The powder method
in x-ray crystallography

Leonid V. Azároff

Professor of Metallurgical Engineering
Illinois Institute of Technology

Martin J. Buerger

Professor of Mineralogy and Crystallography
Massachusetts Institute of Technology

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Elementary x-ray diffraction theory

The general nature of crystals

In the crystalline state the atoms are arranged in patterns which are characterized by periodic repetition in three dimensions. A good two-dimensional analogue of a crystal is a wallpaper pattern. In a wallpaper pattern the motif is an arbitrary design, whereas in a crystal the motif is not arbitrary, but rather a comparatively small collection of atoms representing the chemical composition of the crystal.

Figure 1 shows a two-dimensional analogue of a crystal pattern. The motif consists of several kinds of circles, which can be taken to represent as many kinds of atoms in an actual crystal. From a geometrical viewpoint, the pattern can be thought of as the repetition of the motif at intervals t_1 in one direction and t_2 in another direction. The geometrical motion of repetition is a pure translation; accordingly t_1 and t_2 are called *conjugate translations*. If the motif is a single geometrical point, its periodic repetition by the translations t_1 and t_2 generates an infinite collection of points, a small region of which is shown in Fig. 2. The set of such geometrical points is called a *lattice*. If a motif more complicated than a geometrical point is repeated periodically by translations t_1 and t_2, as in Fig. 1, the entire collection is a two-dimensional pattern (*not* a lattice).

These notions also apply to repetition in three directions. Repetition of a geometrical point generates a *space lattice* (or simply a *lattice*) and repetition of a more complex motif generates a space pattern. If the motif is a group of atoms, as in a crystal, the material body generated by the repetition defined by the three conjugate translations is called a *crystal structure*.

The region determined by the three conjugate translations t_1, t_2, and t_3 is a parallelepiped known as a *primitive cell*. The shape of this cell

does not always have a symmetry as high as that of the pattern of the crystal. When it does not, a larger and more convenient unit parallelepiped is chosen to represent the pattern for most purposes. This unit

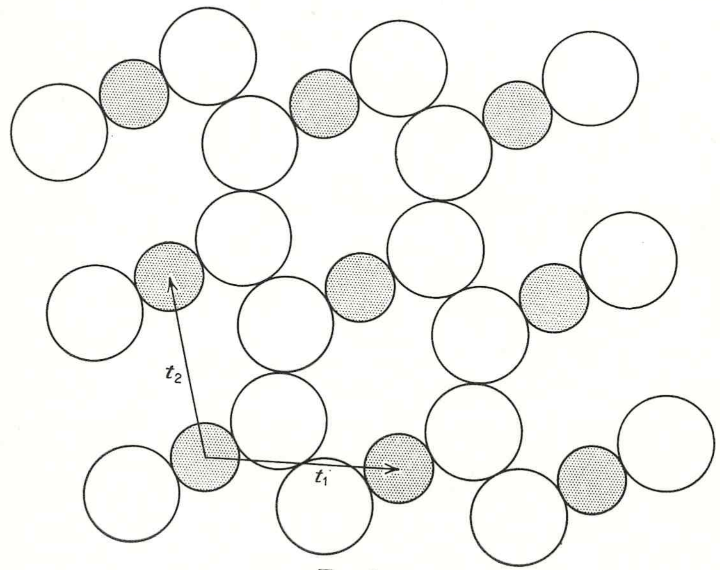

FIG. 1

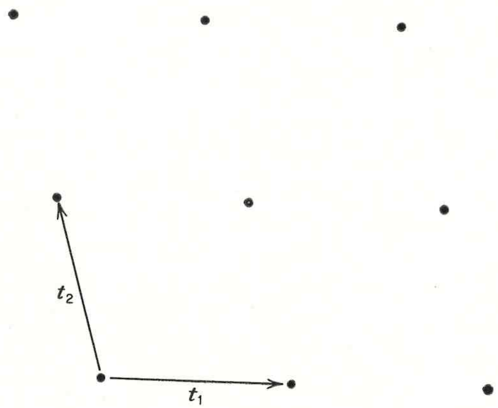

FIG. 2

parallelepiped, which may have a volume of one, two, three, or four primitive cells, is known as the *unit cell*.

