation can fall upon it.
- Unlike other method, the wavelength of the X-ray beam employed does not have a single value.
- From previous section, it has been shows that the diffraction condition is

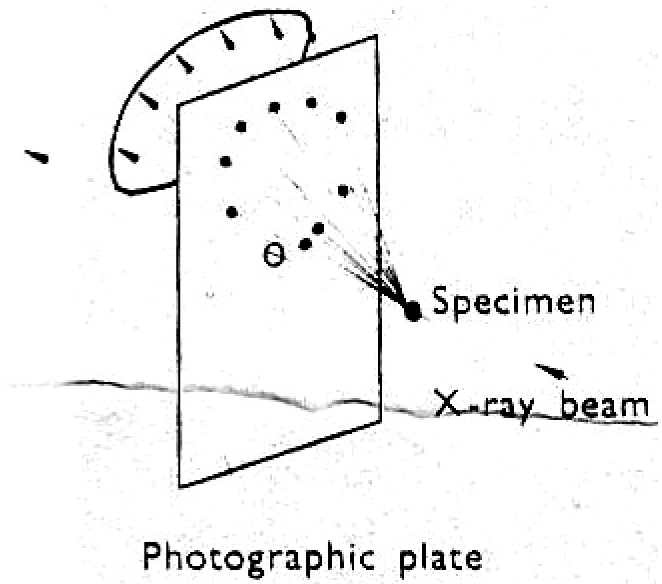
$$\lambda = 2d\sin\theta$$

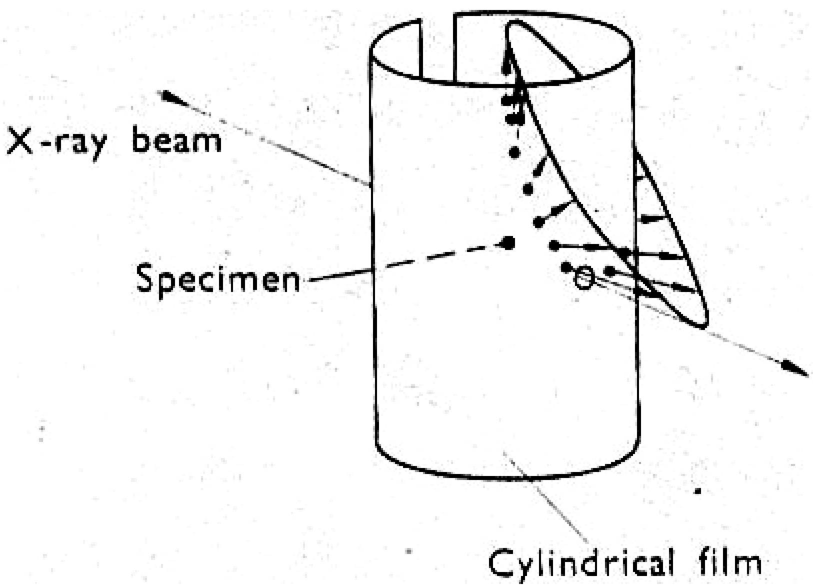
$$2\pi K.a = h\lambda$$

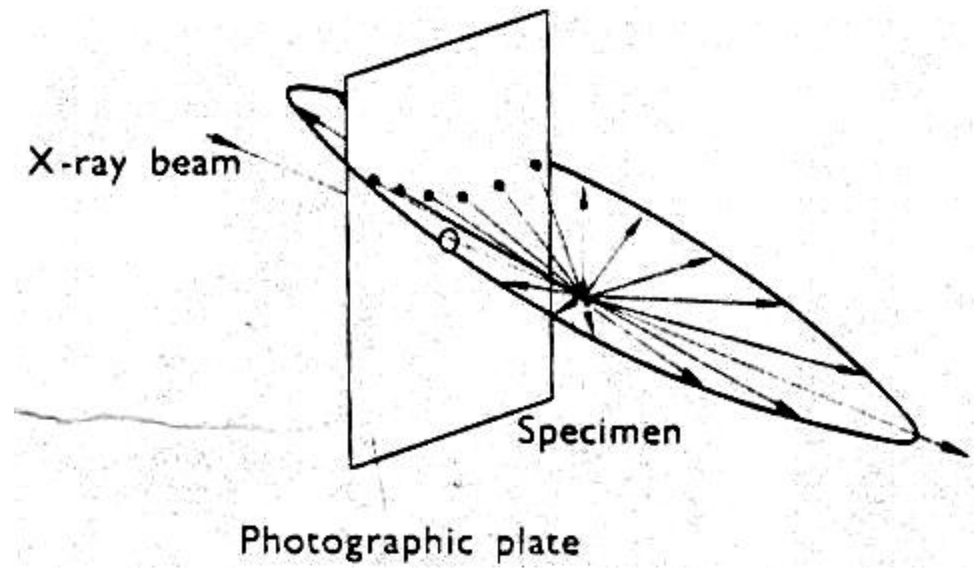
$$2\pi K.b = k\lambda$$

$$2\pi K.c = l\lambda$$

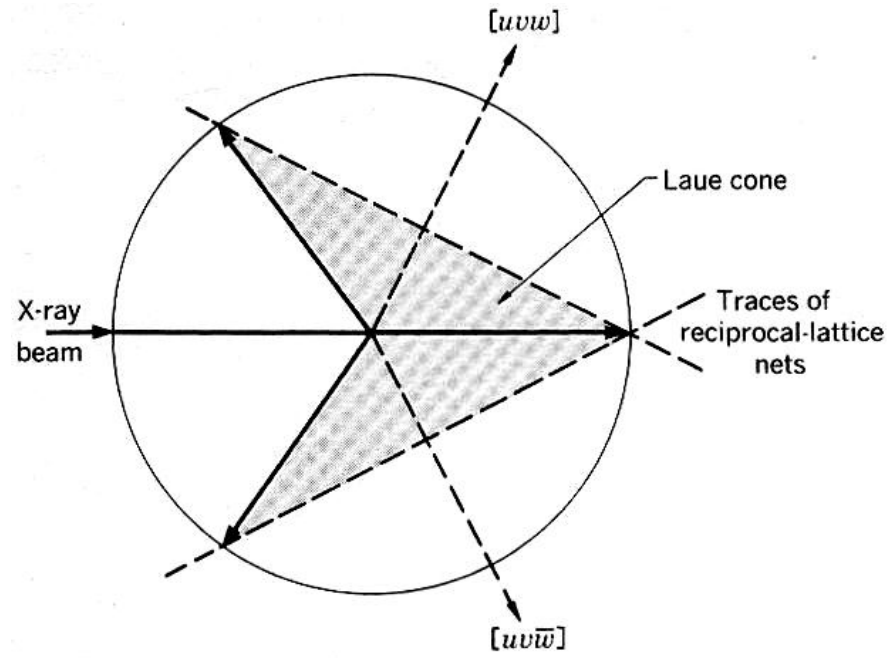
- Three type of Laue photograph can be obtained.
- The spot on these photographs are clustered along well-defined curves $\rightarrow$ Laue cones is observed.

