(a) are the theoretical results obtained and (b) are the results modified roughly in accordance with practice to allow for the greater flux leakage due to the longer solenoid.

The results show that by lengthening the solenoid the same effective flux may be obtained by both a decreased cost of winding and lower energy losses.

To reduce further the size and the cost of the relay, the dimension P should be kept as small as possible; in general the dimensions will give the best efficiency for the winding when the iron core is worked at the maximum permeability. The size of the core, however, should not be so small in relation to the size of the solenoid as to exceed the temperature rating, or in relation to the size of the air gap as to introduce considerable reluctance and flux leakage at the pole faces. For a given solenoid, if it is required to increase the magnetizing force, the ampere turns may be increased either by increase of current or by increase of turns. If the heat rating is not exceeded, the modification may be obtained by increase of current; if the solenoid is originally fully rated as regards temperature, the modification may be obtained by adding turns with the current kept at about its original value.

(To be concluded)

A UNIVERSAL X-RAY SPECTROGRAPH*.

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ABSTRACT. The article describes a compact form of X-ray spectrograph with which the various photographic methods employed in X-ray and crystal analysis can be carried out.

INTRODUCTION

X-RAYS are radiations of the same kind as light, but of much shorter wave-lengths. This identity, although suspected, was not established until the discovery by Friedrich and Knipping at v. Laue's† suggestion that they could be diffracted by crystals. The researches of v. Laue and subsequent investigators‡ on the action of crystals on X-rays not only established the identity of X-rays with light (and hence with heat radiations and with Hertzian waves) and enabled the arrangement of the atoms in crystals to be determined, but also led to the production of X-ray spectra by the use of crystals.

v. Laue's theory of the diffraction of X-rays by crystals can be summarized as follows. A beam of X-rays which passes through a crystal makes each atom there become a centre of secondary radiation. These secondary wavelets have the same periodicities as the incident waves, and the phase differences between the primary and the secondary radiations are the same for all the scattering atoms. The atoms in a crystal being arranged in a periodic space lattice, it follows from elementary principles of interference that some of the secondary vibrations must reinforce each other in certain directions in space (the incident beam being assumed parallel). These intensity maxima in the secondary radiation produce the well-known Laue spots on a photographic plate.

* Manufactured by Messrs Adam Hilger, Ltd.

† Friedrich, Knipping, and Laue, *Ann. d. Phys.* **41** (1913) 971.

‡ Laue, *Jahrb. d. Rad.* **11** (1914) 308; W. L. Bragg, *ibid.* **11** (1914) 346.

The distribution and the densities of the individual spots in a Laue photogram depend obviously both upon the diffracting crystal and upon the qualities of the incident radiations. A certain range of frequencies is required to produce a Laue photograph. In analogy to the term used in the spectroscopy of the visible spectrum, such X-rays are called "white radiations," since they contain a certain continuous range of wave-lengths.

Friedrich and Knipping applied the suggestion of v. Laue by bringing a crystal in the path of a narrow pencil of "white" X-rays. Any particular crystal face could be set at right angles to the axis of the beam, the crystal being mounted on a goniometer. A photographic plate placed at a short distance beyond the crystal received the resulting diffracted beams and recorded them in the form of a number (sometimes over a hundred) of regularly arranged dots. The effect is similar to that produced by the passage of a narrow beam of white light through a three-dimensional grating, the distance apart of whose lines is of the order of a few wave-lengths.

Laue's work resulted in a large number of discoveries. His method is nowadays still successfully applied for determining symmetry properties of crystals. The actual dimensions of a crystal lattice are not obtainable by Laue's method. The measurement of the dimensions of the crystal unit has been made possible by the use of monochromatic X-rays. This discovery was made by W. H. and W. L. Bragg* who established the fundamental "reflection theory" of X-rays.

