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X-Ray Diffraction from Calcite for Wave-Lengths 1.5 to 5 Angstroms

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Theoretical expressions for the coefficient of reflection, percent reflection, and width of the line to be expected from the second crystal of a double spectrometer in the (1, −1) position, based on Darwin's theory of reflection from a perfect crystal, as modified by Prins, are evaluated for calcite for six lines in the region 1.54 to 5A. This region includes, at 3.06A, the critical absorption limit of calcium. With a specially designed double-crystal spectrometer, these properties of the rocking curve from the second crystal for ten wave-lengths, copper $K\alpha$ radiation and nine spectrum lines selected from the uranium M series, are experimentally measured and these results compared with the calculated values. The agreement between the observed and calculated rocking curve widths is excellent throughout the entire region and gives no evidence of mosaic structure in the crystals. The calculated values of percent reflection are consistently above those observed by some 16 percent. Good agreement is obtained for the values of the coefficient of reflection for wave-lengths shorter than 4A including those close to and on either side of the calcium absorption limit. No correction for temperature motion of the atoms has been attempted, but it seems possible that such a correction would give very satisfactory agreement between theory and experiment, showing that calcite surfaces may be obtained for which there is no evidence of mosaic structure from the diffraction of x-rays.

INTRODUCTION

IMMEDIATELY following Bragg's interpretation of the Laue spots in 1912, Darwin attacked the problem of accounting theoretically for the intensity distribution in the diffraction pattern. The original theory developed by Darwin[1,2] is based essentially on the classical treatment of x-rays as a branch of optics and on the assumption of a perfect crystal,[3] and, while the theory is now considered a classic in x-ray reflection, the conclusions and predictions derived, with the exception of the refractive index, did not conform with experiment. Because of the great importance of this problem its solution was pursued by many investigators, mostly from the experimental approach, but the discrepancy between theory and experiment, though considerably decreased with the accumulation of more reliable data, has continued to exist. Darwin explained this discrepancy with the concept of mosaic structure present in real crystals. In 1926, the status of the problem was expressed by Professor A. H. Compton as ". . . there thus seems little hope of being able to apply the theory for a perfect crystal strictly to any real crystal."[4]

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

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

[3] A perfect crystal is defined as one having no grating distortion, no temperature motion of the atoms, of infinite dimensions, and with the reflecting surface defining a grating plane.

[4] A. H. Compton, *X-Rays and Electrons*, D. Van Nostrand Co., page 143, 1926.

In 1930 Prins[5] offered a modification of Darwin's classical electromagnetic treatment by introducing the effects of absorption of the x-rays in the crystal, and, as has been recently pointed out by Allison,[6] the necessity of the concept of mosaic structure, at least in certain specimens of calcite crystals, is no longer acute. It is the purpose of this paper to show what agreement between the modified theory and experiment has been reached for calcite in the wavelength region of 1.5 to 5 angstroms, including at 3.06A, the critical absorption limit of calcium.

THEORETICAL DISCUSSION

To facilitate an understanding of the essentials of this problem, a brief resume of Darwin's treatment is given.

Monochromatic radiation, in the form of plane waves, making a glancing angle near the Bragg angle on a perfect, non-absorbing crystal, is partially reflected and partially transmitted. The intensity of the transmitted component, in passing through the crystal, is diminished by partial reflection at every internal grating plane it encounters; and also, the inverse process is present, defeating the endeavors of the internally reflected components to emerge from the surface and contribute to the intensity of the beam reflected from the crystal as a whole. This interplay between the transmitted and reflected beams was expressed by Darwin through two simultaneous difference equations in terms of the amplitudes T_r and S_r of the transmitted and reflected rays, and the number of grating planes r, measured from the surface, involved in the process. The solution of the equations expresses directly the ratio of these amplitudes for $r=0$, at the surface of the crystal, in a complex quantity since the phase difference of the scattered rays occurs intimately throughout the analysis. The ratio of the intensities of the beams incident on and reflected from the crystal, taken as the square of the modulus of the complex expression, is given in the Darwin equation, with slight change in notation,

$$\frac{I_{\Delta\theta}}{I_0} = \left[\frac{S_0}{T_0}\right]^2 = \left[\frac{a}{\sin\theta_0\cos\theta_0\Delta\theta - \delta \pm \left[(\sin\theta_0\cos\theta_0\Delta\theta - \delta)^2 - a^2\right]^{1/2}}\right]^2 \qquad (1)$$

in which the variable, $\Delta\theta$, is the deviation of the glancing angle of the radiation on the crystal from the angle θ_0 defined by $n\lambda = 2d\sin\theta_0$; δ represents the deviation of the refractive index n from unity $(n=1-\delta)$; and a is the quantity defined by $a/\delta = f(2\theta_0)/f(0)$ where $f(2\theta_0)/f(0)$ is the ratio of the amplitude of a wave scattered by the atom at an angle $2\theta_0$ to that scattered in the forward direction of the incident beam, or, in other words, at zero scattering angle. The sign of the radical is determined by the physical requirement of the conservation of energy, that $I_{\Delta\theta}/I_0$ be always less than or equal to unity.