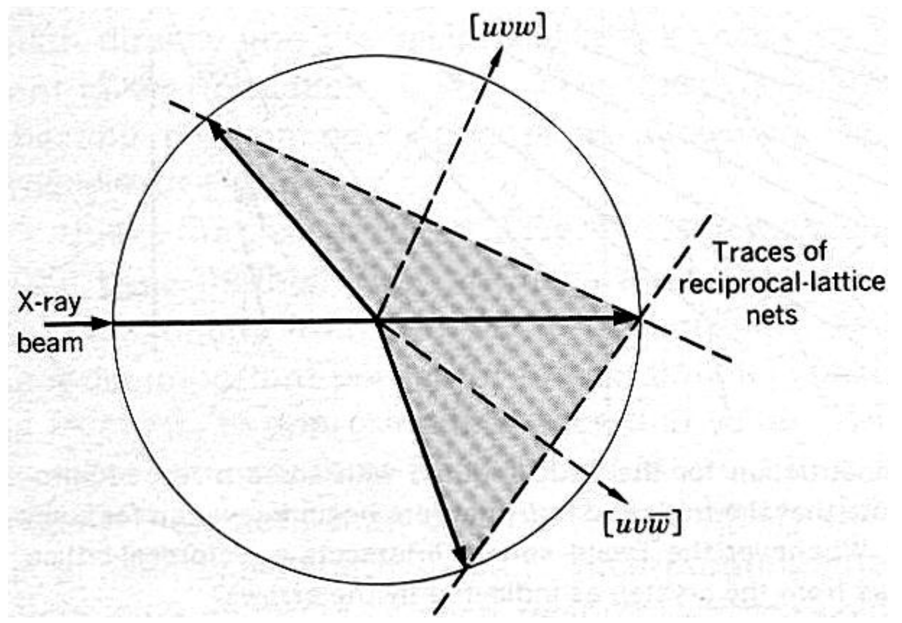




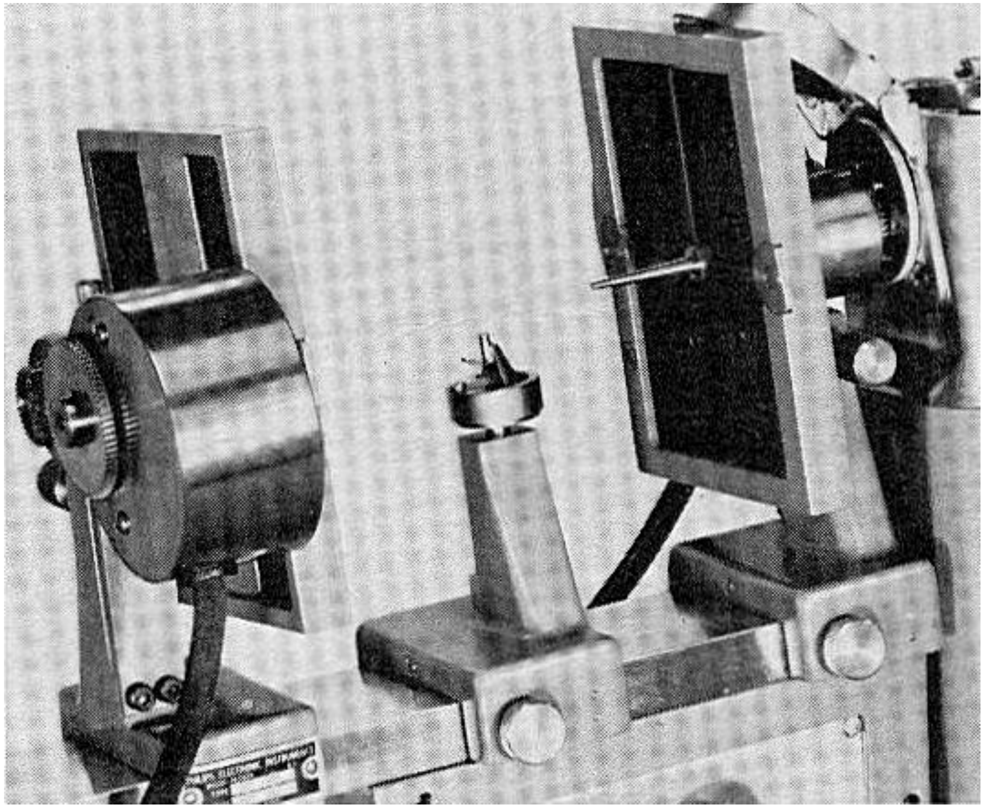


- The axis of the cone is normal to the reciprocal-lattice plane.
- When s symmetry element in the crystal is parallel to the incident x-ray beam, the diffraction cones surrounding the beam are symmetric.
- On the other hand, if the crystal is tilted slightly so that symmetry-equivalent zone axes in the crystal no longer form equal angles with the x-ray beam, the cones are no longer equivalent.





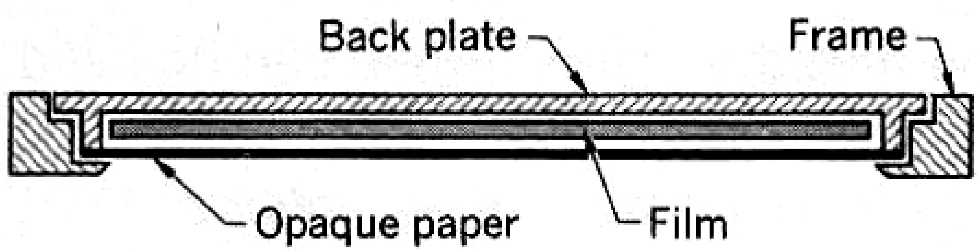
- A film is placed so that the diffracted radiation can be recorded.
- If the crystal is thin enough for the radiation to pass through it, the film may be placed behind the sample (Front-reflection).



- The film can be placed between the radiation source and sample (Back-reflection).
- The incident beam allowed to irradiate the sample through a hole cut in the centre of the film.

Instrumentation

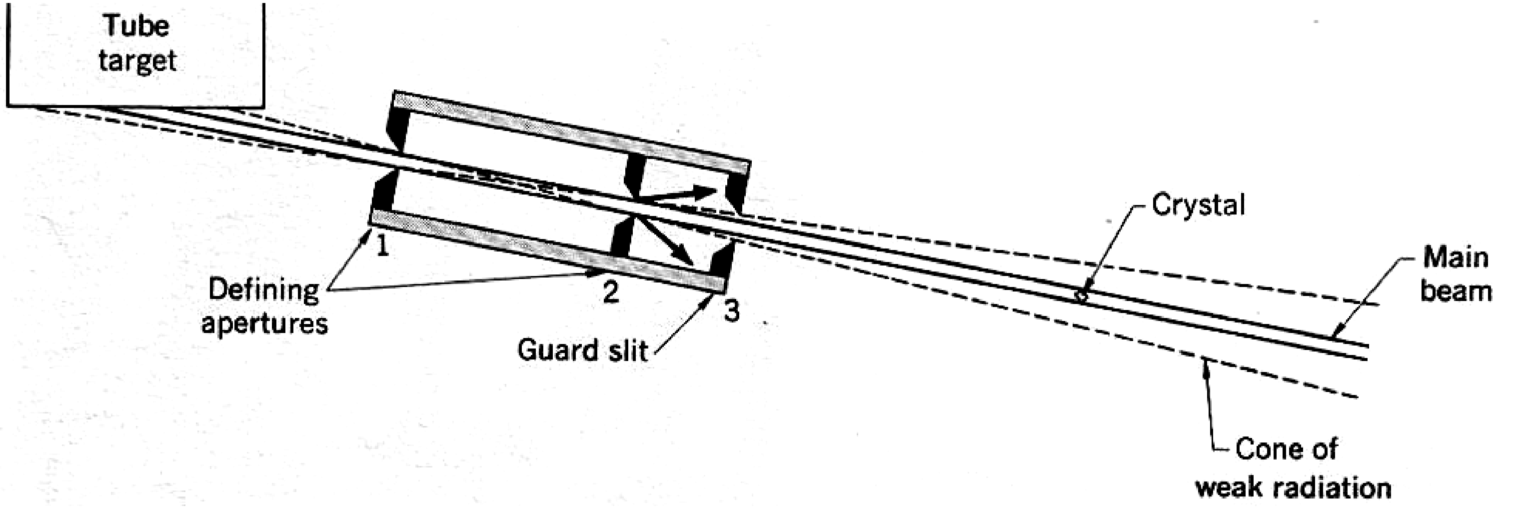
- Flat-plate cameras/films
  - A flat film with a special cassette is used to record the diffraction cones produced in the Laue method.



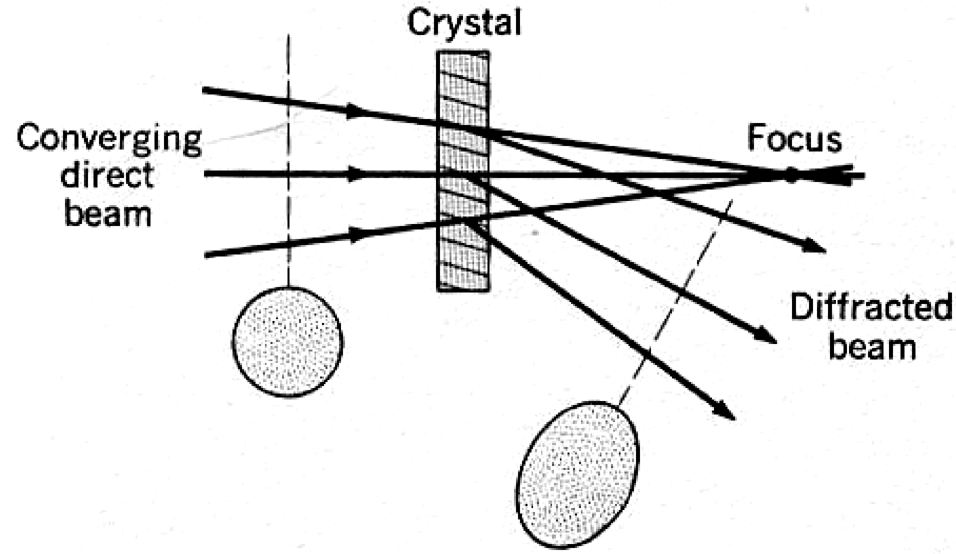
  - The crystal-to-film distance is made quite small (usually fixed at 3 or 5 cm).
  - The short distance has two advantages:

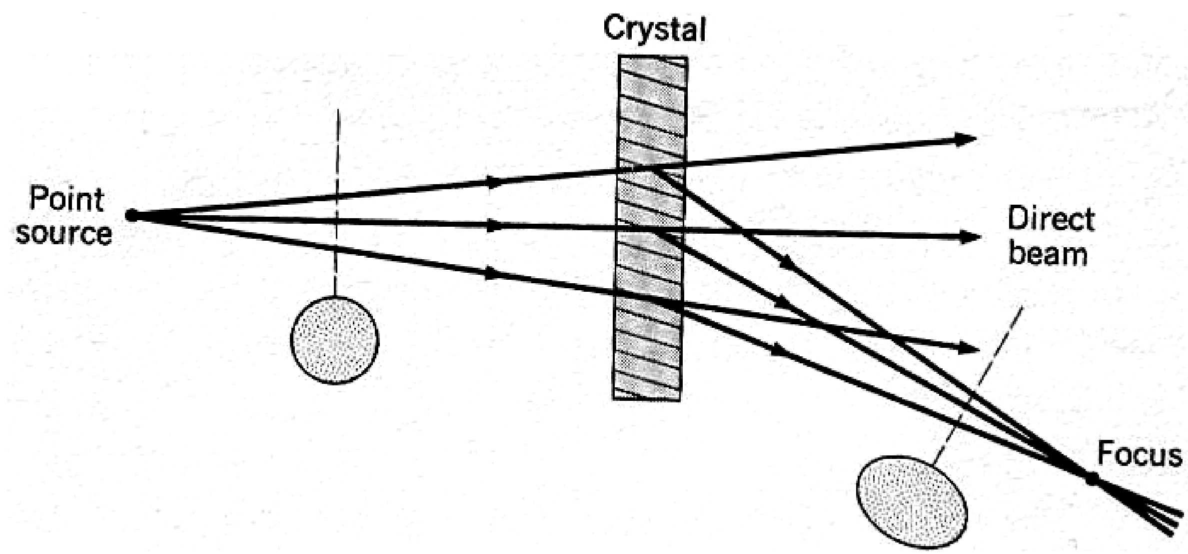
1. Decreases the exposure time
2. Increases the number of reflections intercepted by the film.