For the purposes of discussing x-ray diffraction by crystals it is convenient to consider first a simple motif consisting of one atom. The periodic repetition of this motif by the three translations produces a pattern consisting of an identical atom at each point of a simple pattern be termed a *lattice array* of atoms. Then, for a more complicated crystal, the entire crystal can be regarded as several lattice arrays of atoms each somewhat displaced from one another (Fig. 3). In

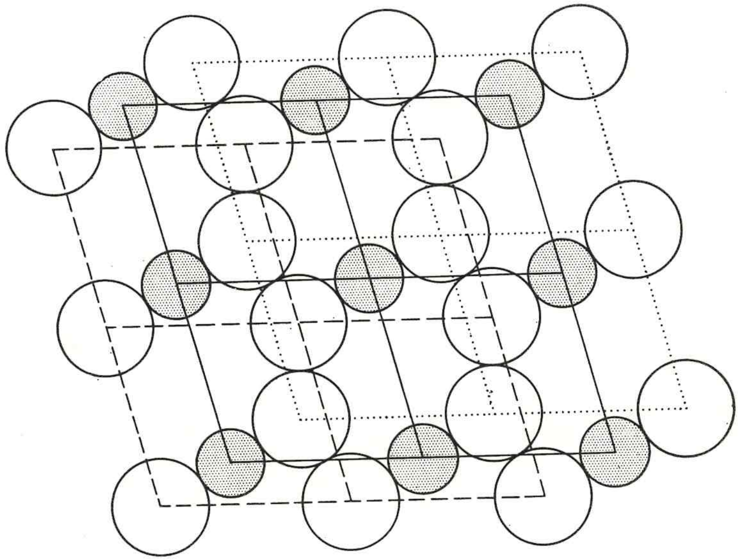

Fig. 3

this way any crystal structure can be decomposed into several parallel lattice arrays.

The diffraction of x-rays by a lattice array of atoms

An atom is an electrical system capable of being disturbed by an external electric field. The fluctuation of the electric field of an impinging electromagnetic wave displaces the electrons of an atom. For this reason they undergo vibration having the same frequency as the electromagnetic wave which, in the present connection, is x-radiation. These accelerating charged particles are themselves the origin of radiation of this frequency. The electrons of an atom, therefore, absorb and reemit x-rays, and in accordance the atoms are said to *scatter* x-radiation.

When a wave front of x-rays impinges on a set of atoms, each atom scatters the x-rays. If the atoms are centered on points in a plane, for example, a plane in a lattice array corresponding to a crystallographic plane (*hkl*), two directions of scattering have special properties, as shown in Fig. 4. In both these directions the distance from the original wave front, to an atom, and on to a new wave front is the same for all atom

locations in the plane. These directions correspond, respectively, to a continuation of the beam in the original direction, and to a reflection of the beam by the plane on which the atoms lie. The scattering by atoms in a plane is, therefore, tantamount to reflection by the plane.

A lattice array of atoms can be regarded as an infinite stack of parallel, equally spaced planes (Fig. 5). Any rational plane (*hkl*) of the lattice

