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ABSOLUTE X-RAY WAVE-LENGTH MEASUREMENTS

By A. P. R. Wadlund

Abstract

Wave-length of the $K\alpha_1$ lines of Cu, Fe, and Mo as determined by a speculum metal grating.—By means of a speculum metal grating, 50 lines to the mm, ruled over a length of 5 mm, the wave-lengths of the $K\alpha_1$ line of copper, iron and molybdenum were determined as 1.5373 ± 0.0008, $1.937(6) \pm 0.002(3)$ and $0.708(3) \pm 0.001(1)$ angstroms respectively. Using the $K\alpha_1$ line of copper the following constants were calculated: the *grating space of calcite* 3.0290 ± 0.0016A, *Avogadro's number* $(6.061 \pm 0.009) \times 10^{23}$ molecules per gram molecule, and the *electronic charge* $(4.774 \pm 0.007) \times 10^{-10}$ e.s.u. A discussion is given of the sources of error involved, of which the most important are those due to the settings on the lines of the diffraction pattern and those due to the inexact setting of the grating.

Introduction

As a result of their work on the diffraction of x-rays by a ruled grating, Compton and Doan[1] made the statement that they saw "no reason why measurements of the present type may not be made fully as precise as the absolute measurement by reflection from a crystal, in which the probable error is due chiefly to the uncertainty of the crystalline grating space." The present investigation was undertaken with the view of getting more precise measurements by this method than is at present possible by the crystal method.

Theory

As was shown by A. H. Compton[2], x-rays are totally reflected from a plane surface when the angle of incidence is sufficiently large. If then, the glancing angle is less than the critical angle for total reflection, a reflection grating may be used for diffracting x-rays and the usual formula of optics holds, viz.:

$$n\lambda = D(\sin i + \sin \phi) \tag{1}$$

where i is the angle of incidence, ϕ is the angle of diffraction for order n, and D is the grating space. Eq. (1) may be written in terms of the glancing angles:

$$n\lambda = D[\cos \theta - \cos (\theta + \alpha)] \tag{2}$$

[1] A. H. Compton and R. L. Doan, Nat. Acad. Sci. **11**, 598 (1925).

[2] A. H. Compton, Phil. Mag. **45**, 1121 (1923).

where θ is the glancing angle of incidence, $\theta+\alpha$ is the glancing angle of diffraction for order n, and hence α the angle between the zero order and the nth order. For the small angles involved it is more convenient to use Eq. (2) in the form

$$n\lambda = D(\alpha\theta + \tfrac{1}{2}\alpha^2 - 4\text{th degree terms} + \text{etc.}) \tag{3}$$

It was found unnecessary to use the 4th and higher degree terms in the present work.

For their more precise diffraction measurements, Compton and Doan used monochromatic radiation, as for example, $K\alpha_1$ of Mo. Thibaud[3] has been able to get beautiful diffraction patterns using general radiation, the complete spectrum being clearly separated and sharp. The method used in the present instance follows closely that of Compton and Doan, rather than that of Thibaud.

Arrangement of Apparatus and Experimental Procedure

The arrangement of the apparatus is shown diagramatically in Fig. 1. A water cooled metal tube X with changeable target and filament was used as the source of x-rays. The general radiation passed through slit S_1, and the particular line whose wave-length it was desired to measure was reflected

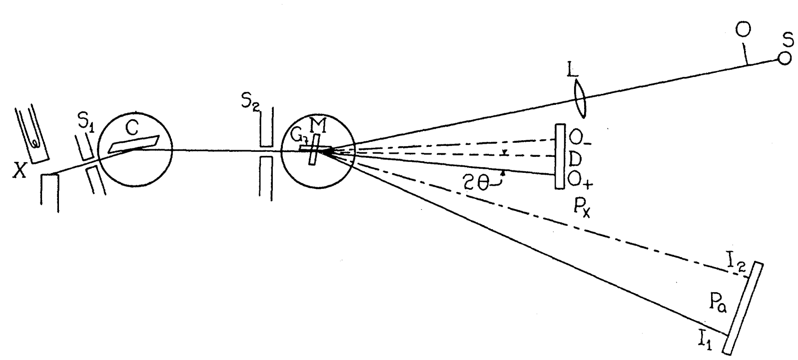

Fig. 1.