- Collimating system
  - The main function of the collimating system is to define a narrow X-ray beam.
  - This can prevent the radiation from striking the film or leaking into the room.
  - Commonly, the system used a series of circular apertures to form a pinhole system or a combination with rectangular openings to form a slit system.



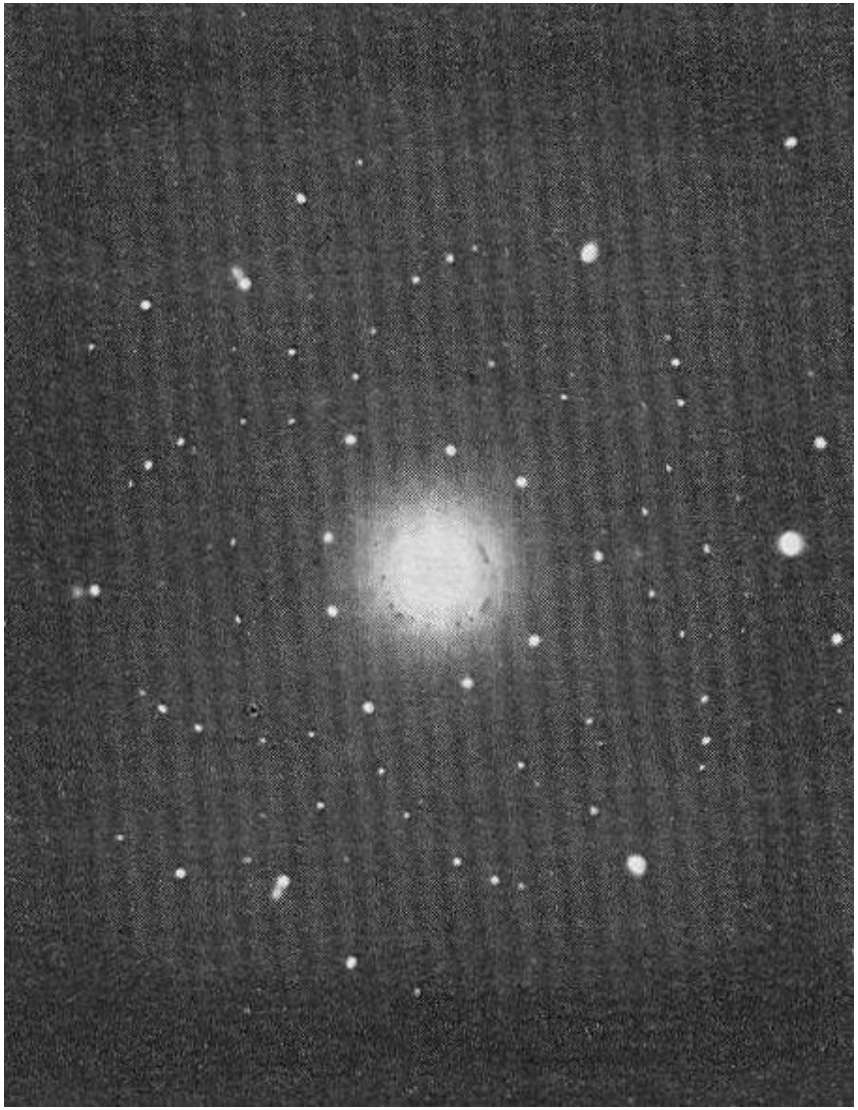
- Shape of reflections
  - It is not possible to obtain a parallel beam of X-ray by simple collimation because the original source emits X-ray uniformly in all directions.





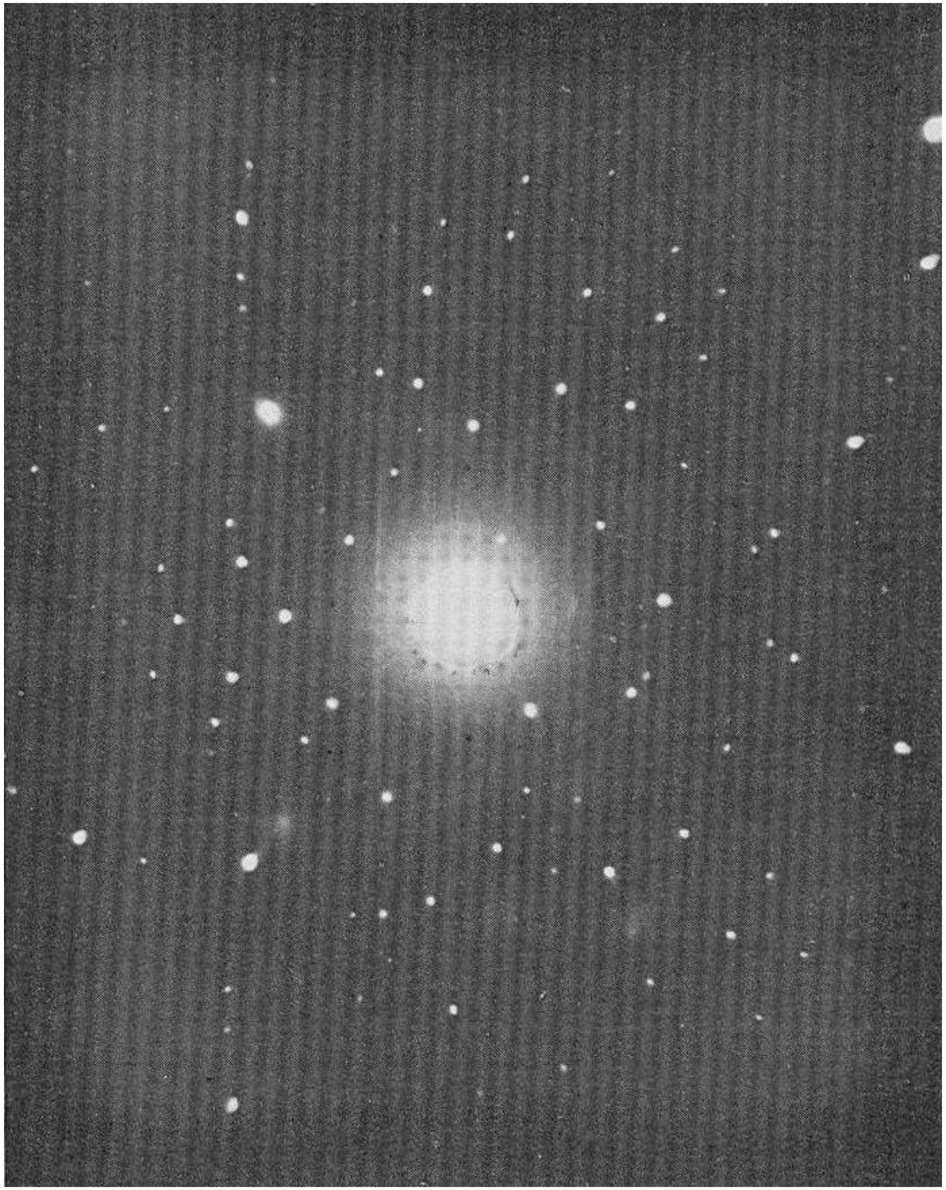
Front-reflection

- The reflections from a set of planes belonging to the same zone form a cone about the zone axis.
- These cones intersect the front-reflection photograph in ellipses (conic sections).
- Silicon crystal oriented with its [111] direction parallel to the incident beam.



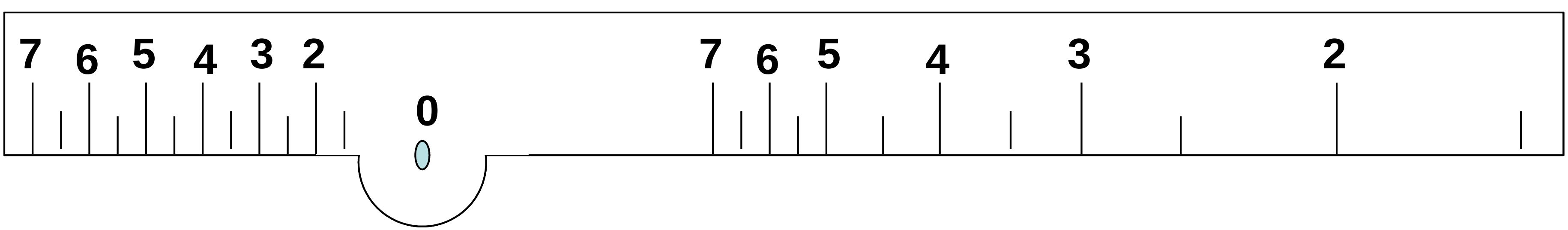
- When the same crystal is displaced slightly from proper alignment with the direct beam, the ellipses become distorted.