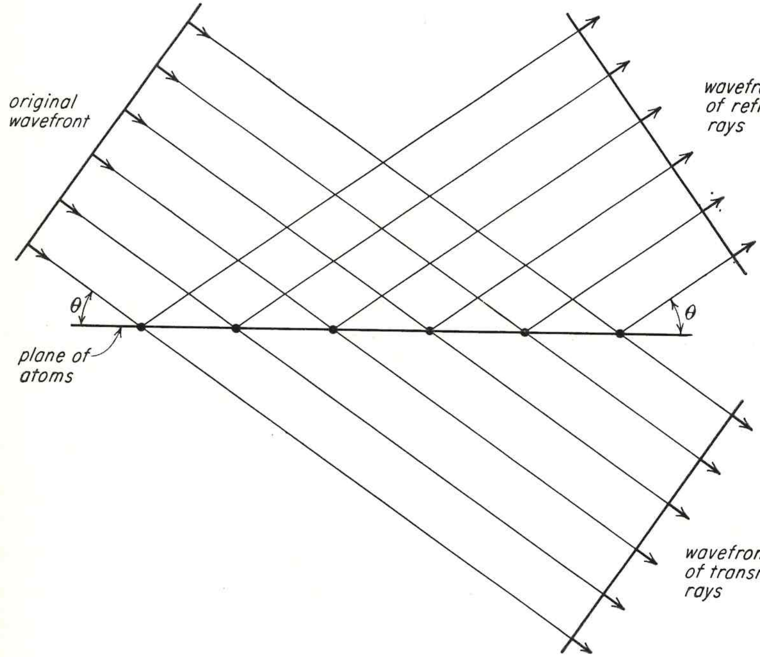

Fig. 4

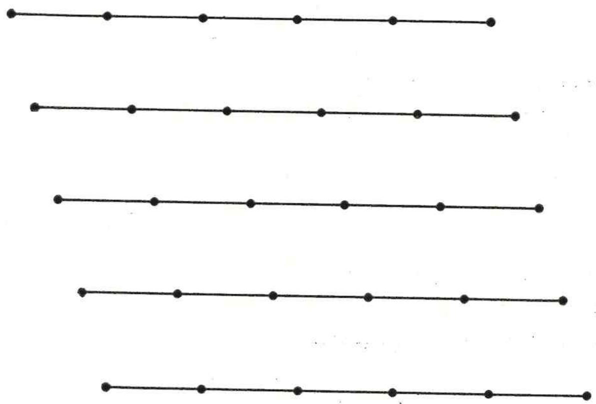

Fig. 5

array can be chosen as the plane in question, and then the whole array can be thought of as a stack of planes parallel to this one. How does such a stack reflect x-rays? The condition for scattering-in-phase by one plane of the stack was established above. If two (or more) are considered (Fig. 6), it is evident that the path length from incoming wave

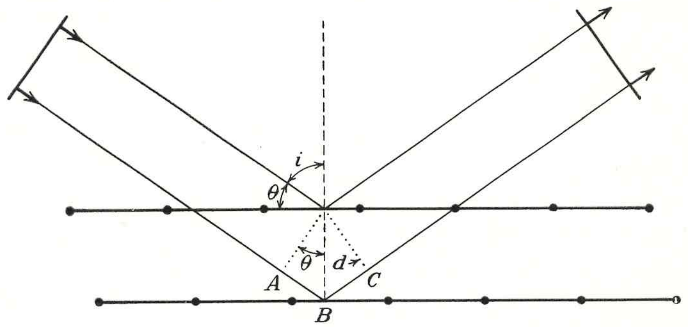

FIG. 6

front, to plane, to scattered wave front is longer in the case of the lower plane. The greater path difference is

$$\Delta = ABC = 2AB. \tag{1}$$

Since

$$AB = d_{hkl} \sin \theta, \tag{2}$$

the total path difference is

$$\Delta = 2AB = 2d_{hkl} \sin \theta. \tag{3}$$

If both these planes are to scatter in phase, the path difference Δ must be an integral number of wavelengths, that is, $n\lambda$ where n is an integer. Therefore, the condition for scattering-in-phase is

$$n\lambda = \Delta = 2d_{hkl} \sin \theta. \tag{4}$$

This condition for scattering-in-phase is known as *Bragg's law*. Note that it is defined in terms of an interplanar spacing d_{hkl} of the lattice, and a *glancing angle* θ. This "glancing angle" is the complement of the angle of incidence i (Fig. 6) of a reflection in geometrical optics.

