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# The Reflecting and Resolving Power of Calcite for X-rays

*By* SAMUEL K. ALLISON
*University of Chicago*

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With a precision double spectrometer, the rocking curves from three pairs of calcites in the (1, −1) positive have been observed for seven wave-lengths from 0.21A, (W $K\alpha_1$) to 2.3A, (Cr $K\alpha_1$). Three quantities were observed at each wave-length, (1) the percent reflection ($P_0$), defined as the ratio of the maximum ionization current obtainable from crystal $B$ to the ionization current produced by the x-rays incident on $B$ from $A$, (2) the coefficient of reflection ($R$), defined as the ratio of the area of the rocking curve from $B$ to the intensity incident on $B$ from $A$, (3) the half width at half maximum of the rocking curve from $B$. One of the pairs (crystals III) was obviously more perfect than the others, and its values of $P_0$, $R$, and $w$ are compared with theory. It is shown that none of the three quantities defined above is simply related to the analogous observations on a single crystal with monochromatic, parallel, incident x-rays, but that numerical predictions of the values of the above quantities may be obtained from somewhat laborious calculations based on Darwin's theory of diffraction by a perfect crystal as modified by Prins to take account of absorption. It is found that the predicted and observed coefficients of reflection are in good agreement in the wave-length range between 0.5 and 2.3A. On the basis of this agreement it is possible to state that calcite surfaces may be obtained for which there is no evidence of mosaic structure from measurements of the coefficient of reflection by double spectrometer methods in the wave-length region between 0.5 and 2.3A.

## EXPERIMENTAL PART

### Introduction

THE experiments reported here are similar to those performed on calcite in previous researches by other investigators.[1] The object of the experiments in the present case was primarily to provide a set of calibrated crystals to use in intensity measurements in this laboratory. The method consists essentially in comparing the intensity reflected from crystal $B$ of a double spectrometer with that incident on $B$ from crystal $A$, the instrument being set in a parallel position. In the present experiments only the (1, −1) position in the notation of Allison and Williams[1] was used.

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[1] A. H. Compton, Phys. Rev. **10,** 95 (1917); Davis and Stempel, Phys. Rev. **17,** 608 (1921) and Phil. Mag. **45,** 463 (1923); Wagner and Kuhlenkampff, Ann. d. Physik **68,** 369 (1922); Allison and Williams, Phys. Rev. **35,** 1476 (1930); Davis and Purks, Phys. Rev. **34,** 181 (1929).

## Apparatus

The double spectrometer used in these experiments is shown in Fig. 1. It was constructed by the Gaertner Scientific Corporation, Chicago, for the author. The principles of construction of the instrument are those previously described by Williams and Allison.[2] The advantages of this design are principally due to the fact that axis $B$ can be rotated about axis $A$, and the ionization chamber can be rotated about axis $B$. This enables the instrument to operate both in the parallel and anti-parallel positions, and allows settings for widely different wave-lengths to be made without moving the x-ray tube. In a design for a double spectrometer recently described by A. H. Compton,[3] the x-ray tube must be rotated about axis $A$ to change from one wave-length to another, which may be a considerable disadvantage. The author's instrument, however, is not designed for accurate *absolute* wave-length determinations, since angular measurements of rotation through large angles about axis $B$ cannot be made with great accuracy. The present instrument is best adapted to the investigation of rocking curves, fine-structures, etc.

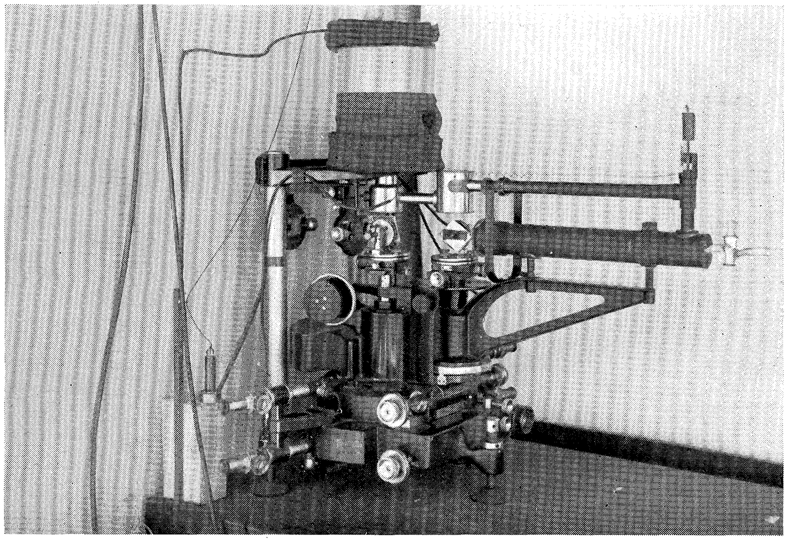

Fig. 1. The double spectrometer. The electrometer (above) is wrapped with wadding to protect it from sudden temperature changes. The instrument stands on a heavy stone slab mounted on concrete piers. The distance from the top of this slab to the shelf supporting the electrometer is 54 cm. Behind the instrument is a lead covered room in which the x-ray tubes are operated.

Although the instrument of Fig. 1 does not differ in principle from the previous one of Williams and Allison, much more care was taken in its construction. Because of the wide range of positions that axis $B$ and the ionization chamber may assume with respect to axis $A$ the problem of properly

[2] Williams and Allison, J.O.S.A. and R.S.I. **18**, 473 (1929).

[3] A. H. Compton, Rev. of Sci. Instr. **2**, 365 (1931).

balancing the weight on the various members is complicated. This problem was much more successfully handled in the present instrument than in its prototype. In particular, the essential requisite of the instrument namely that axis *A* be parallel to axis *B* was carefully worked out by scraping the face plates which connect the axes until as tested by a sensitive spirit level the two were parallel to less than one minute of arc.

The crystal mountings are somewhat more elaborate than those of the previous instrument in that two controlled horizontal translations are possible. In addition to the motion perpendicular to the reflecting face of the crystal, it is possible to shift the entire mounting parallel to the reflecting face. In this way the x-ray beam may be shifted along the surface of the crystal without moving that surface out of the axis of rotation. An attempt to design a plate for mounting the crystals which could readily be removed from the instrument with the crystal on it, stored in a dessicator, and then replaced, was unsuccessful. No scheme was devised such that the plate would return to its position on the axis to the required degree of accuracy (less than 10 seconds of arc) in a series of trials. The entire mounting had to be slid out of the grooved ways provided for the translatory motion in order to remove the crystals from the instrument.

Some distances on the instrument are: between the centers of the two collimating slits, 14.5 cm; from a point halfway between the two slits to axis *A*, 13.2 cm; from axis *A* to axis *B*, 13.8 cm; from axis *B* to the front window of the ionization chamber, 5.8 cm.

The ionization chamber is of the type mentioned in the previous paper by Williams and Allison,[2] and in the present experiments was filled with methyl bromide at one atmosphere pressure. The electrometer was of the Compton type, as manufactured by the Cambridge Instrument Company. It was operated at a sensitivity of 1.84 meters per volt as read on a scale 1.75 meters distant from the mirror of the instrument. It was shown by trial that a linear relationship between scale deflection and voltage on the unearthed quadrants existed at all points of the scale.

Commercial x-ray tubes were used for studies with the tungsten and chromium *K* series. The tube with the chromium target had a special glass window to transmit the radiation. The other wave-lengths used were obtained from tubes of the type previously described by the author.[4] The high voltage for operating the tubes was obtained from the generating plant described by Allison and Andrew.[5] In the experiments in which the $K\alpha_1$ lines of Mo, Cu, Fe, Ag, and the $L\beta_1$ line of Ir were used, the x-ray tubes were run at steady voltages between 30 and 42 k.v., higher values being used for Mo and Ag. Experiments with the Cr $K\alpha_1$ line were conducted at 38.4 k.v. and 26.8 k.v. With this radiation (wave-length 2.28A), about 86 percent was absorbed in the 58 cm air path alone, according to the absorption coefficient found by Spencer.[6] This raises the possibility that if the voltage on the tube is suffi-

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[4] Allison, Phys. Rev. **30**, 245 (1927).