- Silicon crystal with [111] direction displaced by 10° from that of the incident beam.



Gnomonic Projection

- Laue photograph obtained from the Laue method can be used to constructed the Gnomonic Projection.
- By fixing the specimen-to-film distance D at some convenient value, it is possible to construct a ruler.
- Figure shows the special ruler is used.

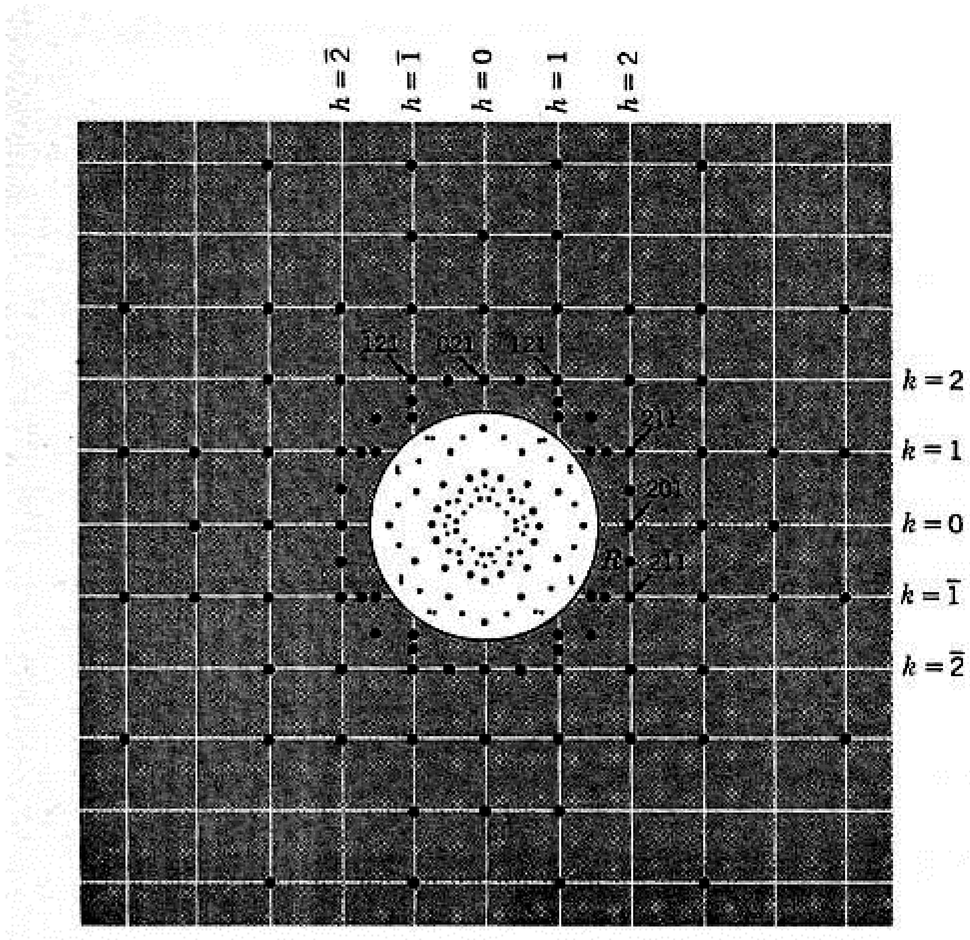


- Figure show a gnomonic projection constructed from a transmission Laue photograph of a cubic MgO crystal shown in the central circle.

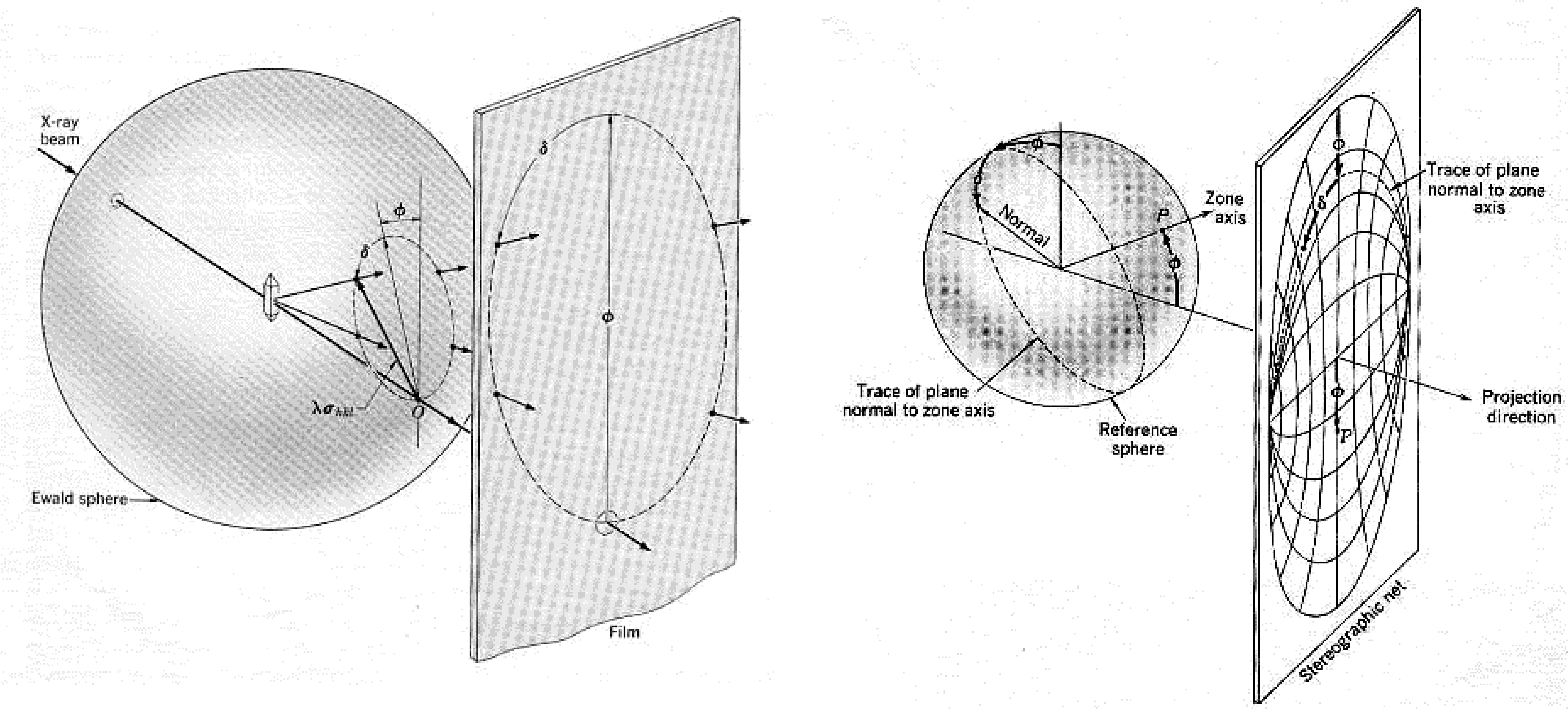
- The X-ray beam parallel to a_3, while a_2 was vertical and a_1 horizontal.

- Since the a2 axis is vertical, the h01 poles are regularly spaced along the central horizontal line.

- Similarly, the 0k1 poles lie along the vertical central line.