from the calcite crystal C. Several crystals were tried and that one used which gave the sharpest lines. The crystal was mounted on a table which could be rotated by a slow motion screw. The monochromatic radiation was then collimated by the slit S_2 about 1/10 mm wide before striking the grating G. The slit S_2 was so designed as to be capable of horizontal motion perpendicular to the x-ray beam and rotation about a vertical axis and a horizontal axis parallel to the beam. The grating was held in place by 3-point contact screws which allowed of considerable adjustment. This holder was in turn mounted on a table which could be moved in two mutually perpendicular directions (parallel to and perpendicular to the beam of x-rays) by slides which were

[3] J. Thibaud, Rev. d'Op. 5, 105 (1926); Phys. Zeits. 29, 241 (1928) (and elsewhere).

actuated by very fine pitch screws. The slides and grating were then placed on a table such as used for the crystal, so as to be capable of rotation about a vertical axis. The whole arrangement was then attached to a carriage which was capable of motion by a screw in a horizontal direction perpendicular to the beam. The diffraction pattern was recorded on the photographic plate P_x. For the purpose of angle measurement a plane-parallel mirror M was mounted on an arm which extended a few cm above the grating and moved as an integral part of the rotating part of the table. The mirror M was so mounted as to be capable of motion of translation along two horizontal directions and rotation about a vertical axis. The mirror could also be tilted giving in essence a motion of rotation about a horizontal axis. As a means of measuring angles through which the grating was rotated, a straight edge O served as an object, the image being formed at P_a where it was photographed.

The actual manipulations involved in obtaining the photographs at P_a and P_x are given in what follows. Having obtained monochromatic radiation through the slit S_2, the grating was carefully aligned photographically, so that the beam which struck the grating was split by the face of the grating at zero glancing angle, the object being to allow of total reflection from two positions approximately 180° apart. The positions of the grating which were to be used were then determined, after which the mirror M was carefully adjusted. The dotted line GD (Fig. 1) is the direct beam; GO_+ the reflected beam from the face of the grating as shown, called positive zero for short; the dot-dash line GO_- the reflected beam in the second position, called negative zero. On the plate P_a, I_1 corresponds to O_+, I_2 to O_-. With this arrangement no negative order was necessary for determining the glancing angle, nor was it necessary to measure the indeterminate distance from the plate P_x to the effective part of the grating. After this preliminary work the actual photographs to be measured were obtained in the following manner. The grating was first moved out of the beam and a short exposure of the direct beam recorded on the film P_x. This place on the film was then protected from further immediate exposure with a strip of lead and the grating moved back to its predetermined position and a short exposure taken to record the negative zero order. The position of the grating was then recorded by an exposure on plate P_a, after which the grating was turned and the positive position recorded. Sufficient time was allowed for the recording of the positive zero order, then the direct beam was uncovered and a lead frame placed in front of the film so that only the central portion of the plate was exposed to the action of the x-rays. When the exposure had been going for a time sufficient to record several orders of the spectrum, and before the plate P_x was removed, a check on the glancing angle was obtained by putting another plate at P_a, recording the position of the grating, then rotating back to get a second negative zero order, the position of which was also determined. When copper or iron radiation was used, there were placed in the paths CS_2 and GD, tanks which could be evacuated, in order to reduce the absorption of these radiations. All parts of the apparatus were rigidly fastened to a concrete pier. The room temperature did not vary more than 1°C during an exposure.

Results

Fig. 2 is an enlargement of a film obtained at P_x, and is typical. It was obtained for $K\alpha_1$ of Cu at a glancing angle of 21′:19″.5 after an exposure of about 30 hours at a distance of approximately 1 meter. The tube was operated at about 30 KV peak. The two negative zero orders are shown at O_-, direct beam at D, positive zero order at O_+, two negative diffracted orders

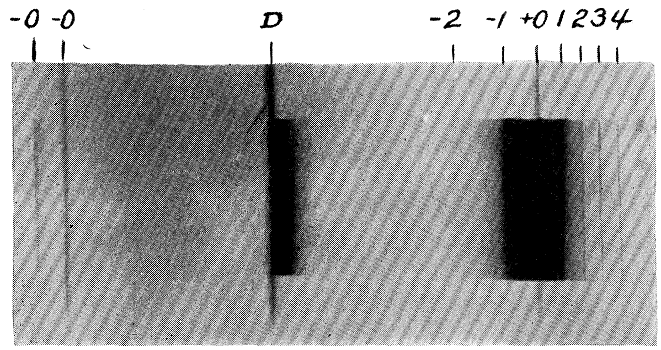

Fig. 2.

at −2 and −1, and four of the six measurable positive diffracted orders at 1 to 4. The 6 positive orders are visible and measurable on the original negative. The broad beam beside D is that part of the direct beam which passed the grating. Fig. 3 shows the type of plate obtained at P_a, the distance MI being about 2 meters.