[5] Allison and Andrew, Phys. Rev. **38**, 441 (1931).

[6] Spencer, Phys. Rev. **38**, 1932 (1931).

ciently high, the radiation reflected at the glancing angle for Cr $K\alpha_1$ may contain little of this wave-length and be mostly second and higher orders of the general radiation. It was shown that this effect did not invalidate the results for chromium by using the instrument as a single crystal spectrometer in the usual way and examining the spectrum, and also by the fact that the rocking curves at the two voltages indicated above for Cr were in agreement. The tungsten $K$ spectrum was obtained from a tube operated at 110 k.v.

**Adjustments**

The instrument was put in adjustment by the procedure previously described by Allison and Williams[1] with some minor refinements in technique. One large improvement over the methods of Allison and Williams resulted from the fact that it was found possible to use a telescope with a Gauss eyepiece in the adjustment of the crystals. This greatly increased the accuracy with which the cleavage faces could be set parallel to the axes of rotation. With the crystal holder removed, a piece of plane parallel glass, mounted on a small block equipped with levelling screws, was placed over the axis. The plane parallel plate and the telescope were adjusted until at two positions of the plate 180° apart the reflected cross-hairs coincided with those in the telescope. The axis of the telescope was then perpendicular to that of the spectrometer. The plane parallel plate was then removed, the crystal in its mounting attached to the axis, and the crystal tilted until the reflected cross-hairs from its face coincided with those in the telescope. In this way it was found possible to set the crystals accurately enough to obtain the minimum rocking curve width in parallel positions at once, and the tilting process previously described by Allison and Williams was not necessary. The telescope was placed roughly 2 meters from the spectrometer, and the crystals could be set with their faces within $\pm 15$ seconds of arc of the axes of rotation by this method.

In agreement with previous observers the rocking curves were found to be independent of the width of the slits used to limit the horizontal divergence of the beam of x-rays. The same slit widths, however, were not used at all wave-lengths. The inadvisability of such a procedure may be realised by considering the area on the crystal face irradiated by the x-ray beam at different glancing angles. For a constant vertical divergence of the beam this area is proportional to its horizontal extent, which to a sufficient approximation is given by

$$s = 2L_c a/L \sin\theta \tag{1}$$

where $L_c$ is the distance from a point midway between the slits to the axis of the crystal, $a$ is the slit width (assumed the same for both slits), $L$ is the distance between the slits, and $\theta$ is the glancing angle. In the experiments on the tungsten $K$ radiation, $\sin\theta = 0.034$, and the irradiated area becomes large relative to that used for softer wave-lengths. The range of wave-lengths present in the beam after reflection from crystal $A$ can be calculated from the slit width and the distance between the slits by the formula

$$d\lambda = \lambda \cot\theta d\theta = (2a\lambda \cot\theta)/L. \tag{2}$$

The various values of $d\lambda$ used are shown in column 4 of Table I. The vertical divergence of the beam was limited by a slit over the front window of the ionization chamber, at a distance of 5.8 cm from axis $B$. The other limitation was the finite size of the focal spot, certainly not greater than 0.8 cm in diameter and 58 cm distant from this slit. The width of the slit in front of the ionization chamber limiting the vertical divergence of the beam in various experiments is given as $h$ in column 5 of Table I. In column 6 of the same table is given the area irradiated on crystal $B$ in cm$^2$, obtained roughly by multiplying the values in column 5 by the appropriate value of $s$ obtained from Eq. (1).

TABLE I. *Adjustments.*

| Radiation | Crystals | $a$ | $d\lambda$ | $h$ | Area irradiated on crystal $B$. |
|---|---|---|---|---|---|
| W $K\alpha_1$ | II, V | 0.012 cm | 6.2 X.U. | 0.8 cm | 1.0 cm$^2$ |
| " | III | 0.012 | 6.2 | 0.5 | 0.65 |
| Ag $K\alpha_1$ | II | 0.030 | 26 | 0.2 | 0.24 |
| " | III | 0.040 | 34 | 0.2 | 0.32 |
| " | V | 0.015 | 13 | 0.8 | 0.48 |
| Mo $K\alpha_1$ | II | 0.030 | 25 | 0.2 | 0.19 |
| " | III | 0.040 | 33 | 0.2 | 0.25 |
| " | V | 0.015 | 12 | 0.8 | 0.42 |
| Ir $L\beta_1$ | II | 0.030 | 25 | 0.2 | 0.12 |
| " | III | 0.040 | 33 | 0.2 | 0.16 |
| " | V | 0.015 | 12 | 0.8 | 0.23 |
| Cu $K\alpha_1$ | II | 0.030 | 24 | 0.2 | 0.09 |
| " | III | 0.040 | 32 | 0.2 | 0.12 |
| " | V | 0.020 | 16 | 0.8 | 0.23 |
| Fe $K\alpha_1$ | II | 0.030 | 24 | 0.2 | 0.07 |
| " | III | 0.040 | 32 | 0.2 | 0.09 |
| " | V | 0.020 | 16 | 0.8 | 0.18 |
| Cr $K\alpha_1$ | II, III, V | 0.030 | 23 | 0.8 | 0.24 |

## Crystals

Five pairs of split calcites were examined in this work. Two of the pairs, calcites I and IV, were examined only for a few wave-lengths and the data are not reported here. The three pairs II, III, and V had freshly cleaved surfaces. They were clear calcites, suitable for the construction of Nicol prisms, but of unknown origin. They were split by a method recommended to the author by Professor Bergen Davis. The sample to be split was mounted on the carriage of a milling machine, in such a way that the lateral motion of the carriage was accurately parallel to the cleavage direction. A very thin circular saw was then run at slow speed and a groove made across the specimen. By continued sawing in this groove a split soon started and the slight jars due to the impact of the saw teeth on the crystal spread it until fissure was complete. The two halves of the crystal were then immediately placed in a dessicator and kept until used. The crystals were parallelopipeds usually from 0.5 to 1 cm thick and some 5 cm on a side.

The ability of the crystal surfaces to give a sharp reflected image of the cross hairs of the Gauss eye-piece was different in the various specimens. It is a rather disconcerting fact that crystals III, which proved to give the highest resolving power for x-rays, were the poorest optical reflectors. Crystals II gave a very clear reflected image, as good as that from a polished glass plate. Crystals V were intermediate between II and III in this respect.

The most extensive investigations were carried out on crystals III, and before these crystals were finally removed from the instrument a test was performed to make sure that the resolving power had not changed during the experiments. On Nov. 19, 1931 these crystals gave a rocking curve of 2.6″ half width at half maximum for Mo $K\alpha_1(1, -1)$. After the investigation of the other wave-lengths was completed, on Jan. 2, 1932, the experiment with Mo $K\alpha_1$ was repeated and again 2.6″ obtained. There is therefore no evidence that the crystals III had changed during the period of experimentation.

### Measurements

From the rocking curves for a given wave-length three quantities were determined. The half width at half maximum, $w$, is the angular range in seconds of arc through which crystal $B$ must be turned to reduce the power entering the ionization chamber to one-half its maximum value. By maximum value is meant the largest ionization current observed, corrected for base-line. This base-line was taken as the ionization current observed when crystal $B$ was rotated from its angular position for maximum reflection through an angular displacement of 6 or more times the half width at half maximum. The percent reflection, $P_0$, is the ratio of the maximum ionization current obtainable by reflection from crystal $B$ to that obtainable from the beam incident on $B$ from $A$. The coefficient of reflection, $R$, is in this paper defined as the ratio of the area under the rocking curve to the ionization current obtainable from the beam incident on crystal $B$ from crystal $A$. Values of $R$ observed and calculated in this paper are based on the radian as the unit of angle.