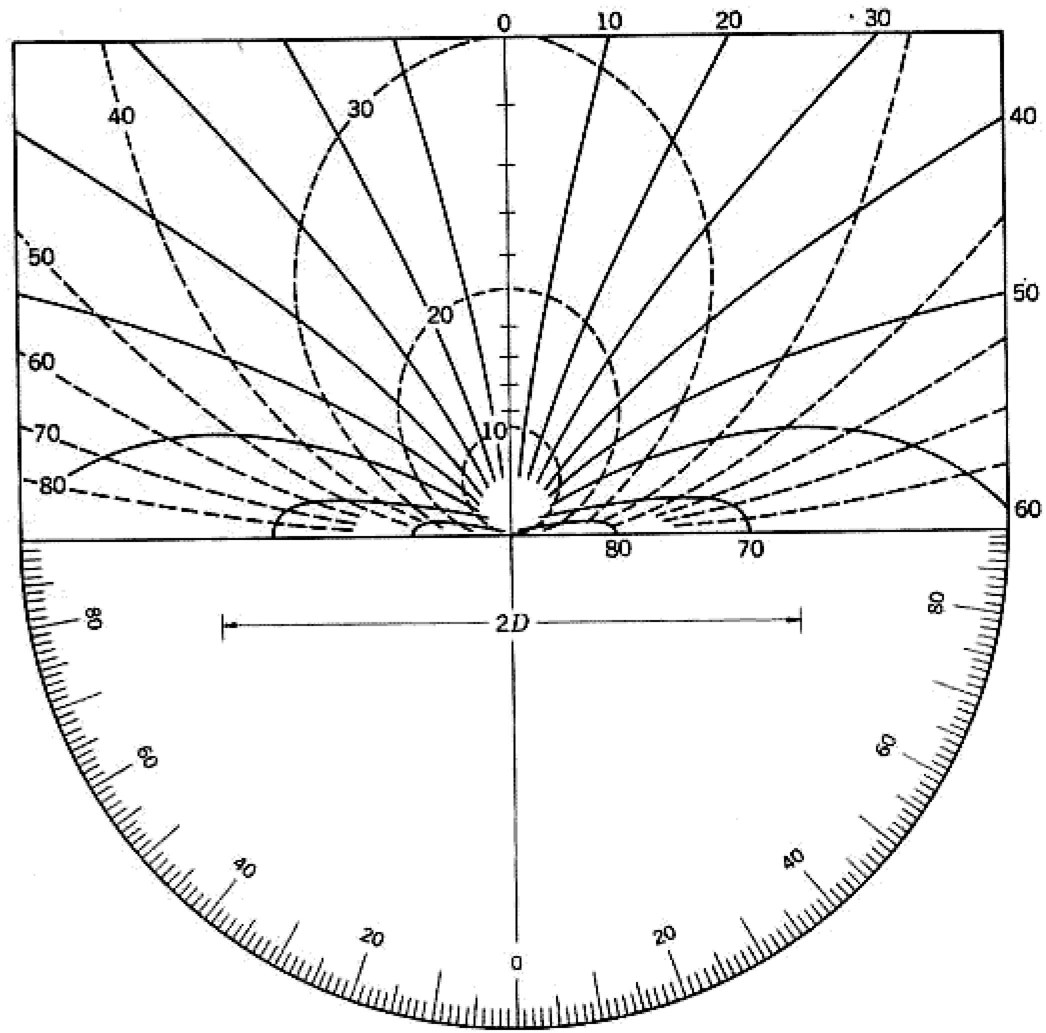
Stereographic projection

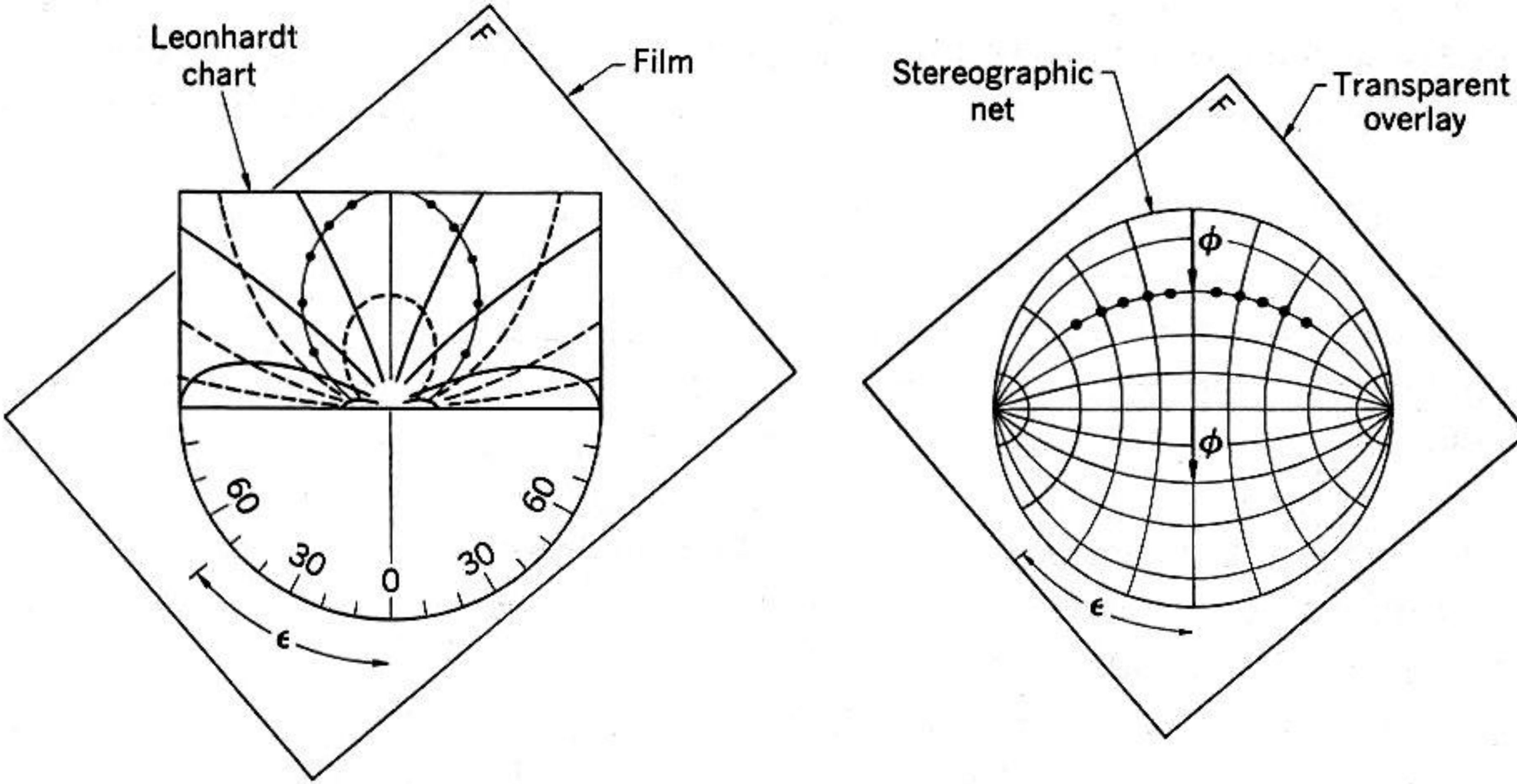


A comparison of the figure suggests that it would be desirable to be able to measure the position of reflections on a front-reflection photograph directly in terms of the two angular coordinates ϕ and δ.

Leonhardt chart

- The ϕ values are sketched by the dashed curves
- The δ values are sketched by the solid lines.

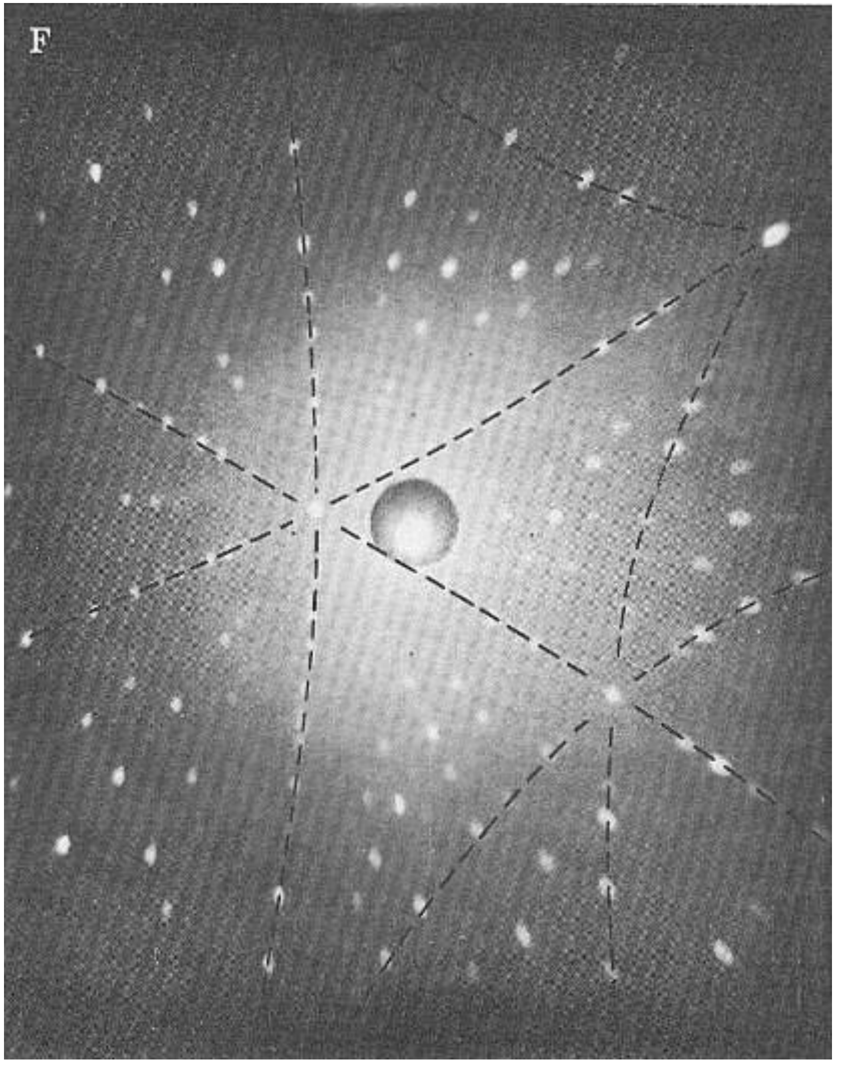




Transferal of angular coordinates from film to stereographic projection with the aid of the Leonhardt chart