When a crystal diffracts x-rays in accordance with Bragg's law, the scattered x-rays are said to constitute a *reflection*. Since the reflection is attributed to the plane (hkl) the reflection itself is designated hkl, written without parentheses.

If (4) is solved for θ there results

$$\theta = \sin^{-1}\left(\frac{\lambda}{2}\frac{n}{d_{hkl}}\right). \tag{5}$$

The term $\lambda/2$ is constant for the experiment. The term n can only have the discrete values of integers, and the term d_{hkl} can only have the discrete values of the spacings of the planes (hkl). Therefore, θ can only have certain discrete values. The possible discrete values are further limited by the fact that the term in parentheses cannot exceed unity.

In most cases it is convenient to avoid the explicit use of n by incorporating it in the indices of the plane. This can be done as follows: Equation (5) can be rearranged to

$$\theta = \sin^{-1}\left(\frac{\lambda}{2\dfrac{d_{hkl}}{n}}\right). \tag{6}$$

The term d_{hkl}/n has a specific meaning. It signifies a spacing $1/n$th that of the spacing of the plane (hkl). This is the spacing of the plane $(nh\ nk\ nl)$. That is,

$$d_{nh\ nk\ nl} = \frac{d_{hkl}}{n}. \tag{7}$$

This can be substituted in the denominator of (6) to give

$$\theta = \sin^{-1}\left(\frac{\lambda}{2d_{nh\ nk\ nl}}\right). \tag{8}$$

One notes that the indices in (8) contain the common factor n. In classical crystallography such indices were not permitted. In x-ray crystallography, however, it is convenient to refer a reflection to a plane whether it has a common factor or not. If it does contain a common factor, this factor is the n of Bragg's law, (4) and (5).

The diffraction by the whole crystal structure

Any crystal structure can be regarded as several mutually displaced lattice arrays (Fig. 3). Each lattice array can diffract x-rays as if reflecting them from a plane (hkl), provided the glancing angle θ is adjusted so that it is one of the discrete solutions of (5). Now consider how the diffraction from several lattice arrays of the crystal structure interacts for a particular reflection (Fig. 7). Let the crystal structure be composed of only two lattice arrays, labeled 1 and 2 in Fig. 7. When (5) is satisfied, all atoms of lattice array 1 scatter in phase with each other, and all atoms of lattice array 2 scatter in phase with each other. But the path from the incoming wave front to array 2 is longer than to array 1. This means that array 2 contributes to the resultant wave scattered by the whole crystal a wave whose phase is behind that scattered by array 1. The resultant scattered wave is not destroyed unless this phase difference is π, and only then if the two amplitudes are equal.

From this several conclusions can be drawn: 1. The full crystal structure scatters at the same glancing angles θ as any of its component lattice arrays. 2. The displacements between the component lattice arrays cause phase differences in their contributions to the net scattered wave.

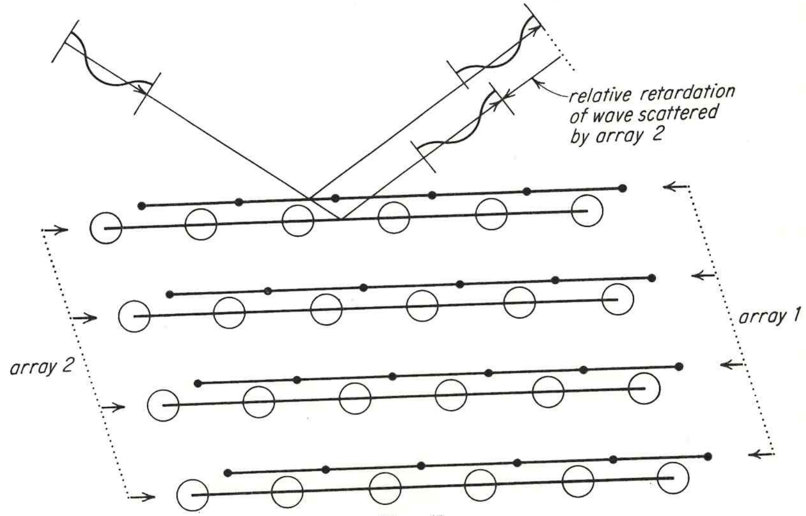

Fig. 7

3. These phase differences tend to reduce their contributions to the intensity from a value which would be obtained if all atoms of the structure scattered in phase.