Obviously the polarization of the incident beam will affect the quantity a and we must further qualify a by the relation $a = Q\delta(F/Z)$ in which Q is the

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

[6] Allison, Phys. Rev. **41**, 1 (1932).

polarization factor, equal to cos $2\theta_0$ and to unity for the two polarized components π and σ, respectively, in which the directions of oscillations of the electric vectors are parallel and perpendicular to the plane of incidence of the radiation on the crystal. The term F/Z is the atomic structure factor divided by the number of electrons in the atom, and is equal to the ratio $f(2\theta_0)/f(0)$ for the σ component.

If we desire to study characteristic radiation, which we know to be completely unpolarized, Darwin's Eq. (1) is to be written in the form

$$\frac{I_{\Delta\theta}}{I_0}=\frac{1}{2}\left[\frac{(F/Z)\delta}{\sin\theta_0\cos\theta_0\Delta\theta-\delta\pm[(\sin\theta_0\cos\theta_0\Delta\theta-\delta)^2-(F^2/Z^2)\delta^2]^{1/2}}\right]^2$$
$$+\frac{1}{2}\left[\frac{(F/Z)\delta\,|\cos 2\theta_0|}{\sin\theta_0\cos\theta_0\Delta\theta-\delta\pm[(\sin\theta_0\cos\theta_0\Delta\theta-\delta)^2-(F^2/Z^2)\delta^2\cos^2 2\theta_0]^{1/2}}\right]^2 . \quad (2)$$

Examination of this Eq. (2) shows that a region of 100 percent reflection exists for each polarized component. The angular extents of these regions are $4\delta(F/Z)$ csc $2\theta_0$ and $4\delta(F/Z)$ cot $2\theta_0$ for the σ and π components, respectively. The intensity distribution of each of the terms in (2) is symmetrical about the corrected Bragg angle θ ($\theta=\delta \sec\theta_0 \csc\theta_0+\theta_0$). The refractive index is implied in the displacement of the axis of symmetry of the diffraction pattern from θ_0 to θ.

Prins' modification

Darwin considered the effect of absorption of the x-rays within the crystal upon his Eq. (1) but concluded that this introduced no essential modification. However, it should be pointed out that Darwin attempted to correct for absorption by assuming that the absorption coefficient accounted for a decrease in intensity quite independent of that due to scattering, which was already adequately treated in the difference equations. Prins reasoned that, in view of our present knowledge, the absorption coefficient includes absorption of two types: first, a coherent process or a diminution of intensity due to interference between the rays coherently scattered at zero scattering angle and the rays of the incident beam, and second, an incoherent or quantum process, such as photoeffect, recoil electrons, etc. Both types of processes must be included in a complete treatment of the problem.

The classical theory of dispersion expresses the index of refraction as a complex quantity, $n=1-\delta-i\beta$, of which the real part, $1-\delta$, is the ordinary refractive index. The coefficient β in the imaginary term, known as the absorptive index, is defined in the relation $\beta=\mu_l\lambda/4\pi$, in which μ_l is the linear absorption coefficient of the medium for radiation of wave-length λ. This classical expression for the index of refraction does not admit of incoherent absorption; however, Prins takes advantage of the experimental value of μ_l, which does include both types of absorption, and replaces δ in Darwin's Eq. (2) by $\delta+i\beta$, thereby incorporating in the theory a correction for incoherent absorption. When this substitution is effected, a similar replacement of a by $a+ib$ must be made because of the relation between a and δ just defined. The quantity b is considered later.

Prins' equation, or the modified Darwin Eq. (1), appears as[7]

$$\frac{I_{\Delta\theta}}{I_0}=\left[\frac{a+ib}{\sin\theta_0\cos\theta_0\Delta\theta-\delta-i\beta\pm\left[(\sin\theta_0\cos\theta_0\Delta\theta-\delta-i\beta)^2-(a+ib)^2\right]^{1/2}}\right]^2. \quad (3)$$

In accord with the previous discussion, this expression applies to the σ-component of polarization only; a similar expression in which $(a+ib)|\cos 2\theta_0|$ is written in place of $(a+ib)$ takes care of the π-component.

We are next confronted with the questions (1) of the phase relations of the scattered waves as a function of the scattering angle, (2) whether or not each electron can be treated as scattering separately, and (3) will the electronic structure factor F/Z be constant for all electrons in the atom irrespective of their various binding energies and different dimensions of the electron shells. We shall assume that the phase shift of coherently scattered radiation is the same in all directions, and that the amplitude scattered as a function of the scattering angle is the same for all electrons. This hypothesis leads to the relation[8]

$$(a+ib)/(\delta+i\beta)=f(2\theta_0)/f(0) \quad (4)$$

for the σ-component, where $f(2\theta_0)/f(0)$ is the ratio of the amplitude scattered at angle $2\theta_0$ to that scattered at zero angle.