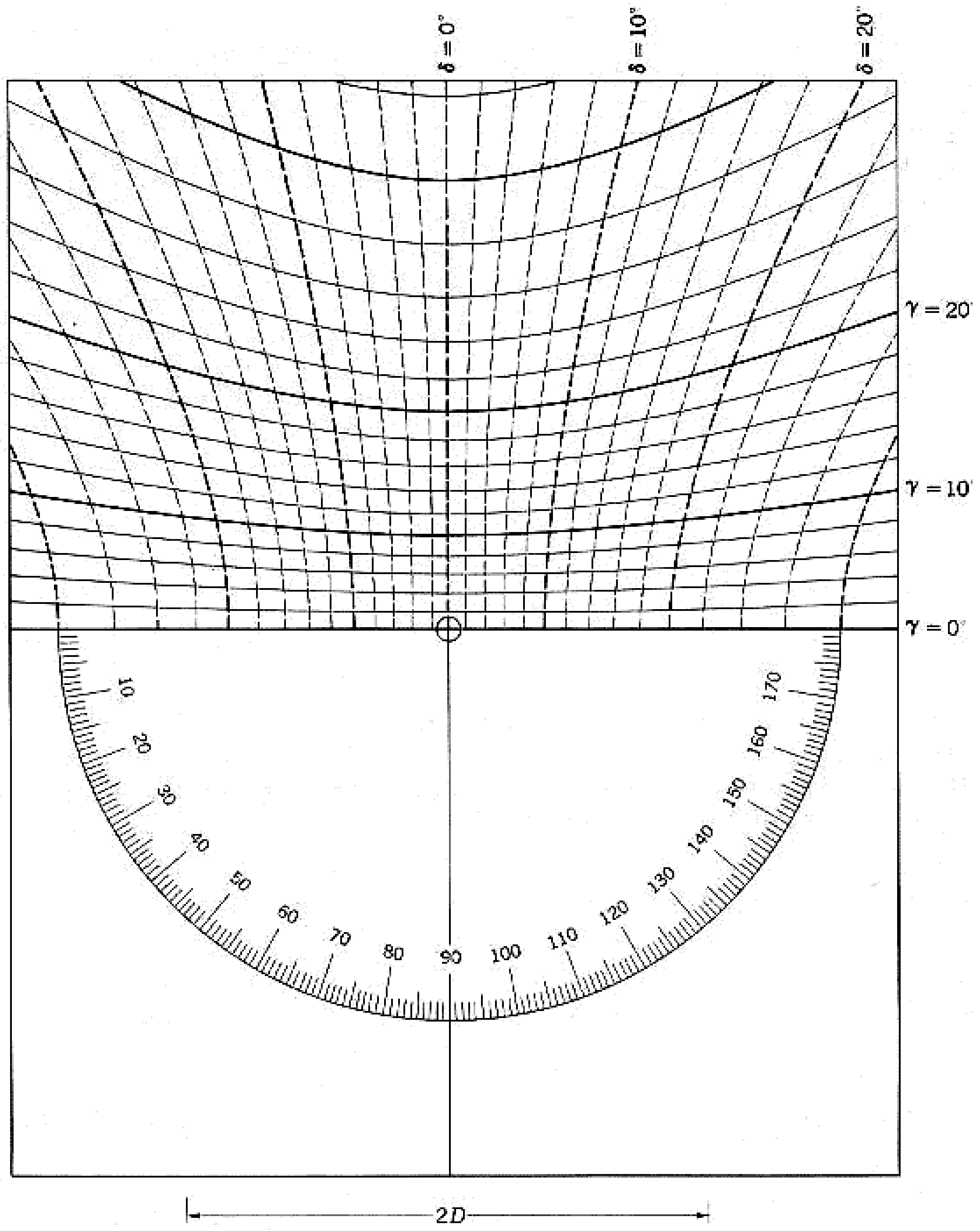
Back-reflection

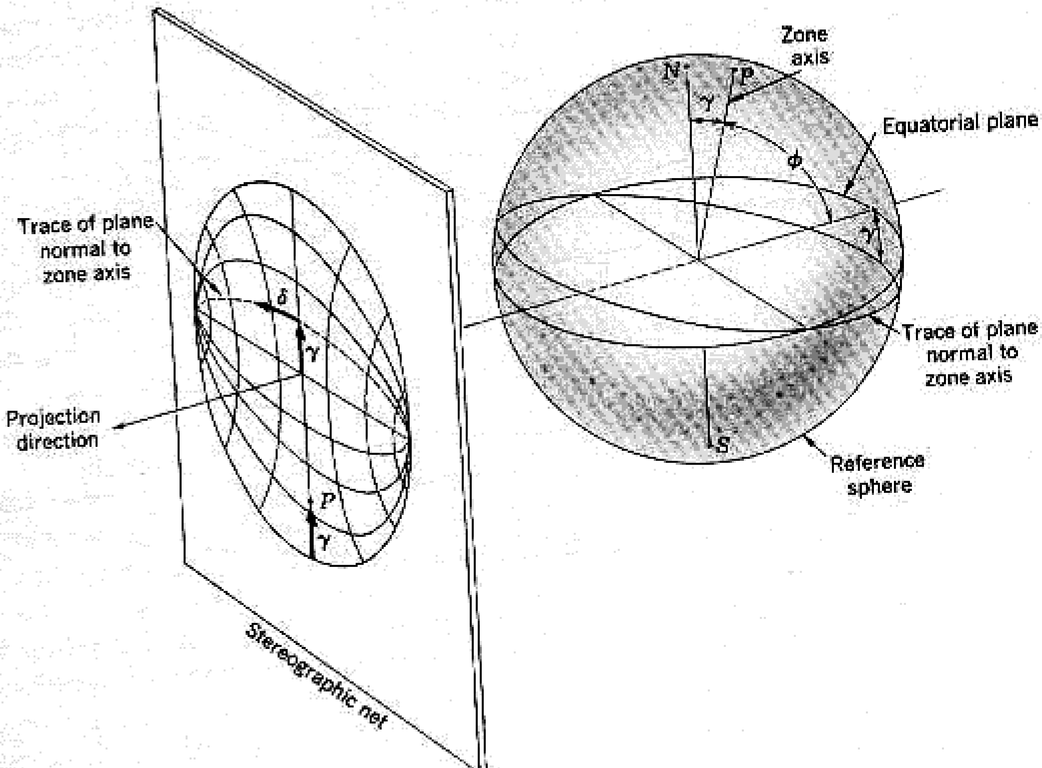
- Back-reflection Laue photograph of a silicon crystal. (distance crystal to film is 3cm)