A regular routine was developed for the recording of rocking curves, the steps of which will now be described. A run was begun with crystal $B$ out of the x-ray beam. The beam reflected from crystal $A$ (which had been set at the proper angle) was allowed to enter the ionization chamber, and the current through the x-ray tube was adjusted until the rate of deflection of the electrometer was between 5 and 10 scale divisions per second. When conditions had become steady, a series of readings, usually three, were made on the beam reflected from crystal $A$. Between these readings the ionization chamber was shifted slightly to make perfectly sure that the entire beam was entering the window. If these three readings agreed to within 1 percent, the ionization chamber was displaced 5° and a reading taken of the diffusely scattered radiation. The difference between the average of the three readings and the base-line reading was taken as proportional to the intensity incident on $B$ from $A$. Except in experiments on W $K\alpha_1$ the base-line was negligible here. Crystal $B$ was then advanced into the beam, and the ionization chamber placed to receive the reflected beam from it. The rocking curve was then taken. Care was taken to obtain readings far enough from the maximum to supply a reliable base. Crystal $B$ was then removed, and the power incident upon it again determined; the average of the initial and final values being used as the intensity incident on $B$ during the taking of the rocking curve. The results are given in Table II. Each value is the result of at least two independent observations.

TABLE II. *Experimental results.*
$w$ = half width at half maximum of rocking curve (seconds).
$P_0$ = percent reflection.
$R$ = coefficient of reflection, in (radians)$^{-1}$.

| Line | λ (X.U.) | $w$ II | $w$ III | $w$ V | $100\,P_0$ II | $100\,P_0$ III | $100\,P_0$ V | $R\times10^5$ II | $R\times10^5$ III | $R\times10^5$ V |
|---|---|---|---|---|---|---|---|---|---|---|
| W $K\alpha_1$ | 208.6 | 4.2 | 2.3 | 7.2 | 33 | 35 | 28 | 2.34 | 1.17 | 2.14 |
| Ag $K\alpha_1$ | 558.3 | 3.8 | 2.2 | 7.0 | 48 | 59 | 34 | 2.15 | 1.53 | 2.38 |
| Mo $K\alpha_1$ | 707.8 | 3.9 | 2.6 | 7.2 | 52 | 63 | 33 | 2.31 | 1.86 | 2.44 |
| Ir $L\beta_1$ | 1155 | 4.8 | 4.1 | 8.1 | 59 | 64 | 37 | 3.49 | 2.95 | 3.24 |
| Cu $K\alpha_1$ | 1537 | 5.6 | 4.9 | 7.8 | 61 | 62 | 46 | 3.92 | 3.46 | 3.91 |
| Fe $K\alpha_1$ | 1932 | 6.8 | 6.2 | 9.9 | 54 | 58 | 42 | 4.45 | 4.18 | 4.45 |
| Cr $K\alpha_1$ | 2285 | 7.7 | 7.1 | 9.3 | 52 | 55 | 42 | 4.73 | 4.68 | 4.37 |

If we examine the data on $w$ in Table II, we see that the $w$ values for crystals III are consistently lower than for crystals II or V. This is taken to indicate that crystals III approach the ideal of a perfect crystal more nearly than do the others investigated, since any mosaic structure would enlarge the angular range over which reflected can take place. The remainder of this report will be concerned with a comparison of the values of $w$, $P_0$, and $R$ observed for crystals III with the predictions of the theory of diffraction by a perfect crystal.

## THEORETICAL PART

### Theory of diffraction of x-rays by an absorbing, perfect crystal

The theory of the diffraction of x-rays from the face of a perfect crystal has been developed by Darwin,[7] and later, Ewald.[8] In the discussion here we shall consider the theory as derived by Darwin. In Darwin's derivation, the absorption by incoherent processes of the x-rays as they penetrate the crystal, is neglected. The absorption due to ejection of photoelectrons or recoil electrons would be considered as an incoherent process in this sense. The result of Darwin's calculations can be expressed in the following form. The ratio of the intensity reflected from the crystal to that incident upon it is

$$\frac{I_{(\beta-\theta)}}{I_0}=\left|\frac{-q}{v+(v^2-q^2)^{1/2}}\right|^2, \tag{3}$$

where

$$v=\left\{2\pi d(\beta-\theta)\cos\theta_0\right\}/\lambda, \tag{4}$$

$$q=-\frac{2\pi d}{\lambda\sin\theta_0}\,\delta\,\frac{F(2\theta_0)}{F(0)}, \tag{5}$$

$$\theta=\theta_0+\delta\sec\theta_0\operatorname{cosec}\theta_0, \tag{6}$$

$$\theta_0=\sin^{-1}\frac{n\lambda}{2d}\cdot \tag{7}$$

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[7] Darwin, Phil. Mag. **27**, 325 and 675 (1914).

[8] Ewald, Phys. Zeits. **26**, 29 (1925).

In the above expressions, $(\beta-\theta)$ is the deviation of the glancing angle from the angle $\theta$, which is the corrected Bragg angle. $\lambda$ is the wave-length of the x-rays in air; $d$, the grating space of the crystal; $n$, the order of the spectrum, and $\delta$ the deviation of the index of refraction from unity. The sign to be used for the radical in the denominator of Eq. (3) is determined by the physical requirement that the ratio on the left hand side of this equation must be less than or equal to one. $F(2\theta_0)$ is the ratio of the amplitude of the wave scattered at angle $2\theta_0$ from the unit cell to the amplitude incident upon it. $F(0)$ is analogous ratio for the wave scattered in the forward direction of the incident beam. Let us first consider the simplified case in which the entire incident radiation is plane polarized in such a direction that the electric vector lies in a plane perpendicular to the plane of incidence of the radiation on the crystals. For the case,

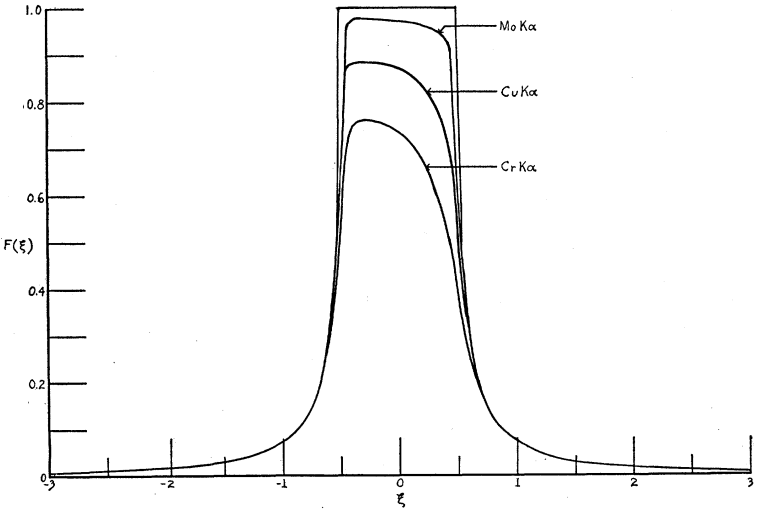

Fig. 2. Theoretical diffraction patterns from a single crystal. The outer curve is Darwin's theory, uncorrected for absorption, the inner curves illustrate Prins' absorption correction. With values of $\xi$ plotted as abscissae, the curves apparently have about the same width at half maximum. If instead of $\xi$, we consider the actual angular deviations from $\theta$, the width increases with wave-length.

$$F(2\theta_0)/F(0) = FZ^{-1} \tag{8}$$

where $F$ is the structure factor and $Z$ the number of electrons in the unit cell of the crystal. In the range $-q<v<q$, Eq. (3) gives rise to 100 percent reflection. If we call this range of angle $\Delta\theta_\sigma$ we have

$$\Delta\theta_\sigma = 4\delta FZ^{-1} \operatorname{cosec} 2\theta_0. \tag{9}$$

In this and following equations, the subscript $\sigma$ indicates that the electric vector of the radiation is perpendicular to the plane of incidence. We shall use this $\Delta\theta_\sigma$ as a unit of measure of angular deviation from the corrected Bragg angle $\theta$, and introduce the quantity $\xi_\sigma$ defined by

$$\xi_\sigma = (\beta - \theta)/\Delta\theta_\sigma. \tag{10}$$

If this $\xi_\sigma$ is introduced into Eq. (3) ,we obtain

$$F(\xi_\sigma) = \left| 2\xi_\sigma + (4\xi_\sigma^2 - 1)^{1/2} \right|^{-2} \tag{11}$$

A plot of $F(\xi_\sigma)$ is shown as the outer curve of Fig. 2.