The Bragg Method of Crystal Analysis

The characteristic feature of the Bragg method of crystal analysis consists in the use of monochromatic radiations. The crystal is placed in the path of a limited X-ray beam of a known wave-length. The atoms in the crystal, under the influence of the incident rays, become again centres of a secondary radiation. It is easily seen that reinforcement of these secondary or scattered waves takes place if the scattering centres are periodically arranged in space. This reinforcement through interference occurs, for a given wave-length, only when the incident beam makes a certain angle with a given set of atomic planes in the crystal. Bragg, in his fundamental theory, showed that the diffraction phenomena of X-rays in crystals can be represented formally as a reflection of the incident rays by the atomic planes in the crystal. The relation which connects the glancing angle θ (the complement of the angle of reflection), the spacing† d, and the wave-length λ was found to be

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

The wave-length is characteristic for a given anticathode; if its numerical value is once determined, any spacing can be calculated from an observation of its glancing angle θ.

The above formula can be generalized in analogy with optical phenomena and is written

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

n is an integer and gives the order of the spectrum‡.

The Bragg method makes it possible to measure the spacings and also, as can easily be seen, the angles between the reflecting planes of a crystalline substance. The knowledge of these two elements is obviously essential for an investigation of crystal structure. Conversely, if the structure of a diffracting substance be known, the wave-length of the radiation can be determined.

* W. H. and W. L. Bragg, *Proc. Roy. Soc.* A **88** (1913) 428.

† The spacing is the measure of the distance between two successive *identical* planes in the crystal.

‡ The meaning of the word spectrum when used in connexion with X-rays is the same as when used in connexion with light. Radiations from a source are so arranged in a spectrum that the position of each component of the radiations is determined by its frequency.

Description of the Various Procedures in Crystal Analysis which are based on the Bragg Method

Out of Bragg's discovery have developed various technical schemes of crystal analysis. In the following the most important photographic methods will be described. One of these is due to de Broglie* and is generally known as the method of the oscillating or revolving crystal.

The X-rays after passing through a slit system (corresponding to the collimator in an ordinary spectrometer) strike the surface of a crystal plate which is kept turning or oscillating round an axis which is parallel to the slit. The monochromatic rays which are reflected strike a photographic plate and record a spectrum. This method is used when accurate measurements of spacings or wave-lengths are required. The accuracy of the measurements depends naturally on the quality of the crystal surface. This method will also give good results if a crystalline powder is used instead of a large single crystal. The powder has to be spread out in a flat layer, the surface of which is now set so as to pass through the axis of rotation. This last mentioned method is a modification of the "powder method," originally given by Debye and Scherrer and Hull†. In the powder method the substance is mounted in powder form at the centre of a cylindrical photographic film. A pencil of monochromatic X-rays falling upon a thin rod of such powdered crystal is diffracted and photographed as a number of curved lines. Lines corresponding to all possible reflecting planes are obtained at once on the film. Such photographs are often very difficult to interpret, but they are very useful for a preliminary examination of substances which are not easily obtainable except in the form of microscopically small crystals. If a complete determination of a crystal structure is attempted, it is advisable to recur to a method which is essentially identical with the one invented by de Broglie. This method, which is the most efficient of the photographic methods, has lately been developed by several X-ray workers (*e.g.* Schiebold and Polanyi‡). Instead of using a large crystal and reflecting the X-rays from one geometrically defined surface, a small crystal which is entirely bathed in a narrow X-ray beam is used. During the exposure the crystal is rotated. The various reflecting planes come in succession into their reflecting positions and the diffracted rays produce a pattern on a photographic plate which is similar in appearance to a Laue photograph. The difference, however, lies in the fact that the pattern is entirely due to the diffraction of monochromatic rays. The calculation of the elements of the unit cell in a crystal from revolving-crystal diagrams is considerably simplified if the crystal is, each time, set in such a way that one of the main zone axes coincides with the axis of rotation. For this purpose the crystal has to be mounted on a goniometer which is attached to the spectrometer table.

A complete investigation of the structure of a crystal involves the determination of its space group. Once the dimensions of the unit cell of a crystal are found by X-ray analysis, all the possible spacings can then be calculated. In the majority of cases it is found that certain reflections which, according to the calculations, ought to be observed, are missing on the photograms. A closer analysis shows that this phenomenon is intimately connected with the distribution of the scattering elements (molecules) in the unit cell. This distribution, or in other terms the space group, can be derived from the distribution of the missing reflections. These missing reflections can easily be found on a revolving-crystal diagram.