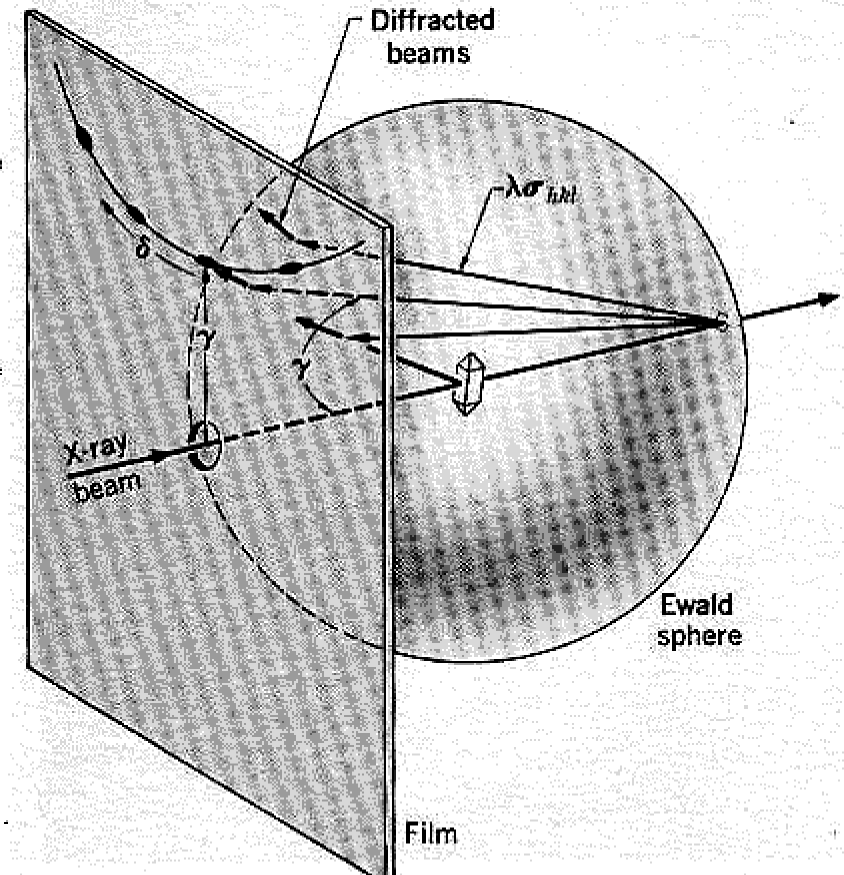


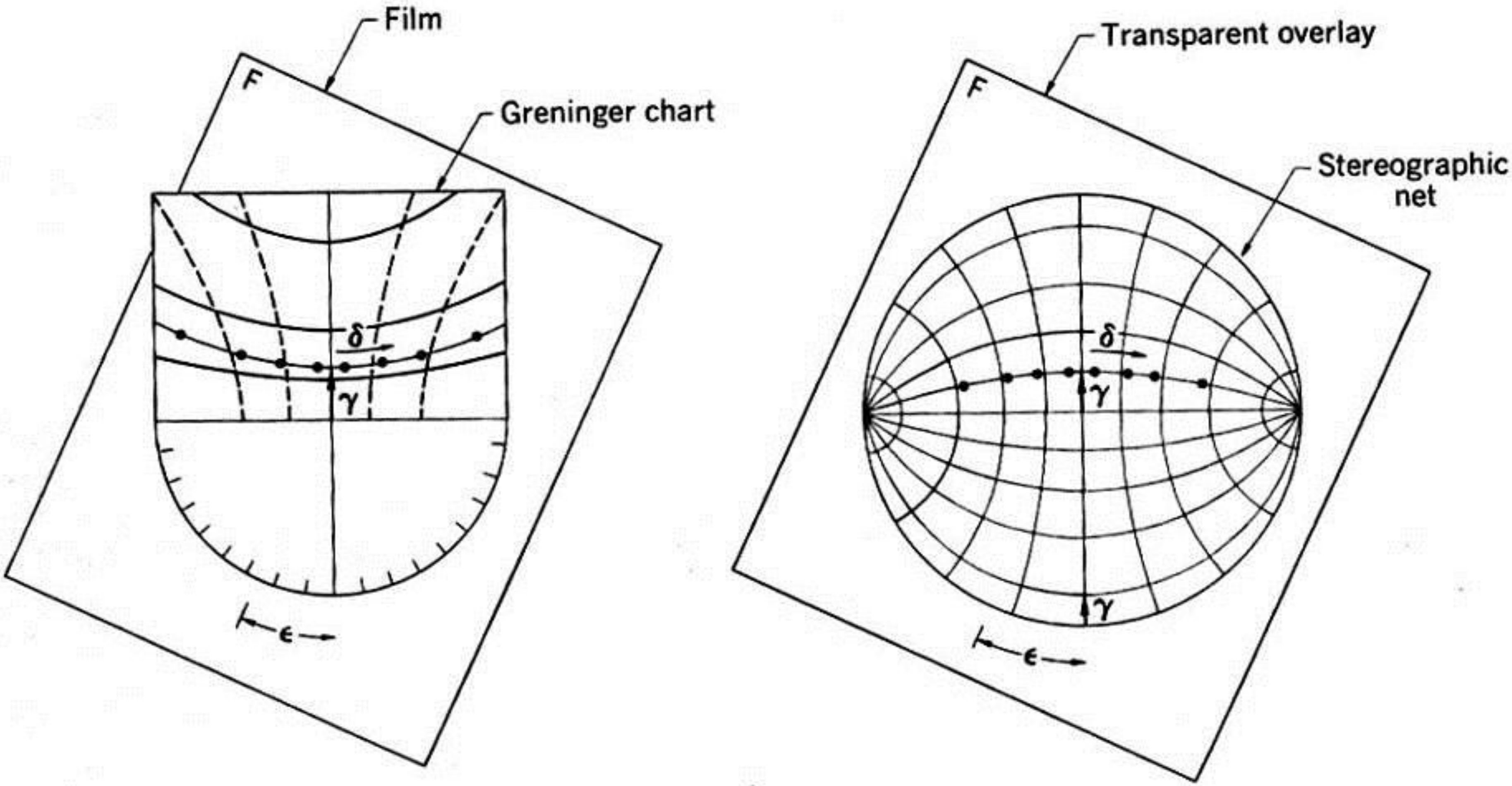
- As in the case of transmission Laue photographs, it is possible to relate the positions of individual reflection spots to the orientation.

- Greninger chart for film to crystal distance D=3cm




Zone
axis
N
P
γ
φ
Equatorial plane
Trace of plane
normal to
zone axis
δ
γ
Projection
direction
P
γ
Trace of plane
normal to
zone axis
S
Reference
sphere
Stereographic net

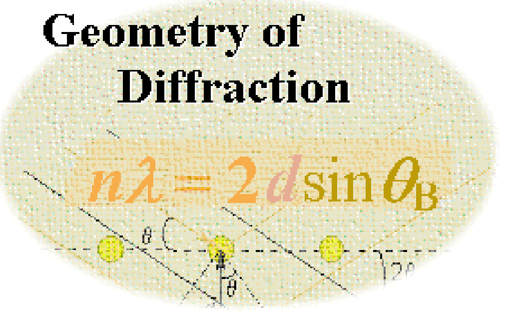

Diffracted
beams
$\lambda\sigma_{hkl}$
δ
γ
γ
X-ray
beam
Ewald
sphere
Film



Transfer of angular coordinates from a back-reflection photograph to a stereographic projection with the aid of the Greninger chart.

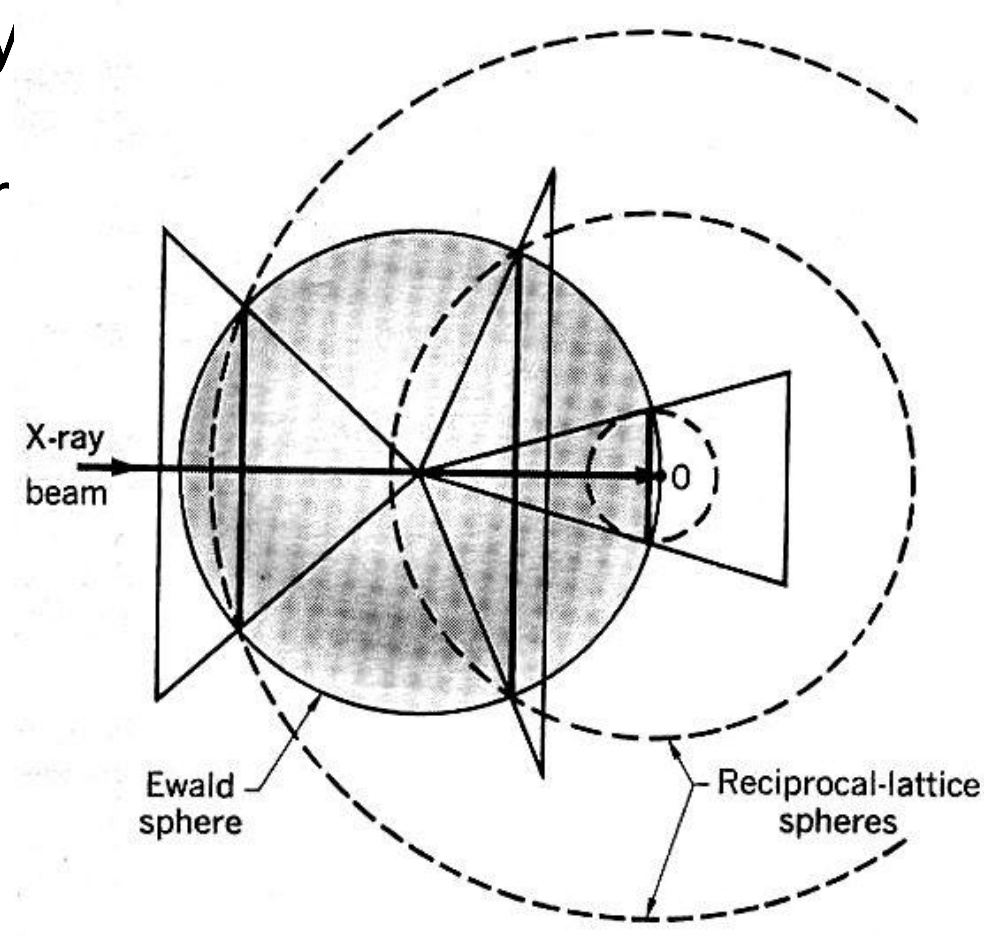
3.6 Powder Method

- The specimen used in the powder method is consisting of large number of tiny crystallites.
- It will be assumed that their orientations are completely random.
- The characteristics of X-ray diffraction effects from a fine-grained crystalline aggregate were first studied by P. Debye and P. Scherrer in Germany in 1916.
- The reciprocal-lattice construction for a powder is self-evidently a superposition of the reciprocal lattice of the individual crystallites comprising it.