Prins[9] has recently modified Darwin's theory in an attempt to take account of the absorption of the x-rays in the crystal by incoherent processes, as mentioned above. It is well known that in the classical dispersion theory, the index of refraction is the real part of a complex number, which number we may represent by $(1-\delta-i\beta)$. The real part of this number, $(1-\delta)$, is the ordinary index of refraction, i.e., the ratio of the phase velocity in vacuum to that in the medium. The imaginary part is related to the linear absorption coefficient $\mu_l$ of the radiation in the medium by

$$\beta = \lambda\mu_l/4\pi. \tag{12}$$

The essential feature of Prins' method is that he has treated the absorption in the classical manner, as if it took place by coherent processes, which in general leads to the substitution of $(\delta+i\beta)$ for $\delta$ when it appears in Darwin's treatment.

We shall take the result of Prins' calculations as it appears in Eq. (11) of his paper. This is, with a slight change of notation,

$$\frac{I_{(\beta-\theta_0)}}{I_0} \tag{13}$$

$$= \left| \frac{d+ib}{(\beta-\theta_0)\sin\theta_0\cos\theta_0-(\delta+i\beta)+(\{(\beta-\theta_0)\sin\theta_0\cos\theta_0-(\delta+i\beta)\}^2-(d+ib)^2)^{1/2}} \right|^2$$

We shall first consider the application of this formula to a crystal composed of atoms of one kind only, in equally spaced planes. Under these conditions the quantity $(d+ib)$ is related to the quantity $(\delta+i\beta)$ as the amplitude of the wave scattered by an atom at angle $2\theta_0$ to the amplitude scattered in the forward direction. In order to be more specific about the relationship between the two quantities, we will adopt the simpler of Prins' two hypotheses, hypothesis *I*. This states that all electrons in the atom may be treated in the same way as regards the amplitude scattered as a function of the scattering angle, irrespective of the level to which they belong. This hypothesis leads to the relation

$$d + ib = (\delta + i\beta)f(2\theta_0)/f(0) \tag{14}$$

where $f(2\theta_0)$ is the amplitude scattered by the atom at the angle $2\theta_0$ from an incident wave of unit amplitude. A more detailed and correct procedure would be to consider the *K*, *L*, *M*, etc. electrons in the atom separately, both with respect to their contributions to $\delta$ and $\beta$, and the angular distribution of the amplitude scattered from them. In this paper, however, the simplified procedure of Eq. (14) will be adopted.

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[9] Prins, Zeits. f. Physik **63**, 477 (1930).

In a crystal such as calcite, which consists of interlaced planes of different kinds of atoms; instead of $(d+ib)$ in Eq. (13), we must introduce a quantity

$$D + iB = \sum_i (\delta_i + i\beta_i) \frac{f_i(2\theta_0)}{f_i(0)} e^{2\pi ni(hx_i+ky_i+lz_i)}. \tag{15}$$

In this expression, $\delta_i$ is the contribution to $\delta$ for the medium from atom $i$. $n$ is the order of the reflection; $h$, $k$, $l$, the Miller indices of the reflecting plane, and $x_i$, $y_i$, $z_i$ the coordinates of the atom $i$ in the unit cell. The summation is to be carried out over all the atoms present in the unit cell. In more common notation, for the $\sigma$ type of polarization defined above,

$$f_i(2\theta_0)/f_i(0) = F_iZ_i^{-1} \tag{16}$$

where $F_i$ is the atomic structure factor of the atom of type $i$, and $Z_i$ is the number of electrons in the atom.

In calculating the values of $D+iB$ by Eq. (15), the author has made a further approximation, namely, that the contributions to $\delta$ and $\beta$ from a given atom $i$ are proportional to the fraction of the total number of electrons in the unit cell contained in the atom in question. If $Z$ is the total number of electrons in the unit cell, this means that

$$\delta_i + i\beta_i = Z_i(\delta + i\beta)/Z. \tag{17}$$

It is clear that more accurate calculations could be made, the best method being perhaps to subdivide the electrons in the unit cell into groups according to their binding energy, but in view of the approximate nature of the graphical calculations to come later it would seem that the somewhat crude assumption of Eq. (17) is permissible.

Substitution of Eqs. (17) and (16) in Eq. (15) gives

$$D + iB = Z^{-1}(\delta + i\beta) \sum_i F_i e^{2\pi ni(hx_i+ky_i+lz_i)}. \tag{18}$$

The summation in Eq. (18) is commonly known as the structure factor $F$, so that finally,

$$D + iB = Z^{-1}F(\delta + i\beta). \tag{19}$$

We are now ready to adapt Eq. (13) to a crystal of more than one kind of atom, and to put it into a form similar to Eq. (11). It should be noted that in Eq. (13) the reference angle is $\theta_0$, the uncorrected Bragg angle, whereas in Eq. (10) the reference angle is $\theta$. In terms of $\theta_0$, the expression for $\xi_\sigma$ in Eq. (10) becomes, after making use of Eq. (6).

$$\xi_\sigma = \frac{(\beta - \theta_0)\sin\theta_0\cos\theta_0}{2\delta FZ^{-1}} - \frac{1}{2FZ^{-1}}. \tag{20}$$

Putting $D+iB$ from Eq. (19) in place of $d+ib$ in Eq. (13), and introducing $\xi_\sigma$ from Eq. (20), we obtain

$$F(\xi_\sigma) = \left| \frac{FZ^{-1}(1 + i\beta/\delta)}{2\xi_\sigma FZ^{-1} - i\beta/\delta + [(2\xi_\sigma FZ^{-1} - i\beta/\delta)^2 - F^2Z^{-2}(1 + i\beta/\delta)^2]^{1/2}} \right|^2. \tag{21}$$

If the effect of absorption is neglected, that is, $\beta=0$, this expression reduces to Eq. (11), Darwin's original form.

The calculation of the shape of the diffraction pattern to be expected from a perfect calcite crystal irradiated at the proper angles by monochromatic, plane, x-rays of wave-lengths 0.708A, (Mo $K\alpha_1$), 1.537A (Cu $K\alpha_1$), and 2.285A (Cr $K\alpha_1$) has been carried out from Eq. (21). The values of $\delta$ were obtained from Larsson.[10] The values of $\beta$ may be obtained from the linear absorption coefficient by Eq. (12). The value of $\mu_l$ was calculated for Mo $K\alpha_1$ in calcite from data collected by A. H. Compton,[11] and extended to other wave-lengths by assuming the validity of the $\lambda^3$ law. The values used are shown in Table III.