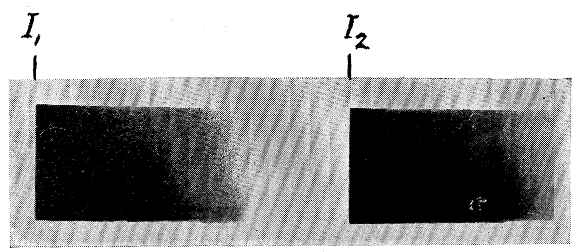

Fig. 3.

Referring to Fig. 1, if $I_1I_2=c$, $MI=d$, $DO_-=a$, $DO_+=b$, $c/d=m$, and $a/b=l$, then

$$\tan 2\theta = m/(l+1) \tag{4}$$

to the degree of accuracy required. Having determined θ it is an easy matter to determine from the measurements $\theta+\alpha$ and hence α. Measurements of the plates P_x and P_a were made on two comparators on different days and results of different observers used. The only distances not measured on the comparator were MI and the grating space. The former was measured by making fiducial marks on a steel tape and comparing the distance between these marks with a standard meter. The grating space was determined with a Geneva spectrometer using the green line of mercury.

The grating used to obtain the diffraction patterns which form bases of measurement throughout this report was of speculum metal. The rulings were 2 cm long and extended over a distance of only 5 mm, the grating space being 2.0000×10^{-3} cm. It was ruled by Mr. Fred Pearson on one of Professor A. A. Michelson's ruling engines and was particularly free from ghosts.

The results obtained from measurements of the plates are given below.

$$\text{Cu } K\,\alpha_1 = 1.5372(5) \pm 0.0003(3)\text{A}$$
$$\text{Fe } K\,\alpha_1 = 1.9376(6) \pm 0.002(1)\text{A}$$
$$\text{Mo } K\,\alpha_1 = 0.7083 \pm 0.0006\text{A}$$

The probable errors are those estimated from the errors in the measured distances involved as explained below. The Cu wave-length is the weighted mean of measurements on two plates showing 6 and 3 orders respectively. The glancing angles of incidence being 0°:21′:19″.5 and 0°:18′:51″.6 respectively. The wave-length for Fe is the result of a calculation on only 1 positive order, the glancing angle of incidence being 0°:23′:38″.0. Although the lines of the plate were not as sharp as on plates for Cu and Mo, the angles were of such magnitude as partly to offset this circumstance. The Mo wave-length is the weighted mean of three measurements on first order spectra only at glancing angles of 0°:7′:55″.6 and 0°:7′:57″.5 and 0°:10′:5″.3. The sharpness of the lines seems to warrant recording the results.

Discussion of the Probable Error of the Results

1. *Errors due to measurements.* The probable errors given in the above table were obtained from Eq. (6) given below. This expression is derived in order to show how the measurements made for wave-length calculation actually enter. Let the symbols used have the significance of those used in Figs. 4 and 5.

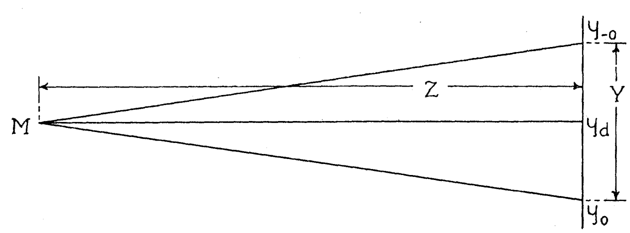

Fig. 4.

A simple calculation shows that Eq. (3) becomes to the degree of approximation required for the calculation of the probable error

$$\lambda = \frac{D}{2n}\left(\frac{\xi_n \zeta_n}{X^2}\right) \tag{5}$$

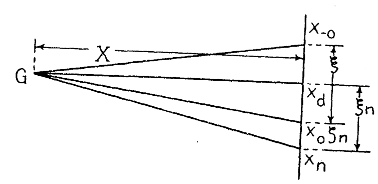

Fig. 5.