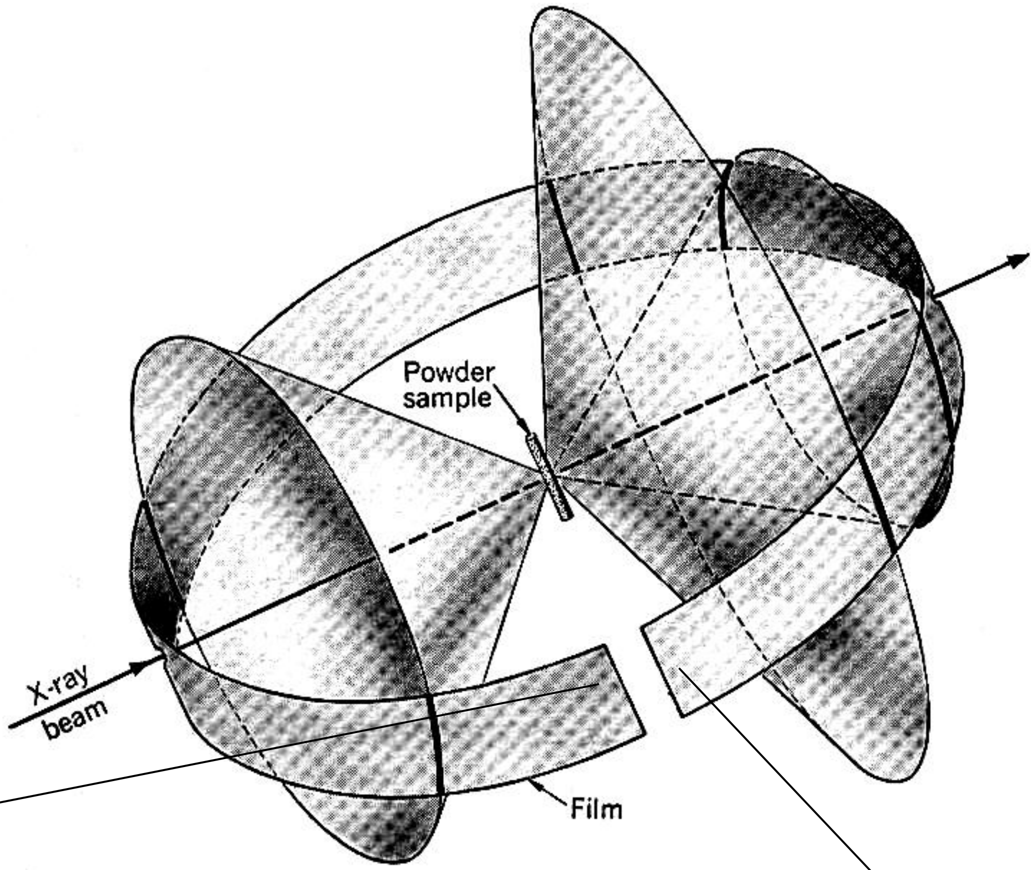


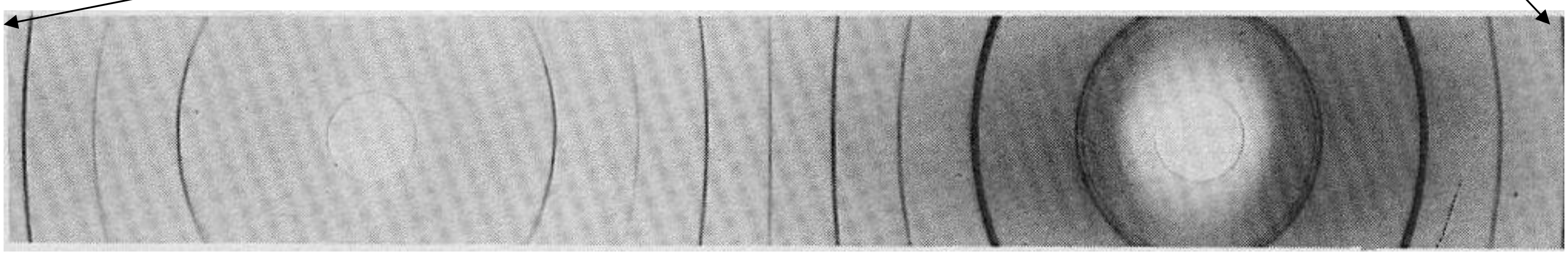
- Consider the reciprocal-lattice construction of a polycrystalline specimen.
- Each crystallite has associated with it a reciprocal lattice whose origin lies on the Ewald sphere.
- Because there are many such crystallites present and their orientation are completely random.
- It is no longer possible to ditinguish the individual lattice.
- Instead, they coalesce into concentric spheres whose radii are the various possible reciprocal-lattice vector.

- As a result of symmetry or chance, many of the reciprocal-lattice vector have the same length.
- So such reciprocal-lattice points come to lie on the same sphere in the reciprocal-lattice construction of a powder..



- Therefore, if we put a cylinder film at the Ewald sphere which constructed the reciprocal-lattice, a pattern from the reflected cone is observed.

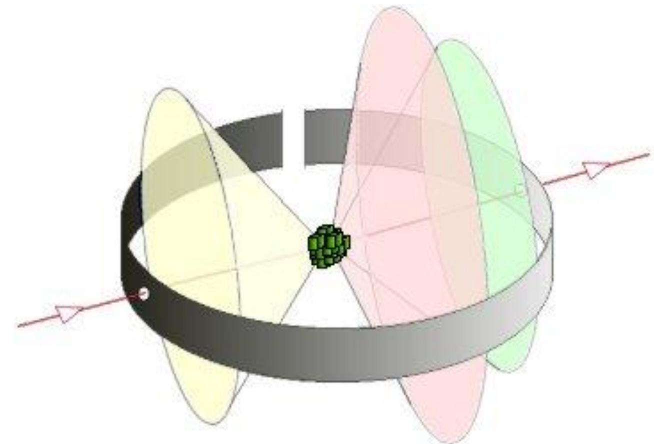


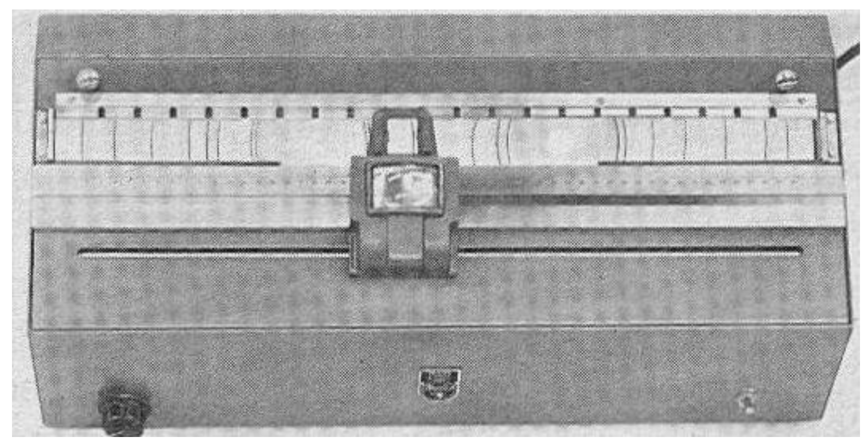


Powder photograph of tungsten

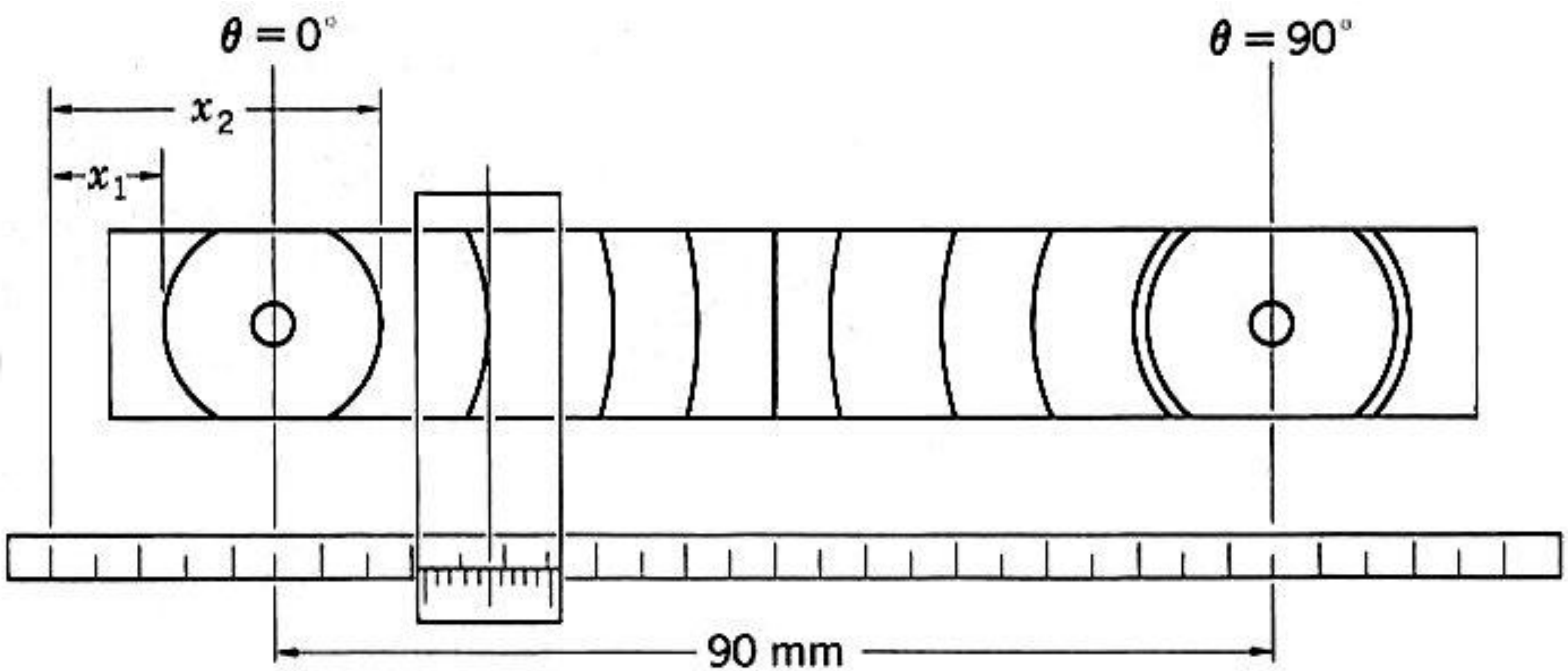
Measurement of d value

- In this method, the film is employed to intercept the diffraction cones.
- The film is split halfway between the point where the direct beam enters and leaves the film.
- The measurement of the distance between a pair of arcs is done using a special film-measuring devices





- The reading are made in succession on two corresponding arcs (left and right) by placing the cross hair at the center of each arc and recording then value to 0.1mm.
- A table of data is made to record the value and obtained the 2 theta value.



Line no.	x_2	x_1	Check x_2+x_1	Arc length $S=x_2-x_1$	Correction $\frac{P}{100} \times S$

Corrected arc length S'	$\theta = \frac{S'}{4}$	Sin θ	$d = \frac{\lambda}{2\sin\theta}$	$Q = \frac{1}{d^2}$	hkl

- The relationship of the diffraction angle θ to the measured arc length S is given by

$$4\theta = \frac{S}{R}$$

$$\theta = \left(\frac{1}{4R} \right) S \quad \text{rad}$$

$$= \left(\frac{180}{\pi} \cdot \frac{1}{4R} \right) S \quad \text{deg}$$