* de Broglie, *Les Rayons-X*, Blanchard (Paris).

† Debye and Scherrer, *Phys. Z.* **17** (1916) 277; **18** (1917) 291: Hull, *Phys. Rev.* **10** (1917) 661.

‡ Schiebold, *Z. f. Phys.* **9** (1922) 180: Polanyi, *ibid.* **7** (1921) 149.

Varieties of X-Rays

It has long been known that an X-ray bulb emits rays of different quality as measured by the amount absorbed in passing through a sheet of metal. The more penetrating rays have been called "hard" and the less penetrating "soft"; although such terms are loose and indefinite, they are convenient as relative indications of wave-length, the harder rays being those of shorter wave-length. Barkla* found that such a mixed beam of X-rays falling upon a metal plate caused it to emit, in general, two beams of homogeneous rays, the one being very much harder or more penetrating than the other, and that these beams were characteristic of the material of the metal plate. It is essential for the production of characteristic rays that the exciting rays should be harder than the emitted rays. Soon afterwards, Kaye showed that the characteristic rays were emitted when the material in question formed the anticathode of a discharge tube. Barkla called these rays the K and L-radiations.

Adopting Bragg's suggestion that a crystal should be used for reflection, Moseley† was able to show that the K-radiation consisted of two different wave-lengths forming sharp spectrum lines, one line—the softer (K_α)—being more intense in each case, and that the wave-lengths are distinctive of the emitting substance. Later Siegbahn showed that the K_α line was a close doublet, and that in addition to the K_β line there was also a fainter, K_γ, of still shorter wave-length.

Moseley recognized four lines in the L spectrum of an element, but it has been subsequently shown that there are a larger number of lines. Largely as the result of the work of Siegbahn‡ and his collaborators, fairly comprehensive tables are available, giving carefully measured values of the wave-lengths of radiations of both series, and in a number of cases also of a much softer series known as the M series. A very considerable number of these rays are absorbed by passing a short distance through air, so that it is necessary to employ a vacuum spectrograph for their measurement. For crystal analysis, however, it is best to employ the $K_{\alpha_1\alpha_2}$ lines of some element such as copper, whose radiations will pass through air but have wave-lengths as long as possible.

Besides the characteristic rays there is always a continuous or "white" spectrum present in the radiation emitted by an X-ray bulb. The wave-length of the most penetrating component of the white radiation depends on the peak voltage, and is given by the well-known formula

$$\lambda = \frac{12.3}{V},$$

where λ = wave-length of end radiation in Å.U. and V = peak voltage in kilovolts.

Applications of X-ray Spectrography

It will be evident from the foregoing that the position of lines or spots in an X-ray spectrum depends upon the elements present in the anticathode of the tube and upon the crystal diffracting the ray. Thus two distinct classes of application are indicated. A known crystal can be used for the determination of wave-lengths, or, working with a known wave-length, the crystal structure can be investigated.

* Barkla and Sadler, *Phil. Mag.* **16** (1908) 550.

† Moseley, *Phil. Mag.* **26** (1913) 1024.

‡ Siegbahn, *Jahrb. d. Rad.* **13** (1916) 296; **18** (1921) 240: Sommerfeld, *Atombau und Spektrallinien*, chap. 3.

Quantitative Estimations

In cases where it is desired to make quantitative estimations of the presence of an element by X-ray methods, the use of the Moll registering microphotometer as used by Coster and Hevesy in their work on hafnium is recommended. Briefly, the method is to mix the substance in question with a known proportion of a neighbouring element in the periodic table and to obtain the spectrum of the mixture when used as an anticathode. If the resulting spectrum be now measured with a microphotometer, the intensity of the lines due to the element investigated can be compared with that of the lines due to the known element admixed with it. Precise measurements of this kind are made graphically by the Moll instrument.