Hence we take as the probable error in the wave-length as calculated from the nth order

$$PE\lambda_n = \frac{D}{2n}\left\{\left(\frac{\zeta_n+\xi_n}{X^2}\Delta x_n\right)^2 + \left[\frac{\xi_n}{X^2}\left(1+2\frac{\zeta_n}{\xi}\right)\Delta x_0\right]^2 + \left(\frac{\zeta_n}{X^2}\Delta x_d\right)^2 + \left(2\frac{\zeta_n\xi_n}{X^2\xi}\Delta x_{-0}\right)^2 + \left(2\frac{\zeta_n\xi_n}{X^2 Y}\Delta Y\right)^2 + \left(2\frac{\zeta_n\xi_n}{X^2 Z}\Delta Z\right)^2\right\}^{1/2} \quad (6)$$

We thus have the probable error of a wave-length determination given in terms of the measurements used in the calculation of this wave-length, the Δ^* signifying the probable error of the measurement*.

The error involved in using Eq. (5), which is an approximation, is equivalent to neglecting—under the radical of Eq. (6)—coefficients of the Δ's in which X^4 enters in the denominator. It is evident that this introduces no appreciable change in the probable error as given by Eq. (6).

In all plates obtained ζ_n was of the order 1/10 to 1/3 ξ_n. Consequently, if the probable error of a setting on x_n, x_0, x_d, x_{-0}, y_0, y_{-0}, (ΔY being equal to $[(\Delta y_0)^2+(\Delta y_{-0})^2]^{1/2}$) are about equal, the most important factors are the first and second; in other words, the most important settings are x_n, and x_0. The probable errors of settings on the various lines of a single plate varied at times by a factor of 3.

As an illustration of the data used in the calculations, the 4th order of the film showing six orders is taken.

$\xi = 2.4010$ cm, $Y = 4.7850$ cm, $Z = 204.00$ cm, $\xi_4 = 1.6596$ cm, $\xi_0 = 1.2700$ cm From these data $X = 102.362$ cm; $\theta = 0°:21':19''.5$; $\alpha_4 = 0°:13':4''.9$; $\lambda_4 = 1.5423$A. For the calculation of the probable error the following additional data are given: $\Delta x_d = \pm 0.00007$, $\Delta x_0 = \pm 0.00006$, $\Delta x_{-0} = \pm 0.00007$, $\Delta x_4 = \pm 0.00018$, $\Delta Y = \pm 0.00011$, $\Delta Z = \pm 0.01$, $\zeta_4 = 0.3896$. Hence $PE\lambda_4 = \pm 0.0009$A.

2. *Consideration of approximations used.* The approximation used in the probable error has been considered above. The statement that it was found unnecessary to use the 4th and higher degree term of Eq. (3) was verified by actually including these terms. That Eq. (4) gives accuracy of the degree required is evident from the following considerations. In deriving Eq. (5) the relation $X = (x_0 - x_{-0})Z/(y_0 - y_{-0})$ was used. It is easy to show from Figs. 4 and 5 that Eq. (4) is really equivalent to using this relation as though it were absolutely correct. That it is not absolutely correct is evident from the way in which plates P_a and P_x were set. P_a was placed so that it was perpendicular to the direct beam, P_x was set so that the perpendicular from the mirror to the film struck half way between the images. If $x_d - x_{-0}$ was equal to $x_d - x_0$ then the above relation would be exact. This was never the case, the ratio of these distances, i.e., $(x_0 - x_d)/(x_d - x_{-0})$ was always greater than 9/10 and less than 11/10. This means that the plate P_x should have been set so that $(y_0 - y_d)/(y_d - y_{-0}) = (x_0 - x_d)/(x_d - x_{-0})$. Calculation shows that the approximation made leads to an inappreciable correction in Z and hence in X and the angles θ and α.

3. *Consideration of true errors.* There remains the consideration of true errors. Inasmuch as in x-ray work of this character only divergent and convergent beams are used, Eq. (1), which is derived for plane waves, is not strictly applicable. Porter[4] has recently derived an expression for a first approximation to the correction which Eq. (3) needs. The conditions imposed by this theory are almost exactly fulfilled in the present experimental arrangement. Calculation shows that the wave-lengths given above should be multiplied by 1.0000037. Consequently this source of error may be neglected.