Positions and intensities of x-ray reflections

The conclusions of the last section can be reformulated in a way which brings out some important characteristics of x-ray reflection. It has been shown that the glancing angles θ at which a crystal may reflect x-rays depend fundamentally on the interplanar spacings d_{hkl} of the lattice. These d's in turn depend only on the dimensions of the lattice. (This relation will be developed in detail in Chapter 6.) They are in no way concerned with the arrangement of atoms in the repeated motif. In the next chapter it will be shown that the position where an x-ray reflection is recorded (or detected) is dependent on θ only. This means that the *set of positions of all the x-ray reflections from a crystal depends only on the dimensional characteristics of its lattice* and does not depend on the arrangement of its atoms. As a consequence, two crystals having the same type and dimensions of unit cell give the same x-ray diagram with regard to location of reflections, even if they have completely unrelated chemical compositions. An example of such a pair is tin tetraiodide,

SnI_4, and rubidium aluminum alum, $RbAl(SO_4)_2 \cdot 12H_2O$. Both these compounds have primitive isometric unit cells of edge 12.2 Å.

On the other hand, the relative intensities of the various reflections *hkl* of a crystal depend upon the way the contributions from its several lattice arrays interfere with each other for the several reflections *hkl*. Therefore, the set of intensities of the reflections *hkl* depends entirely on the arrangement of atoms in the motif.

These conclusions can be brought together as follows: *The locations of the reflections of a crystal depend on the shape and type of its unit cell; the relative intensities of these reflections depend on the arrangement of the atoms within this cell.* The combination of the unit cell and the arrangement of atoms in it comprises the crystal structure itself. Therefore, the locations and relative intensities of the reflections of a crystal are characteristics of the crystal structure. Whether or not the powder diagram of an unknown crystal can be interpreted, at least this diagram is characteristic of the crystal and can be used like a fingerprint to distinguish it from other crystals, and hence to identify it. This is the philosophic basis for using the powder diagram of x-ray reflections in crystal identification.

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Principles of powder photography

Collimating system

In all common x-ray diffraction methods, it is necessary to limit the x-radiation to a small pencil. This is accomplished with a "collimator," which may take the form of a *pinhole system*, or a *slit system*. The principle is illustrated in Fig. 1. The radiation emanating from the focal spot on the target of the x-ray tube is limited by a pair of holes, 1 and 2,

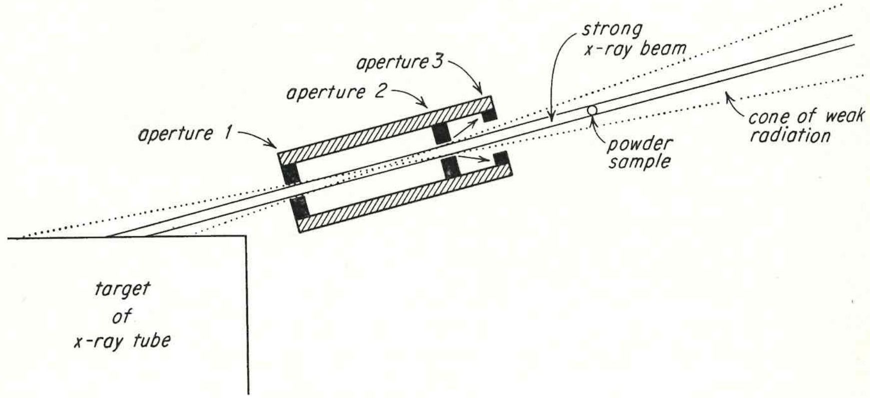


FIG. 1

of the collimator. The holes are small apertures, usually in lead. Since lead has its own x-ray powder diagram, diffraction by the aperture 2 would confuse the diffraction to be studied unless it is removed. Its removal is accomplished by adding another diaphragm, 3, to the sequence. This hole is designed to be large enough to pass the desired x-ray beam defined by apertures 1 and 2, and without being touched by it, but small enough so that the diaphragm intercepts the smallest cone of diffracted radiation arising from aperture 2.