TABLE III. *Values of $\delta$ and $\beta$ used in Eq. (21).*

| $\lambda$ | $\delta$ | $\beta$ | $\beta/\delta$ |
|---|---|---|---|
| 0.708A | $1.87\times10^{-6}$ | $1.31\times10^{-8}$ | 0.007 |
| 1.537 | 8.80 | $2.92\times10^{-7}$ | 0.033 |
| 2.285 | 19.5 | $1.43\times10^{-6}$ | 0.073 |

The value of $FZ^{-1}$ for calcite in the first order from the cleavage faces, based on the atomic structure factors of Bragg and West[12] has been shown by Allison and Williams[1] to be 0.47. All the calculations of this paper have been based on this value, which may be somewhat low, as discussed later. Some of the values of $F(\xi_\sigma)$ for these three cases, both from Eq. (11) (Darwin) and Eq. (21) (Prins) are shown in Table IV.[13]

TABLE IV *Diffraction pattern of a perfect calcite crystal.*

| Eq. (10) $\xi_\sigma$ | $F(\xi_\sigma)$ Darwin | $F(\xi_\sigma)$ Prins Mo $K\alpha_1$ | Cu $K\alpha_1$ | Cr $K\alpha_1$ |
|---|---|---|---|---|
| $-2.13$ | 0.014 | 0.014 | 0.014 | 0.014 |
| $-1.06$ | 0.063 | 0.062 | 0.062 | 0.062 |
| $-0.85$ | 0.106 | 0.105 | 0.105 | 0.105 |
| $-0.64$ | 0.234 | 0.233 | 0.232 | 0.229 |
| $-0.43$ | 1.000 | 0.959 | 0.874 | 0.709 |
| $-0.21$ | 1.000 | 0.973 | 0.881 | 0.758 |
| $\pm0.00$ | 1.000 | 0.971 | 0.870 | 0.735 |
| $+0.21$ | 1.000 | 0.960 | 0.830 | 0.670 |
| 0.43 | 1.000 | 0.924 | 0.702 | 0.503 |
| 0.53 | 0.501 | 0.486 | 0.426 | 0.341 |
| 0.64 | 0.234 | 0.233 | 0.229 | 0.213 |
| 0.85 | 0.106 | 0.105 | 0.105 | 0.103 |
| 1.06 | 0.063 | 0.062 | 0.062 | 0.062 |
| 2.13 | 0.014 | 0.014 | 0.014 | 0.014 |

The calculated values of Table IV are shown graphically in Fig. 2. An interesting feature of the curves corrected for absorption by Prins' method is that

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[10] Larsson, Diss. Upsala 1929. Reported in Siegbahn, Spektroskopie der Rontgenstrahlen, 2nd Ed., (1931) Table XIII, p. 39.

[11] A. H. Compton, X-rays and Electrons, (1926), Table VI–2 p. 182.

[12] Bragg and West, Zeits. f. Krist. **69**, 118 (1928).

[13] A large part of the calculations involved in this paper were made for me by Mrs. G. S. Monk, computer of this laboratory.

they are asymmetrical. The possibility of detecting such a lack of symmetry by double spectrometer measurements will be discussed later.

The areas under the curves of Fig. 2 are important in the theory of intensity of reflection. By integration of Eq. (11) it may be shown that

$$\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma = 4/3. \tag{22}$$

The unit of angular deviation in Eq. (22) is the angle $\Delta\theta_\sigma$, as is shown by Eq. (10). If we adopt more fundamental units, i.e., radians, the area under the diffraction pattern is $4\Delta\theta_\sigma/3$. The areas under the other curves of Fig. 2 were obtained by use of the integraph, and are shown in Table V.[14]

TABLE V. *Values of* $\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma$ *from Eqs.* (*11*) *and* (*21*).

| Line | Darwin | Prins |
|---|---|---|
| Mo $K\alpha_1$ | 1.333 | 1.250 |
| Cu $K\alpha_1$ | 1.333 | 1.122 |
| Cr $K\alpha_1$ | 1.333 | 0.935 |

### Calculation of the shape of the (1, −1) rocking curve for plane polarized radiation

A careful analysis of the operation of the double crystal spectrometer shows that the shape of the rocking curve obtained in parallel positions in the first order could not possibly be that of the curves in Fig. 2, even if perfect crystals were available and the instrument were in correct adjustment. Neither can be the area under a rocking curve be directly compared with the areas under the curves in Fig. 2. The fundamental physical reason for this is that all the theoretical curves previously described were calculated for parallel, monochromatic radiation. Due to the fact that the dispersion is zero in parallel positions, the spectral distribution of the radiation is not important, but, although the first crystal greatly reduces the horizontal divergence of the beam, it does not reduce it to zero, and the beam incident on crystal $B$ is still a divergent one. The author has previously pointed out[15] that the function governing the shape of the rocking curves is

$$\Phi(\xi_{B\sigma}) = \int_{-\infty}^{\infty} F(\xi_\sigma)F(\xi_\sigma - \xi_{B\sigma})d\xi_\sigma. \tag{23}$$

In this expression,

$$\xi_{B\sigma} = (\beta_B - \theta_B)/\Delta\theta_\sigma \tag{24}$$

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[14] It is these areas which, expressed in radian measure, are usually defined as the coefficients of reflection, and it is true that the reflecting power of a single crystal is proportional to them. It is one of the principal objects of this paper to make clear that there is a discrepancy between this definition and the experimental attempts to measure this quantity by the double spectrometer. In this paper, the term coefficient of reflection refers to area under the rocking curve of crystal $B$. This is quite a different thing physically from the areas in Table V.

[15] S. K. Allison, Phys. Rev. **38,** 203 (1931) Eq. (8).

where $(\beta_B - \theta_B)$ is the angular deviation of crystal $B$ from the position in which its reflecting face is parallel to that of $A$. $\Phi(\xi_{B\sigma})$ is the intensity of the beam entering the ionization chamber from a single position of crystal $B$. $F(\xi_\sigma)$ is the diffraction pattern for a single crystal as in Fig. 2. The derivation of Eq. (23) is perhaps made clearer by Fig. 3, in which the course of a ray through the instrument is shown.

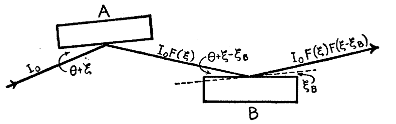

Fig. 3. Course of a ray through the double spectrometer in a parallel position, illustrating Eq. (23).

It is the custom to express the intensity reflected from $B$ in terms of the intensity of the beam incident on $B$ from $A$, which is proportional to the area under the single crystal diffraction pattern. We thus obtain the following expression

$$P_\sigma = \frac{\displaystyle\int_{-\infty}^{\infty} F(\xi_\sigma)F(\xi_\sigma - \xi_{B\sigma})d\xi_\sigma}{\displaystyle\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma} \tag{25}$$

where $P_\sigma$ is the ordinate of the rocking curve from crystal $B$ according to the convention above. The percent reflection, $P_0$, will be given by the value of $P_\sigma$ when $\xi_{B\sigma} = 0$, or

$$P_0 = \frac{\displaystyle\int_{-\infty}^{\infty} [F(\xi_\sigma)]^2 d\xi_\sigma}{\displaystyle\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma}\cdot \tag{26}$$

Laue[16] has discussed the possibility of solving Eq. (23), that is, of determining the shape of the single crystal diffraction pattern from the experimentally determined $\Phi(\xi_{B\sigma})$, and has come to some important conclusions. In the first place, the observed rocking curve ($\Phi(\xi_{B\sigma})$ or $P_\sigma$) will necessarily be an even function, whether or not the single crystal diffraction curves $F(\xi_\sigma)$ are asymmetrical. If we assume that the single crystal diffraction pattern is an even function, then it is possible to find its shape by solution of Eq. (23), otherwise, not. This means that by experiments of the type reported here it is impossible to discover whether the single crystal diffraction patterns are really asymmetrical as in the theory of Prins. If asymmetrical rocking curves are experimentally found, the only legitimate interpretation is that the diffraction patterns of the two crystals used are not identical. It should be remembered that the preceding statement applies only to parallel positions.

[16] Laue, Zeits. f. Physik **72**, 472 (1931).

In view of the findings of Laue, as reported above, the author has not attempted to solve the Eq. (23), using his observed $\Phi(\xi_{B\sigma})$, and discover the nature of the single crystal curve. The procedure adopted has been the reverse of this, namely to calculate $\Phi(\xi_{B\sigma})$ from Eq. (23), using theoretical $F(\xi_\sigma)$'s from Eqs. (11) and (21), and comparing the result with experiment. Calculated values of $\Phi(\xi_{B\sigma})$ are shown in Table VI. These values were obtained mainly by graphical integration.