Consider now the mirror M. The faces of this mirror were plane and parallel to 1/20 of a wave-length of green light which would introduce a constant error in the total angle $y_{-0}My_0$ (Fig. 4) and hence in the angle θ, assuming that the sputtering of the faces of the glass did not change their degree of parallelness. Another true error is introduced by not getting the mirror adjusted so that the two faces would be in the same plane when

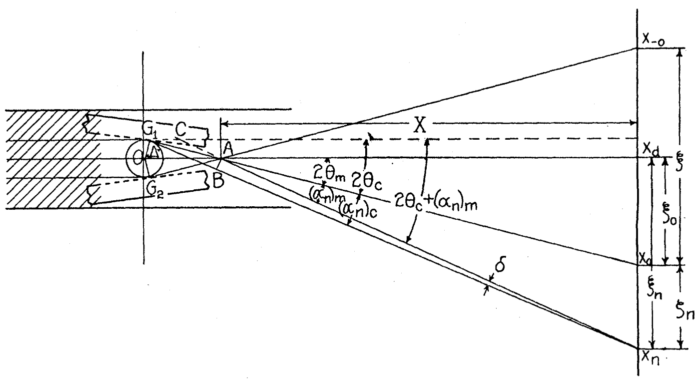

Fig. 6.

rotated through 180°. This adjustment was made to within 0.0025 cm (that is 0.001 inch). Assuming these errors to be in the same direction the error in wave-length is of course most marked in first order calculations, but well within the probable error of a single calculation.

The greatest source of error is that introduced by the inexact setting of the grating. By inexact we mean that the axis of rotation of the grating table may not have been in the plane of the face of the grating. Thus, let O (Fig. 6) be the axis of rotation of the grating table, and Δ the radius of the circle described by the center of the grating. Let G_2 be the position of the grating for obtaining the negative zero order, G_1 the position of the grating for obtaining the positive zero order and the diffraction pattern. The cross-hatched portion is the direct monochromatic beam. The subscripts c and m on the angle denote the angles as they should be (correct) and as measured respectively. From the geometry of the figure $2\theta_c = 2\theta_n$ and δ is the correction which should be made to the measured angle $(\alpha_n)_m$ to obtain the correct angle $(\alpha_n)_c$. A simple calculation shows that:

[4] Alfred Porter, Phil. Mag. **3**, 1067 (1928).

$$\delta \doteq \frac{\Delta}{X}\frac{\zeta_n}{\xi_0} \tag{7}$$

We now define ϵ by

$$\delta = \epsilon(\alpha_n)_m \tag{8}$$

so that

$$(\alpha_n)_c = (\alpha_n)_m(1+\epsilon) \tag{9}$$

Dropping the subscript on the angle θ and the subscript n on the angle α, we have from Eq. (3) $n\lambda_c = D(\alpha_c\theta + \frac{1}{2}\alpha_c^2)$ where λ_c is the correct wave-length. Using Eq. (9) we get $n\lambda_c \doteq n\lambda_m + D\epsilon(\alpha_m\theta + \alpha_m^2)$ i.e. the error in the wave-length is

$$\delta\lambda = (D\epsilon/n)(\alpha_m\theta + \alpha_m^2) \tag{10}$$

From consideration of the manner in which the grating was aligned the probable value of Δ is about 0.0005 cm. This gives, from the data above, for the 4th order of $K\alpha_1$ of Cu, $\delta_4 = 0°:0':0''.3$; $\epsilon_4 = 0.00039$ and $\delta\lambda_4 = 0.0007$A. The same value of $\delta\lambda$ was obtained for all orders of both plates used for the calculation of $K\alpha_1$ of Cu. The values of $\delta\lambda$ for $K\alpha_1$ of Fe and $K\alpha_1$ of Mo were ± 0.001 and ± 0.0009 respectively. The $\pm$ sign is used to allow for the possibility of the grating "running past" the center position by an amount Δ, Fig. 6 shows the grating "running short" by this amount.