Application to a real crystal—Calcite

It will be remembered that thus far we have dealt with reflection from that type of perfect crystal in which the atoms are of one kind only. In order for the equations to apply to a complex crystal, such as calcite, which consists of interlaced planes of different kinds of atoms, certain modifications must be made. We have written $(a+ib)$ as a summation over the various types of electrons in the atom, and we must now sum over the various types of atoms in the unit cell. In place of $(a+ib)$ we shall introduce a quantity $(A+iB)$ defined as

$$\begin{aligned} A+iB &= \sum_j (a_j+ib_j) \\ &= \sum_j (\delta_j+i\beta_j)\left[f_j(2\theta_0)/f_j(0)\right]\exp 2\pi ni(hx_j+ky_j+lz_j) \end{aligned} \quad (5)$$

in which δ_j is the contribution to δ of atom j; n the order of reflection; h, k, l the Miller indices of the reflecting plane; and x_j, y_j, z_j the coordinates of atom j in the unit cell. The summation is to be taken over all the atoms in the unit cell of the crystal.

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[7] This is Eq. (11) in Prins' article, reference 5.

[8] It should be made clear that the writing of this relation (4) implies a somewhat dogmatic answer to each of the three above questions, and that a more accurate working hypothesis would be to consider each shell of electrons separately, both as regards the contributions to δ and β, and also with respect to the electronic structure factor. Then $(a+ib)$ would be written $a+ib=\sum_j (F/Z)_j(\delta_j+i\beta_j)$ where the summation extends over all the electrons of the atom in question.

Alteration of the form of the equation

Before making the numerical calculations of the various quantities for calcite, let us derive the expressions for three important cnaracteristic properties of the theoretical diffraction pattern of the crystal: the percent reflection, the coefficient of reflection, and the width at half-maximum intensity of the reflected line.

First we shall reduce the equation to a less ponderous form. Introduce another variable, x, defined as $x \equiv \sin\theta_0 \cos\theta_0 \Delta\theta/\delta$. The old variable, $\Delta\theta$, expressing in radians the deviation of the glancing angle from the angle θ_0 (given by $n\lambda = 2d \sin\theta_0$), has θ_0 as its reference origin. The variable x has the same reference origin, but represents the fractional deviation of the glancing angle, the unit of deviation being ($\delta \sec\theta_0 \csc\theta_0$). A further change of variable to establish the position θ as the reference origin will be found convenient. We shall define a new variable, l

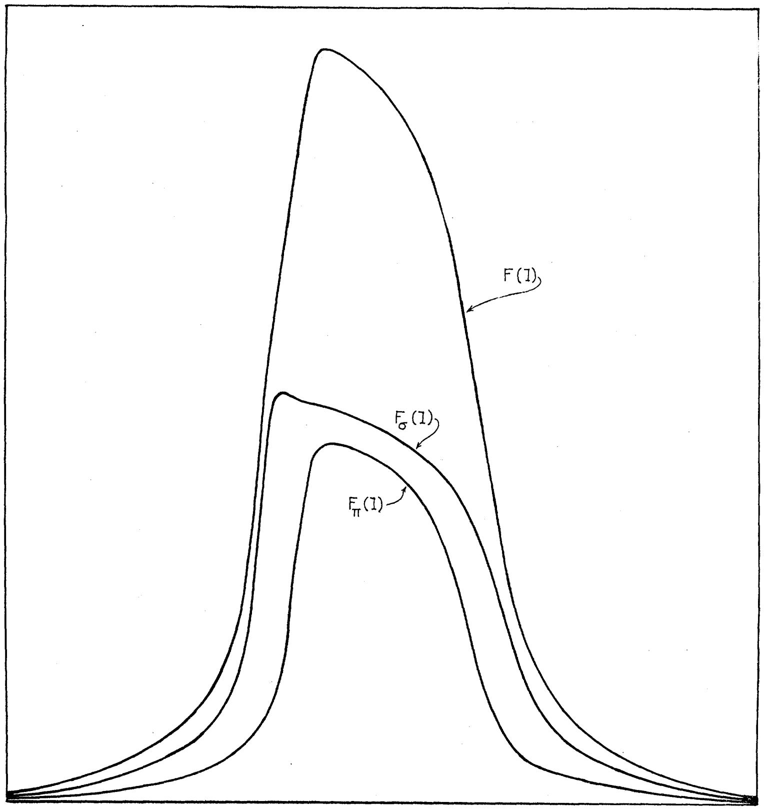

Fig. 1. Theoretical diffraction pattern from a single calcite crystal for $\lambda = 2.299$A. The outer curve, governed by the function $F(l)$, is the sum of the two polarized components, $F_\sigma(l)$ and $F_\pi(l)$. The values of the coordinates from which these curves are plotted are listed in Table I.

$$l \equiv x - 1 = \sin\theta_0 \cos\theta_0 \Delta\theta/\delta - 1. \tag{6}$$

Then Eq. (3) reduces to the form, in l,

$$F_\sigma(l) = \left(\frac{I_l}{I_0}\right)_\sigma = \left[\frac{(A + iB)/\delta}{l - i\beta/\delta \pm \{(l - i\beta/\delta)^2 - [(A + iB)/\delta]^2\}^{1/2}}\right]^2. \tag{7}$$

Physically, $F_\sigma(l)$ is the ordinate of a point, for a given value of l, on the curve of the diffraction pattern to be expected for σ-polarized radiation reflected from a single crystal. This is the form of the equation we shall use throughout the remainder of this paper. As before, the π-component is expressed by a similar function $F_\pi(l)$ obtained by replacing $A + iB$ by $(A + iB) |\cos 2\theta_0|$ in (7). The two components and their sum are plotted for $\lambda = 2.299$A in Fig. 1, and the values of the coordinates from which these curves are drawn are given in Table I.