TABLE VI. *Calculated values of $\Phi(\xi_{B\sigma})$ from Eq. (23). The unit of angle is $\Delta\theta_\sigma$ from Eq. (9).*

| $\xi_{B\sigma}$ | Darwin | Prins | | |
|---|---|---|---|---|
| | | Mo $K\alpha_1$ | Cu $K\alpha_1$ | Cr $K\alpha_1$ |
| 0 | 1.068 | 0.970 | 0.765 | 0.521 |
| ±0.21 | 0.954 | .876 | .694 | .475 |
| ± .43 | .786 | .727 | .566 | .401 |
| ± .64 | .590 | .552 | .434 | .308 |
| ± .85 | .396 | .378 | .272 | .212 |
| ±1.06 | .209 | .200 | .161 | .135 |
| ±1.60 | .077 | .070 | .063 | .052 |
| ±2.13 | .040 | .036 | .033 | .029 |
| ±2.66 | .024 | .022 | .020 | |
| ±3.19 | .019 | .014 | .013 | .012 |

## Calculation of the shape of the rocking curve with unpolarized incident radiation

Before comparing the calculations summarized in Table VI directly with experiment, we must consider the fact that after reflection from crystal $A$, the beam incident on crystal $B$ is partially polarized. Since the radiation used was in each case a characteristic emission line of the target, it is known that the radiation incident on crystal $A$ was completely unpolarized. We may then arbitrarily divide up the beam incident on $A$ into two components of equal intensity, one polarized so that its electric vector is perpendicular to the plane of incidence (subscript $\sigma$) and one with its electric vector parallel to the plane of incidence (subscript $\pi$). We then treat each component separately in its passage through the apparatus. In Darwin's treatment, the extent of the region of 100 percent reflection with $\pi$-polarization is

$$\Delta\theta_\pi = 4\delta F Z^{-1} \operatorname{cosec} 2\theta_0 \cos 2\theta_0 = 4\delta F Z^{-1} \cot 2\theta_0 \tag{27}$$

which is to be compared with Eq. (9). We now introduce the quantities

$$\xi_\pi = (\beta - \theta)/\Delta\theta_\pi = \xi_\sigma \sec 2\theta_0 \tag{28}$$

and

$$\xi_{B\pi} = (\beta_B - \theta_B)/\Delta\theta_\pi = \xi_{B\sigma} \sec 2\theta_0 . \tag{29}$$

By use of the preceding three equations, the derivation of the rocking curves for radiation polarized so that its electric vector lies in the plane of incidence ($\pi$-polarization) may be accomplished simply by changing the subscript $\sigma$ to $\pi$ in all the equations in which it appears up to and including Eq. (26). In adding the contributions from $\sigma$- and $\pi$-components to obtain the unpolarized values, it must be remembered that the angular unit in which $\sigma$

and $\pi$ quantities are expressed is different. (Compare Eqs. (27) and (9).) We shall adopt the angular unit $\Delta\theta_\sigma$ in the following equations dealing with unpolarized radiation, and change quantities expressed in terms of $\Delta\theta_\pi$ to their values in terms of $\Delta\theta_\sigma$. We then obtain

$$P = \frac{\Phi(\xi_{B\sigma}) + \Phi(\xi_{B\pi})\cos 2\theta_0}{\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma + \int_{-\infty}^{\infty} F(\xi_\pi)d\xi_\pi} = \frac{\Phi(\xi_{B\sigma}) + (\cos 2\theta_0)\Phi(\xi_{B\sigma}\sec 2\theta_0)}{(1 + \cos 2\theta_0)\int_{-\infty}^{\infty} F(\xi_\sigma)d\xi_\sigma} \qquad (30)$$

where $P$ is the ordinate of the rocking curve, that is, the ratio of the ionization current obtained from a setting of crystal $B$ to the current obtained from the radiation incident on $B$ from $A$. If $\xi_{B\sigma} = 0$ in Eq. (30), that is, the two crystals are accurately parallel, it reduces to Eq. (26), which means that the percent reflection, $P_0$, is independent of the polarization. This, of course, is not true of the coefficient of reflection, $R$.

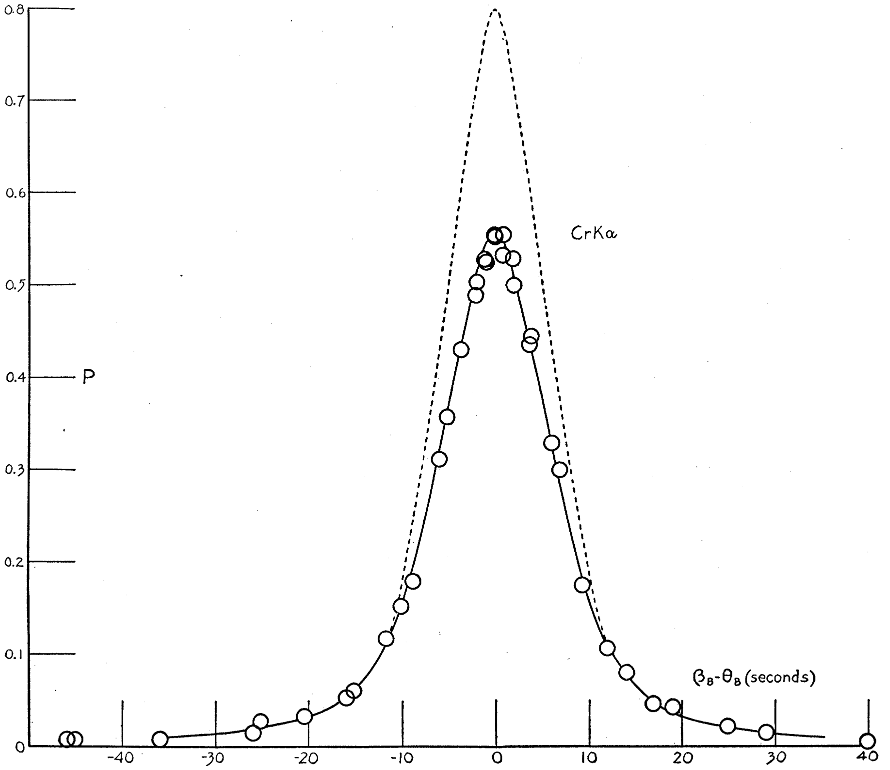

Fig. 4. Comparison of observed and calculated rocking curves for Cr $K\alpha_1$. The dotted curve is the rocking curve calculated from Darwin's theory, in which absorption in the crystal is neglected. The solid curve is the curve derived from Prins' theory. The circles represent experimental points. The points are not fitted to the curve in any way, for instance by an adjustable constant.

The use of Eq. (30) will be illustrated by a sample calculation of a point on the rocking curve for Cr $K\alpha_1$ $(1, -1)$ according to Prins. The denominator of Eq. (30) can be obtained from a knowledge of the Bragg angle for Cr $K\alpha_1$ on calcite, with the values in Table V. Its value is $(1+0.715)$ $(0.935)=1.603$. Let us consider a setting of crystal $B$ such that $\xi_{B\sigma}=0.64$. From Table VI we find $\Phi(\xi_{B\sigma})=0.308$. The value of $\xi_{B\sigma}$ sec $2\theta_0$ is $0.64\times 1.40=0.896$. From interpolation of Table VI, we find $\Phi(0.896)=0.194$, and $\Phi(0.896)\cos 2\theta$ is 0.139. Thus $P$ for this setting of the crystal is 0.279.

The calculated values of $\Delta\theta_\sigma$ from Eq. (9) are shown in Table VIII. They are computed for $FZ^{-1}=0.47$, using $\delta$-values from Table III, with the exception of W $K\alpha_1$, where $\delta$ is extrapolated by assuming a variation with $\lambda^2$. The rocking curves to be expected from calcite for Cr $K\alpha_1$ $(1, -1)$ with unpolarized radiation from Darwin's and Prins equations can be plotted from the calculated values shown in Table VII.