Production of the powder diagram

The principles involved in the production of a powder diagram can be appreciated by considering the simplified experimental arrangement shown in Fig. 2. An x-ray beam is defined by the pinhole system, just described. A photographic film is then placed normal to the x-ray beam. The powder sample is introduced into the path of the x-ray beam. As the beam travels through the powder sample, it meets thousands of powder grains, each a tiny crystal in a different orientation. Among these

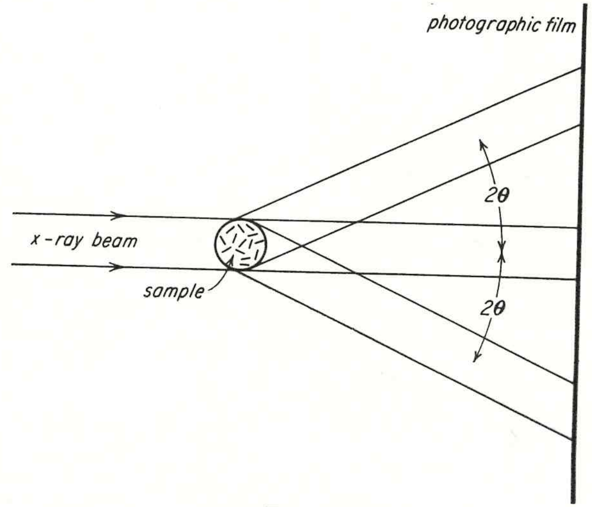


FIG. 2

grains many are so oriented that a particular set of planes (hkl) makes the appropriate glancing angle θ (for that plane) with the x-ray beam. Such grains are in position to reflect x-rays. The reflection occurs in a direction making an angle 2θ with the direct x-ray beam. The locus of directions making an angle 2θ with a given direction is a cone of half-opening angle 2θ (Fig. 2). For each solution of the Bragg equation

$$\theta = \sin^{-1}\left(\frac{\lambda}{2}\frac{n}{d_{hkl}}\right) \qquad (1)$$

there exists such a cone.

Considering a particular cone (Fig. 3), the separate reflections from all crystals which satisfy (1) for a particular n/d_{hkl} lie along the directrices of a certain cone of half angle 2θ. If the experimental arrangements are appropriate, these diffracted rays are sufficiently numerous so that the cone is densely outlined by rays. These rays cut the photographic plate in a circle which is continuous if the rays along the cone are sufficiently dense. From a measurement of the radius of the circle, and the known crystal-to-film distance, it is an easy matter to compute the cone angle, and eventually determine θ.

The use of a flat film severely limits the maximum angle 2θ which can be recorded. A much greater range of 2θ can be recorded if the film is wrapped on a cylindrical form coaxial with the specimen, with the axis of the cylinder at right angles to the x-ray beam, as shown in Fig. 4*A*. Only a narrow strip of film is required. With this arrangement, the cone