Percent reflection

The three properties, percent reflection, coefficient of reflection, and line width of the rocking curve, are experimentally determined with a double-crystal spectrometer, by a method to be discussed in the experimental part of this paper. Hence, for purposes of comparison between theory and experiment, it is desired to obtain expressions for the intensity distribution in the theoretical diffraction pattern as formed by the second crystal, or in twice-reflected radiation.

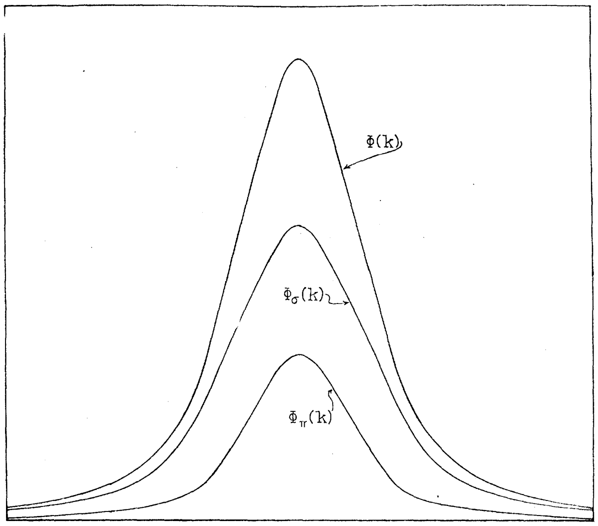

Fig. 2. Theoretical diffraction pattern from a second calcite crystal for $\lambda = 2.299$A. The polarized components represented by the function $\Phi_\sigma(k)$ and $\Phi_\pi(k)$ are added together to give the total theoretical diffraction pattern drawn as the outer curve. This pattern is to be compared with the experimental rocking curve obtained with the double-crystal spectrometer in the (1, −1) position. The coordinate values used in plotting these curves are given in Table I.

The total integrated intensity of a characteristic x-ray line reflected from the first crystal is given by

$$\int_{-\infty}^{\infty} F(l)dl = \tfrac{1}{2}\int_{-\infty}^{\infty} F_\sigma(l)dl + \tfrac{1}{2}\int_{-\infty}^{\infty} F_\pi(l)dl \tag{8}$$

assuming that each polarized component of the incident beam is of equal intensity. This expression (8) also represents the total intensity incident upon the second crystal of the spectrometer.

To treat the reflection from the second crystal, we shall introduce a new variable, k, defined as the deviation, measured in the same units as l, of the glancing angle of the radiation on the second crystal from that angle for which the two crystals are parallel. The doubly reflected intensity is given, considering both components of polarization, by

$$\Phi(k) = \tfrac{1}{2}\Phi_\sigma(k) + \tfrac{1}{2}\Phi_\pi(k) = \tfrac{1}{2}\int_{-\infty}^{\infty} F_\sigma(l)F_\sigma(l-k)dl + \tfrac{1}{2}\int_{-\infty}^{\infty} F_\pi(l)F_\pi(l-k)dl. \tag{9}$$

The function $\Phi(k)$ for a given value of k, is the ordinate of a point on the curve of the theoretical diffraction pattern from the second crystal. The two components and their sum, representing the complete theoretical diffraction pattern are plotted for the wave-length $\lambda = 2.299$A in Fig. 2, and the coordinate values used are given in Table I.

TABLE I. *Theoretical diffraction pattern formed by a single calcite crystal for $\lambda = 2.299A$.*

l	$F_\sigma(l)$	$F_\pi(l)$	$F(l)$
2.5	0.010	0.005	0.015
2.0	0.015		
1.5	0.030	0.015	0.045
1.0	0.073	0.035	0.108
0.8	0.125	0.057	0.182
0.7		0.076	
0.6	0.268	0.090	0.358
0.5	0.428	0.170	0.598
0.4	0.581	0.300	0.881
0.3	0.672	0.495	1.167
0.2	0.727	0.617	1.344
0.1	0.766	0.684	1.450
0.0	0.795	0.725	1.520
−0.1	0.818	0.750	1.568
−0.2	0.839	0.766	1.605
−0.3	0.851	0.722	1.573
−0.4	0.871	0.370	1.241
−0.5	0.727	0.179	0.906
−0.6	0.299	0.111	0.410
−0.7		0.077	
−0.8	0.126	0.057	0.183
−1.0	0.074	0.035	0.109
−1.5	0.030	0.015	0.045
−2.0	0.015		
−2.5	0.010	0.005	0.015

Theoretical diffraction pattern formed by a second calcite crystal for $\lambda = 2.299A$.

k	$\Phi_\sigma(k)$	$\Phi_\pi(k)$	$\Phi(k)$
0.0	0.6310	0.3565	0.9875
±0.2	0.5800	0.3185	0.8985
±0.4	0.4886	0.2335	0.7221
±0.6	0.3876	0.1510	0.5386
±0.8	0.2660	0.0815	0.3475
±1.0	0.1735	0.0480	0.2215
±1.5	0.0686	0.0220	0.0906
±2.0	0.0368	0.0120	0.0488
±2.5	0.0218	0.0050	0.0268