TABLE VII. *Theoretical form of the calcite rocking curve* Cr $K\alpha_1$ *(1, −1).*

| $\xi_{B\sigma}$ | $\beta_B-\theta_B$ (seconds) | $P$ Darwin | $P$ Prins |
|---|---|---|---|
| 0.0 | 0 | 0.798 | 0.557 |
| ± .21 | 2.27 | .698 | .496 |
| ± .43 | 4.64 | .540 | .396 |
| ± .64 | 6.91 | .370 | .279 |
| ± .85 | 9.18 | .229 | .183 |
| ±1.06 | 11.4 | .125 | .116 |
| ±1.60 | 17.3 | .045 | .045 |
| ±2.13 | 23.0 | .024 | .025 |
| ±2.66 | 28.7 | .015 | .016 |
| ±3.19 | 34.5 | .011 | .010 |

TABLE VIII. *Values of* $\Delta\theta_\sigma$.

| Line | $\lambda$ | cosec $2\theta$ | $\Delta\theta_\sigma$ radians | $\Delta\theta_\sigma$ seconds |
|---|---|---|---|---|
| W $K\alpha_1$ | 0.2086A | 14.44 | $4.4\times 10^{-6}$ | 0.91 |
| Mo $K\alpha_1$ | 0.7078 | 4.31 | 15.2 | 3.14 |
| Cu $K\alpha_1$ | 1.537 | 2.04 | 33.7 | 6.96 |
| Cr $K\alpha_1$ | 2.285 | 1.43 | 52.4 | 10.8 |

The calculated rocking curves and the experimental points for Cr $K\alpha_1$ taken on crystals III are shown in Fig. 4. It is seen that the calculated rocking curve agrees within the experimental error with that obtained experimentally. The half width at half maximum of the theoretical curve is 6.9″, the observed value is 7.1″. The percent reflection $P_0$ is 0.557 from Table VII; the observed value is 0.554. It is of interest to note that according to the analysis of the action of the double spectrometer presented in this paper, even if the diffraction pattern from each of the two crystals could be treated by Darwin's equation, the observed percent reflection would only be 0.798 as against 1.00 which has been expected by some writers.

The shape of the rocking curve to be expected from Prins' theory has been calculated for Mo $K\alpha_1$, Cu $K\alpha_1$ and Cr $K\alpha_1$. The rocking curve to be expected from W $K\alpha_1$ has been calculated from Darwin's equation directly. The resultant $P_0$'s and half widths at half maximum, $w$, are compared with experiment in Fig. 5. The resolving power is calculated from a previous definition of the author,[17] which is

$$\lambda/d\lambda = D\lambda/2w. \tag{31}$$

This is to be interpreted as the resolving power which the instrument would have in the (1, 1) position with the same crystals. $D$ is the dispersion of the instrument in the (1, 1) position.

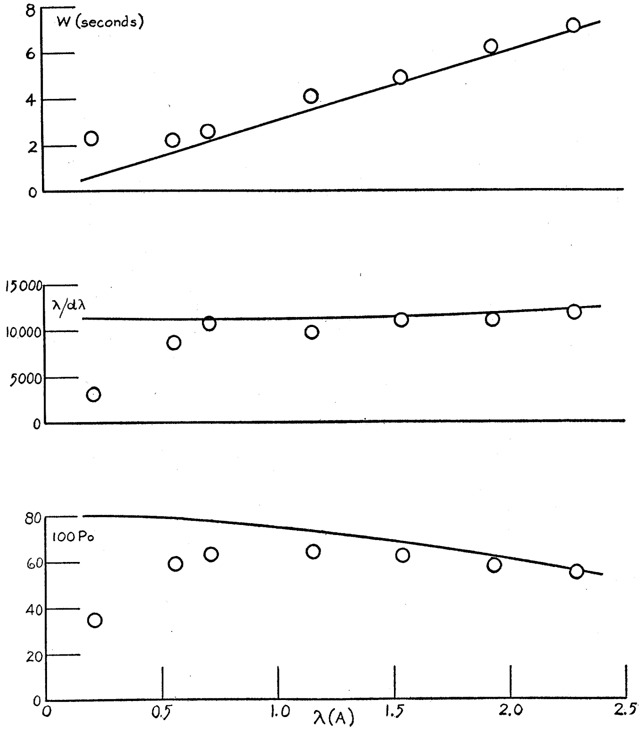

Fig. 5. The half width at half maximum ($w$), resolving power ($\lambda/d\lambda$), and percent reflection ($P_0$) of calcites III compared with theoretical values deduced from Prins. The solid curves are theoretical values, the points, experimental ones.

## Calculation of the coefficient of reflection

In order to calculate the coefficient of reflection as defined in this paper we must find the area under the $P$ curve (rocking curve) with the radian as the unit of angular measure. Thus

$$R = \Delta\theta_\sigma \frac{\int_{-\infty}^{\infty} [\Phi(\xi_{B\sigma}) + \Phi(\xi_{B\sigma} \sec 2\theta) \cos 2\theta] d\xi_{B\sigma}}{(1 + \cos 2\theta) \int_{-\infty}^{\infty} F(\xi_\sigma) d\xi_\sigma} \tag{32}$$

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[17] S. K. Allison, Phys. Rev. **38**, 203 (1931), Eq. (21) 208.

or, finally,

$$R = \frac{\int_{-\infty}^{\infty} \Phi(\xi_{B\sigma}) d\xi_{B\sigma}}{\int_{-\infty}^{\infty} F(\xi\sigma) d\xi_\sigma} \frac{1 + \cos^2 2\theta}{1 + \cos 2\theta} 4\delta F Z^{-1} \operatorname{cosec} 2\theta. \tag{33}$$

The values of the integral in the numerator of Eq. (33) have been obtained by graphical integration of curves plotted from the data of Table VI, and are shown in columns 3 and 4 of Table IX. Columns 6, 7, and 8 of Table IX show the calculated and observed coefficients of reflection.

TABLE IX. *Calculation of R from Eq. (33) and comparison with observations.*

| Line | $\lambda$ | $\int_{-\infty}^{\infty}\Phi(\xi_{B\sigma})d\xi_{B\sigma}$ Darwin | Prins | $\frac{1+\cos^2 2\theta}{1+\cos 2\theta}$ | $R\times10^5$ Darwin | Prins | Obs. |
|---|---|---|---|---|---|---|---|
| W $K\alpha_1$ | 0.209A | 1.631 | — | 0.999 | 0.536 | — | 1.17 |
| Mo $K\alpha_1$ | 0.708 | " | 1.537 | 0.987 | 1.85 | 1.84 | 1.86 |
| Cu $K\alpha_1$ | 1.54 | " | 1.238 | 0.940 | 3.87 | 3.49 | 3.46 |
| Cr $K\alpha_1$ | 2.28 | " | 0.917 | 0.881 | 5.65 | 4.53 | 4.68 |

A graph of the information in Table IX, together with $R$ values measured by other observers is shown in Fig. 6. Only the experimental data obtained in these experiments on crystals III are included in Fig. 6.