Description of Instrument

As arranged for investigations on large crystals and powder layers, the instrument is shown in Fig. 1. It consists of a bar *A* of triangular section upon which slide two carriers *B* and *C* for the plate-holder *D* and slit *E* respectively. This bar passes through the axis of rotation of a small divided circle *F* which carries the crystal mount *G*. An oscillating

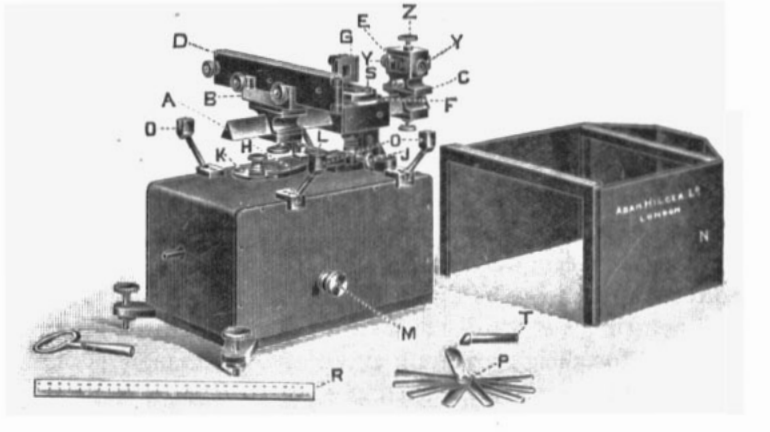

Fig. 1. Instrument arranged for work with single crystal by the Bragg Method.

movement through a given angular range is imparted to the circle *F* by means of a lever *H* which can be clamped to the axis of the circle by the screw *J*. The free end of the lever *H* is kept in contact with the rim of a cam *K* by means of a spring *L*, the cam being mounted on the shaft of a spring motor enclosed in the main body of the instrument, which is provided with levelling screws. The knob *M* operates a lever for starting and stopping the motor. During an exposure, the lead screen *N*, for preventing fogging of the plate by stray X-radiation, is put in position on the supports *O*.

The crystal mount *G* consists of a vertical plate with lead screen, to which the crystal can be attached with soft adhesive wax; it is provided with a tilting adjustment about a horizontal axis. The mount can be traversed in a slide across the rotating table *F* so as to bring the face of the crystal up to the axis of rotation. The edge of the table is divided in degrees to facilitate the setting relative to the lever in order to register lines upon each side of the normal to the photographic plate.

The slit consists of two brass blocks, 26 mm. long, which can be clamped at a known distance apart, one of a number of "feeler" gauges *P* being inserted between the jaws before clamping.

The plate-holder *D*, which is attached to its carrier by two milled-headed screws, is designed to take plates $4\frac{3}{4} \times \frac{3}{4}$ inches (12 × 1·9 cm.) which can be cut from standard

sized plates (half-plate size). It is provided with a black paper screen, so that the instrument may be used in daylight without risk of fogging the plate, and no special sheath for the plate is necessary.

The distance between the centre of rotation of the crystal table and the surface of the photographic plate can be measured with the aid of a steel rule *R*, divided in millimetres, and a gauge which takes the place of the plate-holder, the face of the gauge occupying the same position as the sensitized surface of the photographic plate. The centre of rotation is determined by a fiducial mark upon a pin *T* which can be inserted in the table when the crystal mount is removed. This is quickly done by unscrewing the retaining screw *S* of the spring stop and sliding the mount out of its groove.

Three interchangeable cams give angles of oscillation of 5°, 10°, and 15° respectively.

By removing the crystal mount *G*, moving up the carriers *B* and *C* close to the circle *F*, and making use of a spring clip attached to *C*, the instrument is at once available for taking photographs by Hull's transmission method.