The percent reflection is defined as the ratio (multiplied by 100) of the maximum reflected intensity to the intensity of the beam incident upon the crystal. In the diffraction equations, the maximum intensity is reflected when $k = 0$, and the expression[9] for percent reflection P becomes

$$P = \frac{\int_{-\infty}^{\infty} F_\sigma^2(l)dl + \int_{-\infty}^{\infty} F_\pi^2(l)dl}{\int_{-\infty}^{\infty} F_\sigma(l)dl + \int_{-\infty}^{\infty} F_\pi(l)dl}\,. \tag{10}$$

Coefficient of reflection

The coefficient of reflection is defined as the ratio of the integrated intensity of the beam reflected from the second crystal to the intensity of the beam reflected from the first crystal only. The integrated intensity from the second crystal refers to the area under the rocking curve obtained by varying k throughout the entire region of reflection. Hence, the expression[9] for the coefficient of reflection R can be written

$$R = \delta \sec \theta_0 \csc \theta_0 \frac{\int_{-\infty}^{\infty} \Phi_\sigma(k)dk + \int_{-\infty}^{\infty} \Phi_\pi(k)dk}{\int_{-\infty}^{\infty} F_\sigma(l)dl + \int_{-\infty}^{\infty} F_\pi(l)dl} \cdot \tag{11}$$

in which $\Phi_\sigma(k)$ and $\Phi_\pi(k)$ are defined in Eq. (9). The unit of angular measure, $\delta \sec \theta_0 \csc \theta_0$, is placed in the expression (11) in order to convert the units of the coefficient of reflection into radians.

Width of diffraction pattern

Eq. (9) when plotted for various values of k gives the contour of the theoretical diffraction pattern of an x-ray line reflected from the second crystal, Fig. 2. From this graph the width at half-maximum is obtained in terms of the variable k, and is converted into radians by multiplying by the angular unit $\delta \sec \theta_0 \csc \theta_0$. This value, $W_{1/2}$,

$$W_{1/2} = [W_k]_{1/2}\delta \sec \theta_0 \csc \theta_0 \tag{12}$$

should correspond with the width at half-maximum of the ionization rocking curve of the x-ray line measured with the double-crystal spectrometer in the $(1,-1)$ position.

CALCULATIONS

As Allison[6] points out, the shape of the rocking curve obtained experimentally with a double spectrometer in the parallel position is not to be compared with that given in Fig. 1, but rather with the shape represented in

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[9] When obtaining the total reflected intensity from Darwin's Eq. (2), it is true that

$$\int_{-\infty}^{\infty} f_\pi(\Delta\Theta)d(\Delta\Theta) = |\cos 2\Theta_0| \int_{-\infty}^{\infty} f_\sigma(\Delta\Theta)d(\Delta\Theta)$$

and the integrated intensity reflected from a single crystal, assuming an unpolarized incident beam, can be written

$$J = (1 + |\cos 2\Theta_0|)/2 \int_{-\infty}^{\infty} f_\sigma(\Delta\Theta)d(\Delta\Theta).$$

However, when dealing with the complex expression of Eqs. (3), (7) or (9), this simple $\cos 2\theta_0$ relation between the two components is no longer true due to the fact that the integration must be performed along the real axis. Consequently, each component must be calculated separately. In Allison's recent paper,[6] the $\cos 2\theta_0$ relation is assumed to hold, and in consequence thereof, as Professor Allison himself points out in a letter to the editor in this issue of the Physical Review, his equations and computed values are somewhat in error.

Fig. 2 which is governed by the function $\Phi(k)$, Eq. (9). It would perhaps be a more direct comparison to determine experimentally the $\Phi(k)$ and, by means of Eq. (9), derive an experimental rocking curve from the first crystal which could then be compared with the theoretical function $F(l)$ represented in Fig. 1. However, this procedure has been shown[10] mathematically impossible unless $F(l)$ be assumed to be an even function, that is to say, symmetrical about the axis $l=0$, which assumption, of course, defeats the purpose. In this paper we shall take for granted the validity of Eq. (3) and, on this basis, calculate the $\Phi(k)$, then check the agreement between the values so computed and the experimental values. The three properties, percent reflection, coefficient of reflection, and line width, are chosen for this check because they are perhaps the most distinctive characteristics of the rocking curve that can be experimentally measured.

Evaluation of constants in $F(l)$

The values of the refractive index δ for calcite are taken directly from the experimental dispersion curve given by Larsson[11] in which values of δ/λ^2 are plotted in the region 1.5 to 4A. The δ/λ^2 values to 5A are taken from the curve plotted from classical dispersion theory.