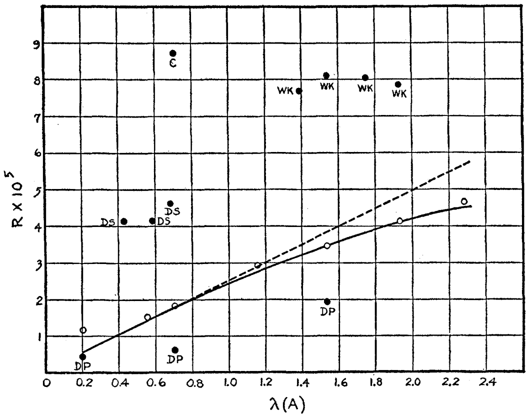

Fig. 6. Calculated and observed values of the coefficient of reflection ($R$). The dotted curve represents values calculated from Darwin; the solid curve, values from Prins. The open circles are experimental values of crystals III. The solid circles are points by other observers. *C*—Compton;[1] *WK*—Wagner and Kuhlenkampff;[1] *DS*—Davis and Stempel;[1] *DP*—Davis and Purks.[1]

## Discussion of results

The most obvious comment to be made on the agreement of observed and calculated coefficients of reflection from 0.5 to 2.3 A as illustrated for crystals III on Fig. 6 is that the agreement is very surprising since no temperature corrections have been applied. The coefficient of reflection should decrease with rising temperature. The calculation of the temperature correction for a complicated crystal such as calcite is difficult and has not been attempted. The value of $(\sin \theta)/\lambda$ for all the present measurements is 0.165 which is comparatively small, and the temperature correction is proportional to this. There is, however, some evidence that the value $FZ^{-1}=0.47$ used here is too small. This value was based on the structure factors of Bragg and West.[12] More recently James and Brindley[18] and Pauling and Sherman[19] have published tables of structure factors. The exact value of $FZ^{-1}$ depends on the particular electronic structure assumed for the molecule $CaCO_3$ as it appears in the crystal. By assuming arrangements from $Ca^{+2}$, $C^{+4}$, $O^{-2}$ to $Ca^0$, $C^0$, $O^0$ we get values of $FZ^{-1}$ which in the table of James and Brindley range from 0.472 to 0.500, and from 0.496 to 0.518 in the table of Pauling and Sherman. If these newer structure factors are preferable to the older values, the value of 0.47 as used in this paper is somewhat too low.[20] It is quite possible that this choice of a low structure factor is compensated by failure to make a temperature correction, thus giving the agreement of Fig. 6. This agreement does not extend to wave-lengths as short as W $K\alpha_1$ (0.2086A), and large deviations are apparent in the quantities plotted in Fig. 5 at this wave-length also. The laws of scattering of these relatively hard wave-lengths are undoubtedly different from the laws applicable in the range 0.5 to 2.3A, a large fraction of the scattering taking place by the Compton process. It is the opinion of the author that this lack of agreement shows that the theory of diffraction by a perfect crystal should be re-investigated in this shorter wave-length region.

If the coefficients of reflection observed by Davis and Purks and entered in Fig. 6 are correct,[21] they present a very serious difficulty, since they are far below the perfect crystal values. The Davis and Purks rocking curve widths for W $K\alpha_1$ $(1, -1)$ were 2.5 seconds full widths at half maximum. The author has been unable to find any calcite specimens that even approach this small value, the values obtained ranging from 4.6 to 14.4 seconds in various specimens. The high values of the coefficient of reflection observed by other authors and entered in Fig. 6 are probably due to the use of calcite surfaces considerably less perfect than those used in the present experiments.

The general statement that these results confirm Prins' modification of Darwin's theory is incorrect in a very important aspect. The present results show that some sort of absorption correction to Darwin's results is needed, but really give no information at all as to the exact shape of the diffraction pattern from a single crystal. In particular, the present results give no information for or against the asymmetrical nature of the patterns in Prins' theory. The fact that the calculated and observed values of $P_0$ are appreciably dif-

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[18] James and Brindley, Phil. Mag. **12**, 81 (1931).

[19] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

[20] I am indebted to W. H. Zachariasen of this laboratory for stimulating discussions of these matters.

[21] Recent communications from Professor Davis state that on repeating the experiments of Davis and Purks under discussion, the rocking curves from the same sample of calcite were found to be wider than at first reported.

ferent for wave-lengths other than Cr $K\alpha_1$ (at Mo $K\alpha_1$ calculated, 0.776; observed, 0.63) may be taken as evidence that the shape of the single crystal diffraction pattern is not exactly that of Prins. The value of $P_0$ is quite sensitive to the shape of the pattern, and independent of the polarization. For instance, let us compare three functions all having maxima equal to unity. If the shape of the diffraction pattern for a single crystal were given by exp $(-\xi^2)$, we should find $P_0=0.71$ from Eq. (26). In the same way if $F(\xi)=(1+\xi^2)^{-1}$, $P_0=0.500$, and if $F(\xi)=(1+\xi^2)^{-2}$, $P_0=0.625$.

A further question of interest is related to the possibility of finding other calcite surfaces as good as those of calcites III in this research. A. H. Compton[3] has reported rocking curves for Mo $K\alpha_1$ $(1, -1)$ of 5 seconds full width at half maximum which agrees with the present results. Hoyt[22] has reported rocking curves under the same conditions somewhat less than 5 seconds wide. Allison and Williams,[1] found a full width at half maximum of 6 seconds. In view of these results it does not seem that such calcite surfaces are exceedingly rare. There is no evidence from the experiments reported here that the width of the rocking curve is a constant for a given piece of calcite, that is, a large sample from a known source. In the author's experiments different splits from the same large piece showed different widths.

Darwin, and other workers following him, have interpreted high values of $R$, for instance, those of Wagner and Kuhlenkampff in Fig. 6, as evidence for a mosaic structure of crystals. The present research shows that it is possible to obtain calcite surfaces for which there is no evidence of mosaic structure from measurements of the coefficient of reflection by double spectrometer methods in the wave-length region from 0.5 to 2.3A. Presumably the effects of a secondary structure as postulated by Zwicky[23] would not influence the present results.

*Note added in proof:* Since completion of this article more accurate calculations of theoretical curves have been carried out by eliminating the assumption of Eq. (17). This assumption states that the absorption correction can be rightly applied by assuming that the absorption of an atom in the unit cell is proportional to the fraction of the total number of electrons in the unit, all contained in the atom in question. This is rather far from correct in the absorption by the calcium atoms in calcite for wave-lengths shorter than the $K$-absorption limit of calcium. The more rigorous calculations direct from Eq. (15) show slight changes in the theoretical values, but do not invalidate in any way the general conclusions of this article. These new calculations will appear in a paper to be submitted from this laboratory in the near future.

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[22] A. Hoyt, Paper delivered at the Washington Meeting of the American Physical Society, April, 1932.

[23] Zwicky, Phys. Rev. **40,** 63 (1932).

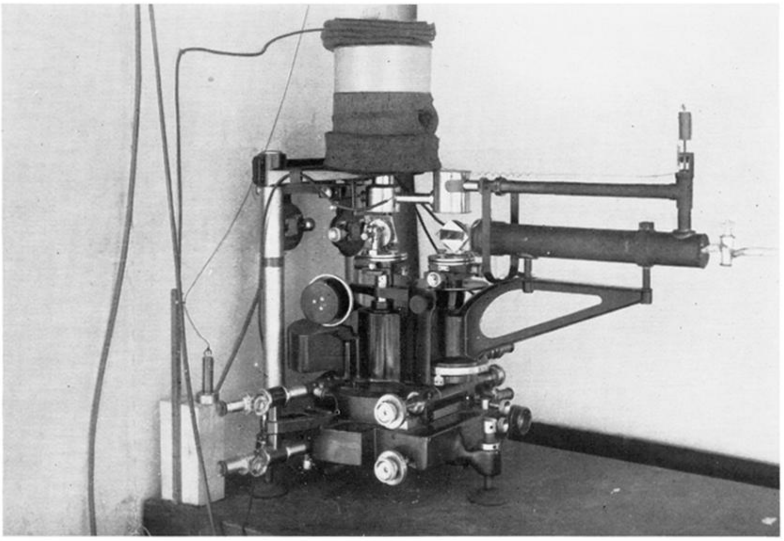

Fig. 1. The double spectrometer. The electrometer (above) is wrapped with wadding to protect it from sudden temperature changes. The instrument stands on a heavy stone slab mounted on concrete piers. The distance from the top of this slab to the shelf supporting the electrometer is 54 cm. Behind the instrument is a lead covered room in which the x-ray tubes are operated.