A simple interchange of parts, which can be effected in about one minute, transforms the instrument into a Debye spectrograph as shown in Fig. 2. The slit jaws, crystal mount,

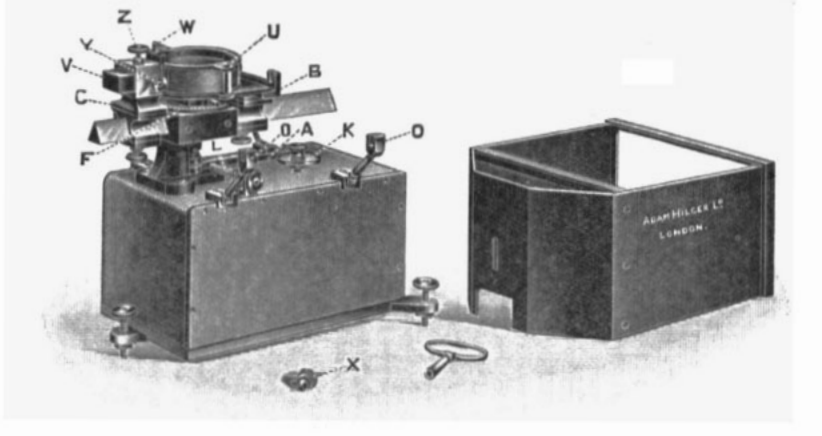

Fig. 2. Instrument arranged for analysis of powders by the Debye Method.

and plate-holder are removed and the carriers *B* and *C* moved up to support a circular camera *U*, 6 cm. in diameter, which carries a photographic film. The camera is so disposed that the powder holder can be inserted in the centre of the table *F*, advantage being taken of the oscillating motion for this method of working also. In place of the slit is mounted a brass block pierced with an aperture 1 mm. in diameter. The circular end of this block fits into an aperture of the camera and points directly to the powder holder in the centre. To allow of insertion of this block a circular hole is cut in the film by means of the film cutter *X*.

The motor is such as to give about 60 oscillations per hour to the crystal and to run nearly five hours without rewinding.

If the instrument is used for the Laue method or the revolving-crystal method, the crystal mount *G* (Fig. 1) is replaced by a two-circled goniometer *A* (Fig. 3). The slit system *B* with its carrier *C* (Fig. 1) is removed and replaced by an arrangement which is shown in Fig. 3. The X-rays pass through a narrow cylindrical channel in a brass rod *B*, the axis of which points towards the centre of the goniometer circles. A lead shield *C* prevents the stray radiation from striking the photographic plate. The plate-holder *D* (holding a quarter-plate) is attached to the same carrier as shown in Fig. 1. A circular

camera is very often useful if revolving-crystal photographs are wanted. A photographic film wrapped in black paper replaces the plate in this case. The film is kept in its position by means of spring clips.

Revolving-Crystal Method

The revolving-crystal method consists in mounting the crystal with a main zone axis parallel to the axis of rotation and in revolving it during the exposure. The revolving cam *K* (Fig. 1) is replaced by a bevel wheel *E* (Fig. 3). An arm *F* which turns round a vertical axis is swung into position as shown in Fig. 3 and clamped by a screw *G*. This arm carries the shaft, which, by means of a worm gear, transmits the rotary motion to the spectrometer table.

The crystal is attached to the end of a pin *H* with soft adhesive wax. The actual setting is done optically (distant light signal and telescope) if the crystal possesses sufficiently good reflecting surfaces. If not, the setting has to be done by using an X-ray photograph (crystal set at random).

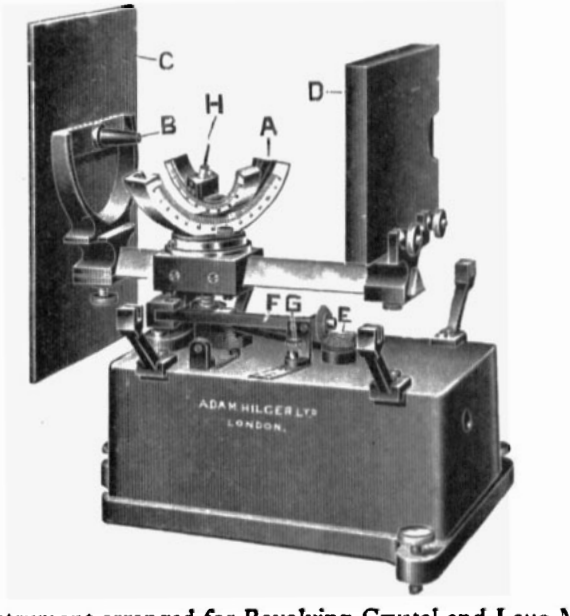

Fig. 3. Instrument arranged for Revolving-Crystal and Laue Methods.