A search through the literature for absorption coefficients of calcite in this wave-length was unsuccessful, and it was necessary to resort to an approximate method for their calculation. An extrapolation of the absorption coefficient of each element in the crystal using the λ^3 or the $\lambda^{2.8}$ law would yield values too much in error to be useful. Jönsson[12] in his investigations finds a linear relation between the product $Z\lambda$ and $(\mu_l/\rho)_K\,(W/AZ)$ where μ_l is the linear absorption coefficient, ρ the density of the element of atomic weight W and atomic number Z, and A Avogadro's number. The factor μ_l/ρ is expressed for the region between the K and L absorption limits, and if $(\mu_l/\rho)_L$ is desired $(\mu_l/\rho)_K$ must be converted to the L region by the factor E_K/E_L where E_K and E_L are the energies of the K and L levels respectively. Then, for any value of $Z\lambda$, determined by the element and wave-length in question, the corresponding value of $(\mu_l/\rho)_K$ is taken from Jönsson's tables. In this manner, the mass absorption coefficients of calcium, carbon, and oxygen are obtained for the wave-lengths selected in this study. The mass absorption coefficients are converted to atomic, and, by addition, the molecular, and, thence, the linear absorption coefficients of calcite are evaluated. This empirical method gives reasonably good values as checked (within approximately 5 percent) with Spencer's experimental measurements on oxygen and argon.[13]

The factor β, previously defined in the relation $\beta=\mu_l\lambda/4\pi$, is readily calculated as soon as μ_l is determined.

The evaluation of A and B, which have been defined in the summation (5) over the unit cell, is accomplished in the following manner.

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

[11] Axel Larsson, Inaugural-Dissertation, Uppsala (1929).

[12] Edvin Jönsson, Inagurual-Dissertation, Uppsala (1928).

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

The quantity δ_j may be considered as the deviation of the index of refraction from unity for a substance formed by removing all the atoms from the calcite unit cell except the atom j. The unit cell of calcite contains two molecules of $CaCO_3$. All the electrons in the oxygen and carbon atoms are so loosely bound with respect to the quantum energies of the wave-lengths employed in these experiments that their dispersion may be considered normal. This means, taking carbon as an example, that[14]

$$\delta_c = (e^2\lambda^2/2\pi mc^2)N_c \tag{13}$$

where N_c is the number of electrons per cubic centimeter in calcite due to one of the carbon atoms in the unit cell. As mentioned above, the calculations are carried out on the assumption that each atom in the crystal contains a number of electrons equal to its atomic number, that is, the calculations are made for non-ionized calcium carbonate. On this assumption

$$N_c = 6/v = 3A\rho/M \tag{14}$$

where V is the volume of the unit cell of calcite, M the molecular weight, A Avogadro's number, and ρ the density. The δ_j values for carbon and oxygen are calculated from Eqs. (13) and (14), and the value of δ_{ca} is then determined by subtracting $\delta_c+3\delta_O$ from the δ value observed by Larsson according to the formula

$$\delta_{ca} = \delta/2 - \delta_c - 3\delta_0. \tag{15}$$

The δ_j values employed here thus depend partly upon the classical dispersion theory and partly upon Larsson's experimental results.

The β_j values for each atom in the unit cell are determined from the linear absorption coefficients obtained by the method of Jönsson mentioned above.

By the factor $f_j(2\theta_0)/f_j(0)$ in Eq. (14) is meant the ratio of the amplitude scattered from the atom j at the scattering angle $2\theta_0$ to that scattered in the forward direction. This ratio is evaluated from tables of structure factors.[15,16] The recent work of Glocker and Schäfer[17] indicates that this ratio is a function of wave-length and changes near a critical absorption discontinuity of the atom. We shall not attempt to take this effect into consideration, due to the small amount of data available, and shall apply the same values to all wave-lengths in the calculations.

We have assumed the electronic structure of calcite to be $Ca^0C^0O_3^0$, and by averaging the values in the structure factor tables referred to above, we obtain

$$\frac{f_{ca}(2\theta_0)}{f_{ca}(0)} = 0.768$$

$$\frac{f_c(2\theta_0)}{f_c(0)} = 0.650 \tag{16}$$

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[14] A. H. Compton, reference 4, page 210.

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

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

[17] Glocker and Schäfer, Zeits. f. Physik **73**, 289 (1931).

$$\frac{f_O(2\theta_0)}{f_O(0)} = 0.775.$$

The exponential term in Eq. (5) expresses the phase differences between the waves scattered from the several atoms in the unit cell. The coordinates of the atoms are

Calcium	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$
Carbon	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Oxygen	$\frac{1}{4}$	$\frac{\bar{1}}{4}$	0	$\frac{\bar{1}}{4}$	0	$\frac{1}{4}$
	0	$\frac{1}{4}$	$\frac{\bar{1}}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{2}$
	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{3}{4}$

Substituting these coordinates in the exponential term we find that the waves scattered from the two calcium atoms reinforce each other in the first order; and likewise for the two carbon atoms. The contributions of four of the six oxygens disappear by destructive interference, leaving only two oxygen atoms effectively scattering. The expansion of Eq. (12) therefore takes on the form

$$A + iB = 2\left[(\delta_{ca} + i\beta_{ca})\frac{f_{ca}(2\theta_0)}{f_{ca}(0)} + (\delta_c + i\beta_c)\frac{f_c(2\theta_0)}{f_c(0)} + (\delta_O + i\beta_O)\frac{f_O(2\theta_0)}{f_O(0)}\right] \tag{17}$$

and the summation can now be accomplished. The constants A and B are determined by equating them to the real and to the coefficient of the imaginary terms respectively.