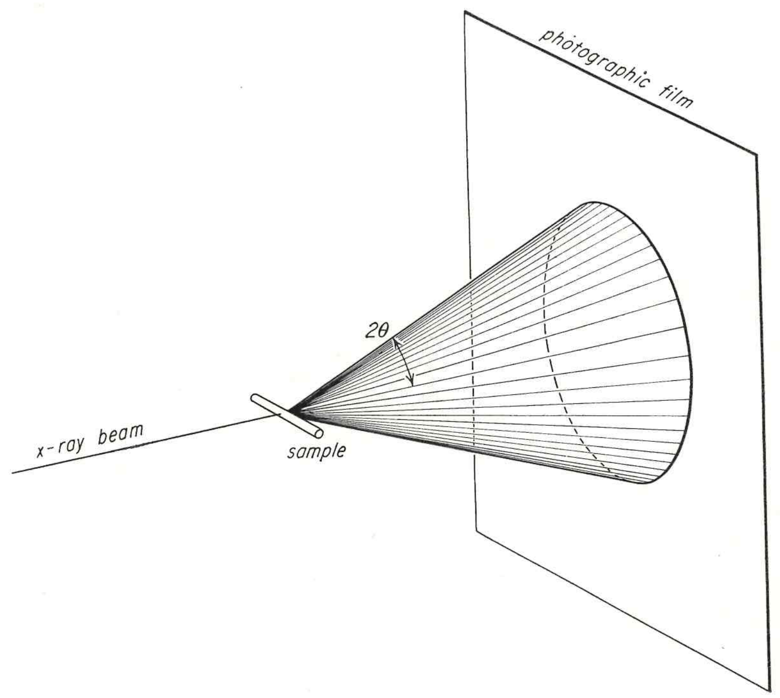


Fig. 3

intersects the cylinder in a curve; that part of the curve which is caught by the narrow strip of photographic film is a nearly circular arc. The distance S between similar arcs (Fig. 4*B*) corresponds to 4θ, and if R is the radius of the film, this distance is

$$S = R \cdot 4\theta, \tag{2}$$

(θ expressed in radians)

$$\therefore\ \theta = \frac{S}{4R}. \tag{3}$$

It is evidently an easy matter to determine θ for each cone by measuring

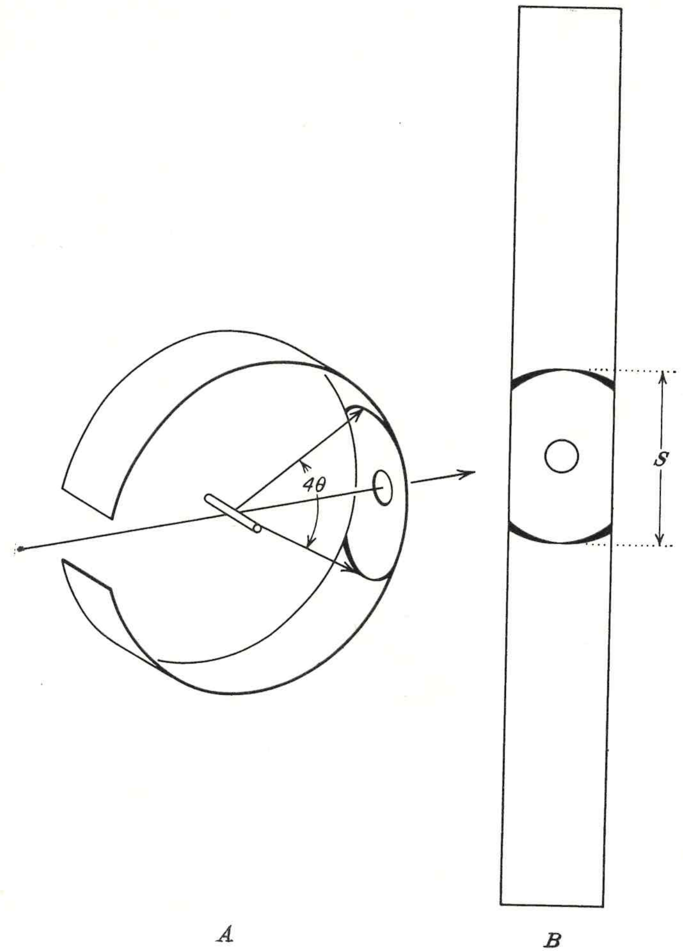
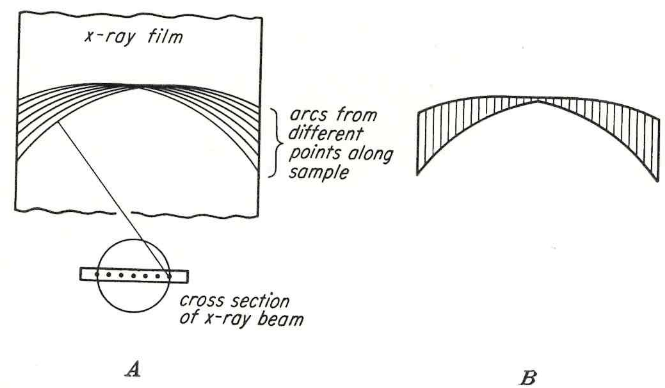