Laue Method

In the Laue method the crystal is in a fixed position relative to the incident beam of X-rays. It is usually set in such a way that one of its planes is at right angles to the beam. The setting of the crystal can be done by successive adjustments controlled by X-ray photographs. If the crystal has optically reflecting surfaces, the setting is preferably done by an optical method, as follows. A small metal tube, which has a mirror attached to one of its ends (surface of the mirror perpendicular to the axis of the tube), is pushed over the "collimator" tube *B* (Fig. 3). A small light source (pea lamp) is placed at a distance of a few yards from the instrument and a telescope or a sight is placed so as to receive the reflected light from the source. The crystal is then shifted by moving the goniometer circles until the particular surface reflects the light into the telescope. The surface of the crystal plane and the mirror surface are then parallel. The mirror surface being perpendicular to the incident beam, the same holds for the crystal surface. The small error in the setting which is due to the crystal being at a certain distance from the mirror can be neglected.

Plates I and II, Figs. 4–7 illustrate the various types of photographs obtainable with the instrument, using the different methods described.

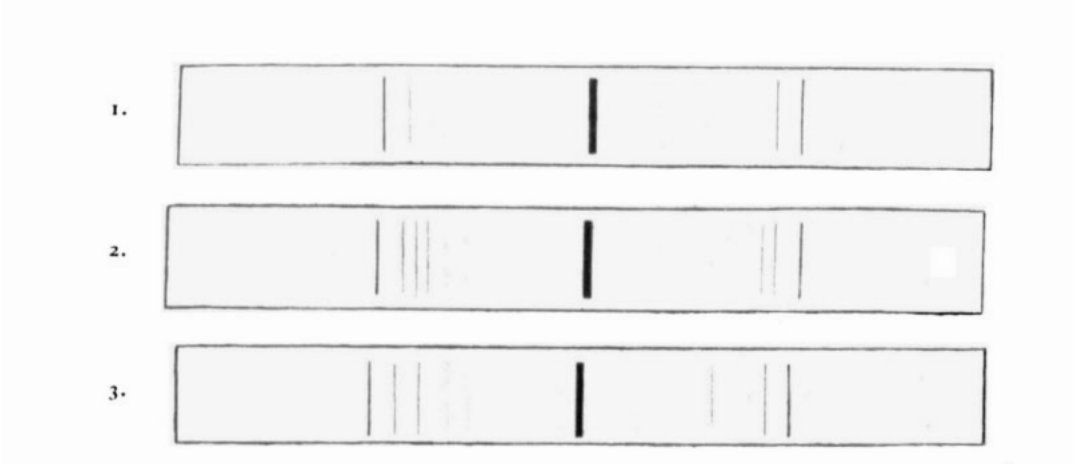

Fig. 4. Spectra taken with the Bragg Arrangement, using Shearer Type Tube, slit width 0·02 mm., and Plate distant about 6 cm. from Rocksalt Crystal.

1. K_α and K_β of copper, exposure 15 minutes.
2. L series of platinum, exposure 30 minutes
3. K_α and K_β of copper, and L_α, L_β of mercury, exposure 30 minutes.