The calculations outlined above yield the following values, presented in Table II, for the six selected wave-lengths:

TABLE II. *Evaluation of the constants in Eqs. (7) and (9) for calcite.*
λ = wave-length; θ = glancing angle; μ_l = linear absorption coefficient;
δ = deviation of refractive index from unity.

λ (angstroms)	$\lvert\cos 2\theta\rvert$	δ $\times 10^6$	μ_l	β/δ (cm)	A $\times 10^6$	B $\times 10^6$
1.537	0.8712	8.753	208	0.0211	4.457	0.185
2.299	0.7120	19.21	615	0.0424	9.716	0.815
2.941	0.5286	28.32	1190	0.0710	13.50	2.010
3.114	0.4716	32.59	265	0.0106	15.78	0.345
3.902	0.1702	53.47	493	0.0149	26.54	0.795
4.937	0.3283	86.60	890	0.0207	43.20	1.792

Calculation of R, P, and $W_{1/2}$

All the constants in the functions $F(l)$ and $\Phi(k)$ are now determined and the theoretical values for the percent reflection, Eq. (10), the coefficient of reflection, Eq. (11), and the width of the diffraction pattern, Eq. (12), can be calculated. The computations were carried out by laborious graphical integration,[18] and the results are presented in Table III.

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[18] The author wishes to express his indebtedness to Mrs. Ardis Monk, computor of this laboratory, for her generous cooperation in assisting with these calculations.

TABLE III. *Calculated values of R, P, and $W_{1/2}$ for calcite.*
R = coefficient of reflection (radians), P = percent reflection, $W_{1/2}$ = half width at half maximum intensity (seconds of arc).

λ (angstroms)	$\int_{-\infty}^{\infty} F_\sigma(l)dl$	$\int_{-\infty}^{\infty} F_\pi(l)dl$	$\int_{-\infty}^{\infty} F_\sigma^2(l)dl$	$\int_{-\infty}^{\infty} F_\pi^2(l)dl$	$\int_{-\infty}^{\infty} \Phi_\sigma(k)dk$	$\int_{-\infty}^{\infty} \Phi_\pi(k)dk$	Angular unit $\times 10^6$ radians	$W_{1/2}$	P	R $\times 10^5$ radians
1.537	1.16	1.00	0.824	0.678	1.34	0.983	35.65	4.94	69.2	3.82
2.299	1.03	0.677	0.631	0.357	1.06	0.456	54.71	7.45	57.7	4.86
2.941	0.86	0.340	0.425	0.107	0.695	0.114	66.73	8.61	44.3	4.49
3.114	1.14	0.510	0.829	0.315	1.28	0.243	73.91	8.70	69.1	6.80
3.902	1.13	0.120	0.796	0.041	1.28	0.0144	108.52	15.05	67.0	11.2
4.937	1.09	0.268	0.707	0.115	1.15	0.0715	183.13	23.50	60.4	16.4

EXPERIMENTAL PART

As was mentioned in the introduction of this paper, experimental work upon the problem of x-ray reflection from crystals has been undertaken by many investigators, but little agreement exists among the reported results. The experimental results for calcite are represented graphically in Fig. 6 of Allison's paper.[6] The inconsistencies of these results among themselves in all probability can be attributed to the various degrees of perfection in the crystals employed by the different investigators. The present experiments are an attempt to measure systematically the aforementioned three properties of reflection for one pair of calcite crystals through a comparatively large range of wave-lengths, from 1.5 to 5 angstroms. Allison has recently reported[6] a similar study for the same crystals, crystals II of his paper, in the region 0.21 to 2.28A using in his investigations a different double spectrometer. A second object of these experiments is to complete the calibration of the crystals for use in relative intensity measurements in the entire region 0.21 to 5 angstroms.

Apparatus

Air at atmospheric pressure is more or less opaque to x-rays of wave-lengths 2 to 5 angstroms and in order to perform these experiments a specially designed vacuum double-crystal ionization spectrometer was constructed. In Fig. 3 is given a photograph of this instrument. The two collimating slits, the two crystals, and the ionization chamber are supported on a heavy circular steel bed-plate, and a large metal cylindrical cap, shown in an elevated position in the photograph, can be lowered to the plate, enclosing the contents in an airtight chamber. The x-ray tube, with an uranium target whose position can be adjusted with respect to the tube itself while in operation by means of a sylphon connection, is clamped to the side of the cylindrical tank, and brought into alignment with the slits by sliding the tank on the stopcock grease which effects the seal between the tank and the bed-plate. Outside control of the second crystal and the ionization chamber is managed by having long, concentric tapered bearings, sealed with stop-cock grease, extending through the bed-plate. Details of the design and construction of this apparatus have been reported in an earlier paper by the author.[19]

Measurements

Nine lines selected from the uranium M series[20] from 2.299 to 4.937A and the copper $K\alpha$ radiation, 1.537A were used in the measurements. The lines of wave-lengths 1.537A and 2.299A overlap the region investigated by Allison,[6] and the good agreement between the results measured with the two different spectrometers can be considered experimental evidence that the properties of the rocking curves are really characteristic of the crystals themselves and not a function of the apparatus.