Fig. 4



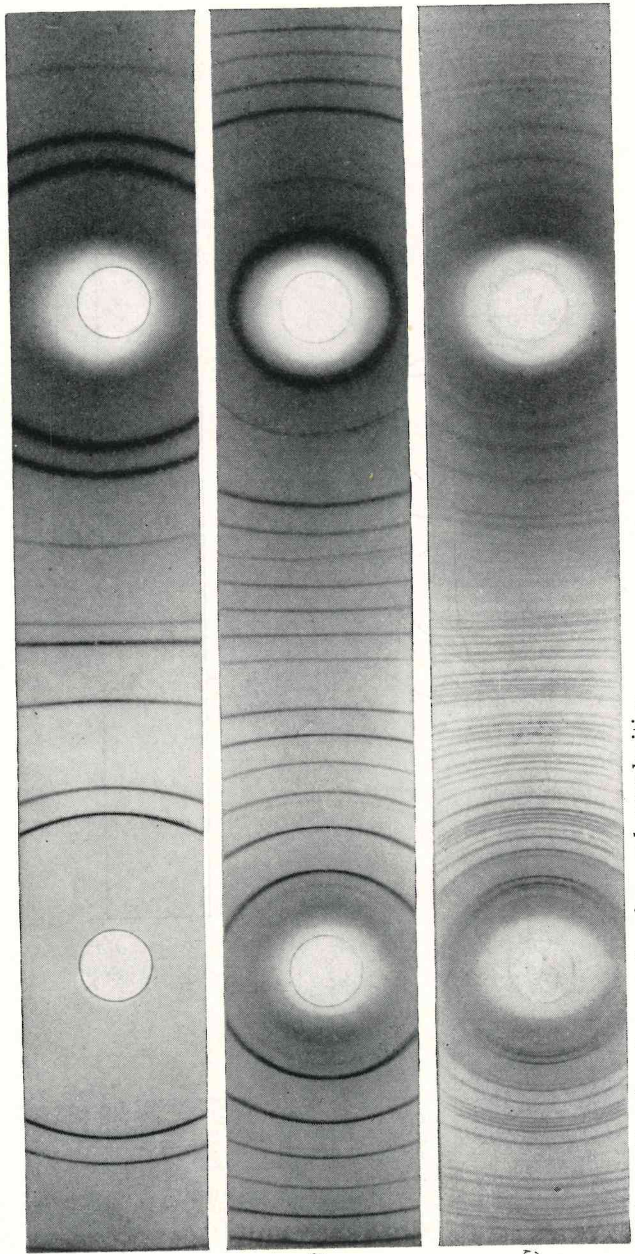


FIG. 6. Powder photographs of several complexities.
A. α-Brass, isometric, a = 2.942 Å.
B. PbTe, isometric, a = 6.439 Å.
C. PbCl, orthorhombic, a = 4.535 Å, b = 7.62 Å, c = 9.05 Å.

It is customary to use a specimen whose shape is that of a tiny cylinder coaxial with the film cylinder (Fig. 4*A*). This tends to give a "shape" to the arc recorded on the film. The reason for this is shown in Fig. 5*A*. Each element of length of the sample produces an arc, and these individual arcs are displaced depending on the location of the element of length producing them. The result is a "shaded arc" (Fig. 5*B*).

Some actual powder photographs are shown in Fig. 6.