Conclusions

1. *Wave-lengths of $K\alpha_1$ of copper, $K\alpha_1$ of iron, $K\alpha_1$ of molybdenum.* The final results for the wave-lengths of $K\alpha_1$ of Cu, $K\alpha_1$ of Fe, and $K\alpha_1$ of Mo are as given below, the column at the right being the values taken fromSiegbahn.[5]

Cu $K\alpha_1 = 1.5373 \pm 0.0008$	1.53730A
Fe $K\alpha_1 = 1.937(6) \pm 0.002(3)$	1.93230A
Mo $K\alpha_1 = 0.708(3) \pm 0.001(1)$	0.70759A

2. *The crystal grating space of calcite.*[6] The crystal grating space using the wave-length of $K\alpha_1$ of Cu given above is calculated as follows. If we let the subscript 1 denote the value of the various quantities as used in crystal wave-length determinations we have $d = d_1\lambda/\lambda_1$ where d is the crystal grating space (calcite in the present experiment). Taking $d_1 = 3.02904$A and $\lambda_1 = 1.53730$A we obtain

$$d = 3.0290 \pm 0.0016\text{A}$$

3. *Avogadro's number.* If we let N represent Avogadro's number, then

$$N = \frac{nM}{\rho d^3\phi(\beta)} = \frac{nM}{\rho d_1^3\phi(\beta)}\left(\frac{\lambda_1}{\lambda}\right)^3 = N_1\left(\frac{\lambda_1}{\lambda}\right)^3$$

[5] "The Spectroscopy of X-rays" (Ox. Univ. Press 1925) p. 105.

[6] Since the preliminary publication of these results (A. P. R. Wadlund, Proc. Nat. Acad. Sci. July, 1928) a paper by E. Bäcklin (Inaugural dissertation, Uppsala Universitets Arsskrift 1928) has come to my attention in which he determines the grating space of calcite from grating measurements on the Kα line of aluminum. He finds d = 3.033 ± .003A.

where n represents the number of molecules in each elementary rhombohedron, M is the molecular weight of calcite, ρ is the density of calcite, $\phi(\beta)$ is the volume of rhombohedron the distance between whose opposite faces is unity and the angle between whose edges, β, is that between the axes of the crystal.

Hence, if we take $N_1=6.061\times10^{23}$ we get

$N=(6.061\pm.009)\times10^{23}$ molecules per gram molecule.

4. *The charge on the electron.* We obtain the electronic charge e from

$$e=\frac{Mc}{10Nz}=\frac{Mc}{10N_1z}\left(\frac{\lambda}{\lambda_1}\right)^3=e_1\left(\frac{\lambda}{\lambda_1}\right)^3$$

where M is the molecular weight of silver, let us say, z its electrochemical equivalent, and c is the velocity of light. If we take $e_1=4.774\times10^{-10}$ e.s.u. there results

$$e=(4.774\pm.007)\times10^{-10}\text{ e.s.u.}$$

It will be seen that these values of N and e are only slightly less precise than those determined by Millikan's oil drop measurements (6.061 ± 0.006 and 4.774 ± 0.005 respectively) and that they agree exactly with those determinations.

This experiment was undertaken at the suggestion of Professor A. H. Compton whom the writer wishes to thank for his keen interest and for the valuable suggestions he has made. Acknowledgment of the suggestions of Dr. J. A. Bearden is also made and indebtedness is due Dr. R. L. Doan who had designed much of the apparatus before the writer started work. An expression of thanks is also extended to Professor and Mrs. G. S. Monk who made measurements on some of the plates.

Ryerson Physical Laboratory,
University of Chicago.
August 24, 1928.

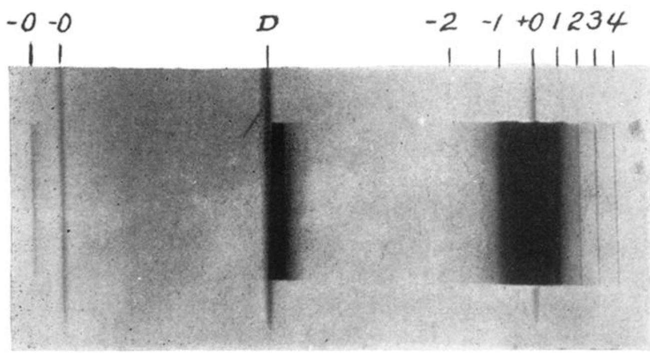

Fig. 2.

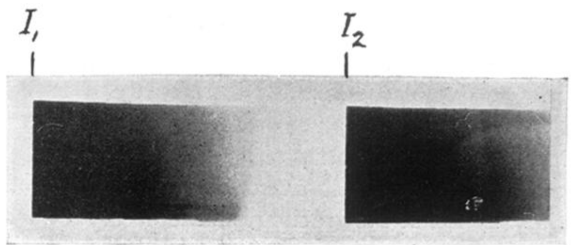

Fig. 3.