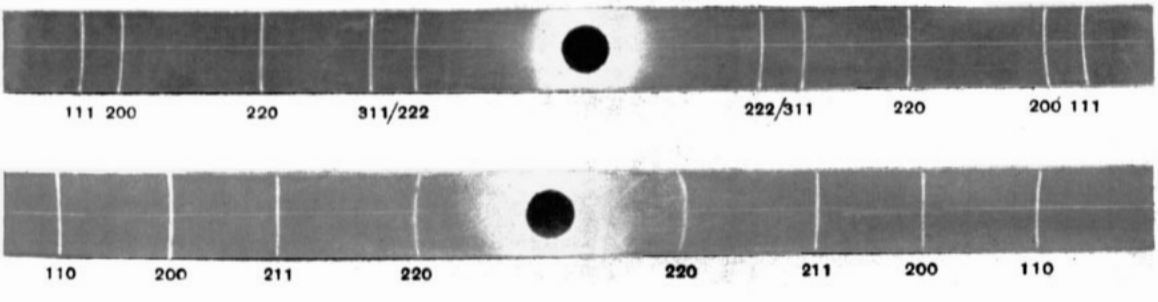

Fig. 5. Crystallograms taken with the Debye Camera, showing (top) Crystal Structure of Copper and (bottom) Crystal Structure of Iron.

In both cases a Shearer tube with iron anticathode was used; exposure 1 hour.

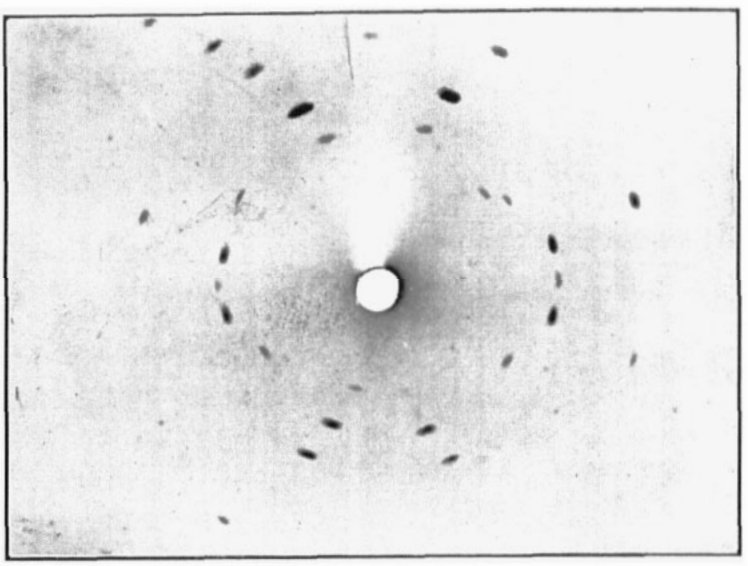

Fig. 6. "Rotating-Crystal" Crystallogram showing the Crystal Structure of Benzil. The C axis of the Crystal is set parallel to the axis of rotation.

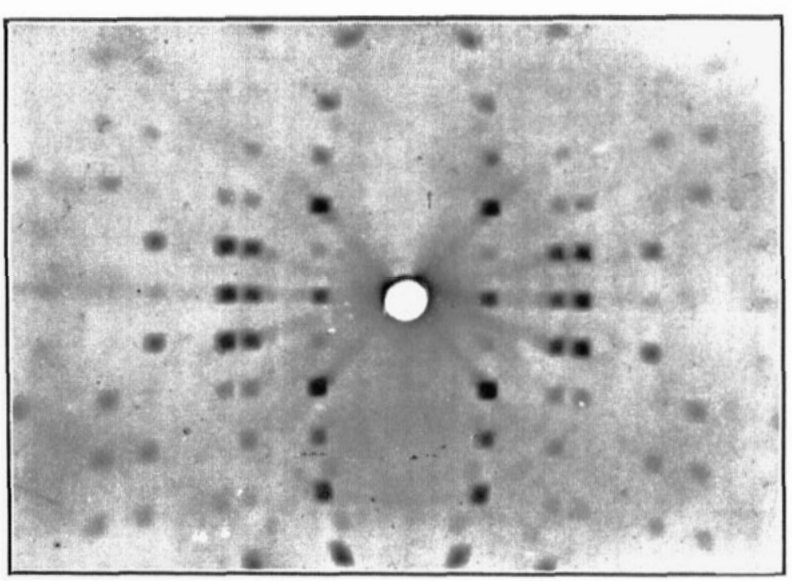

Fig. 7. Laue Crystallogram obtained from Benzil (trigonal). The Incident Beam is normal to one of the prism faces. The prism-axis is vertical, the Crystal being set by optical adjustment. Exposure 3 hours.