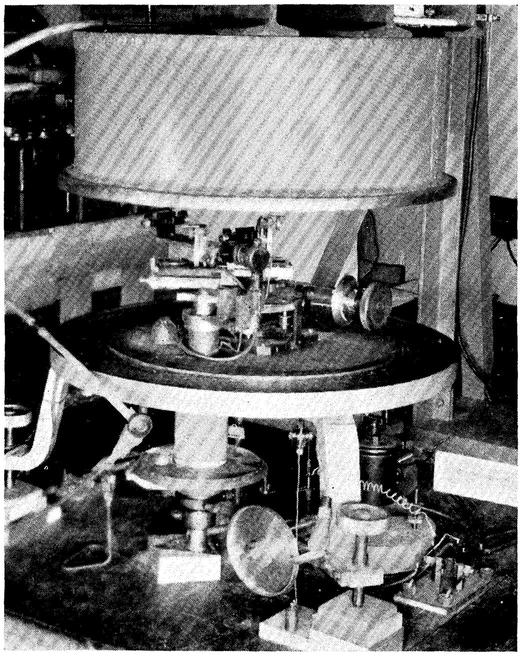

Fig. 3. Photograph of the double-crystal vacuum spectrometer.

By observing the ionization rocking curve obtained in the $(1, -1)$ position by rotating the second crystal throughout the entire range of reflection, and the intensity of the x-ray beam reflected from the first crystal only, that is, with the second crystal removed from its position so that it does not intercept the beam, one gathers all the data necessary for measurements of the percent reflection, the coefficient of reflection, and the width of the line. A regular routine, very similar to the one described by Allison,[6] was adopted in recording these data.

[19] Parratt, Phys. Rev. 41, 553 (1932).

[20] The wave-lengths of the uranium M series are taken from the tables of Siegbahn, *Spektroskopie der Roentgenstrahlen*, Julius Springer, 1931.

The accumulation of tungsten sputtered on the cellophane window between the x-ray tube and the tank, and also on the face of the target, absorbs the soft x-rays very strongly, and a correction for the exponential diminution of intensity due to this cause was found necessary. This correction was effected experimentally by taking a series of measurements with the x-ray tube operating smoothly and without change of power over a period of at least four hours and observing the intensity drop as a function of time.

In order to check the presence of any possible deterioration of the crystals, such as would affect their resolving power, measurements with the selected spectrum lines were taken in the order of increasing wave-length. About two months after the first measurements had been begun, a second series was completed, having taken the wave-lengths in the order opposite to that of the first. If the surfaces of the crystals had changed in this period of time a consistent deviation in the measured properties would have been apparent, particularly in the widths of the lines and in the percent reflection at the short wave-lengths. No such deviation was observed.

The experimental measurements are listed in Table IV. Each value is the average of at least two, usually five, independent observations. The values for the same properties computed from the theoretical equations are also included in the table for ease of comparison.

TABLE IV. *Experimental and calculated values of* $W_{1/2}$, P, *and* R.
$W_{1/2}$ = half-width at half-maximum intensity (seconds of arc), P = percent reflection, R = coefficient of reflection (in radians).

λ	$W_{1/2}$		P		$R\times10^5$	
A	obs.	calc.	obs.	calc.	obs.	calc.
1.537	5.00	4.94	60.5	69.2	3.80	3.82
2.299	7.50	7.45	50.7	57.7	4.81	4.86
2.745	9.10		43.1		4.62	
2.941	9.10	8.61	39.1	44.3	4.35	4.49
3.114	9.15	8.70	57.4	69.1	6.70	6.80
3.514	13.00		57.3		8.35	
3.708	14.20		57.7		9.30	
3.902	15.25	15.05	57.8	67.0	10.40	11.20
4.322	18.60		58.1		11.97	
4.937	23.70	23.50	51.0	60.4	14.00	16.40

DISCUSSION OF RESULTS

The experimental and calculated values of the three properties of reflection are presented graphically in Figs. 4, 5, and 6.

The agreement, close to experimental error, of the line widths throughout the entire region gives no evidence for the presence of mosaic structure in the crystals.

The calculated values of the percent reflection are consistently high, but this is not surprising when one considers that the percent reflection is particularly sensitive to the shape of the pattern, being proportional to the square of the ordinate, Eq. (10). This disagreement may be accounted for by the temperature motion of the atoms, to be discussed presently, or it may reflect an inherent inadequacy of Eq. (7) to correctly represent the diffraction pattern.

The comparison of the calculated and observed values of the coefficient of reflection should be considered in connection with the next paragraph. As seen in Fig. 6 the observed values lie below those calculated, and, in fact, another pair of calcite crystals, crystals III reported by Allison,[6] give experimental values of 3.46 and 4.68×10^{-5} radians for wave-lengths 1.537 and 2.285A, respectively, which are even lower than those observed for crystals II given in Fig. 6. This indicates that the theoretical values uncorrected for the kinetic motion of the atoms due to temperature are somewhat too high. The deviation at $\lambda=4.937$A between the two curves of Fig. 6 may be due to the uncertainty of the value of δ at this wave-length, the value used being taken from the theoretical dispersion curve since Larsson's work[11] did not

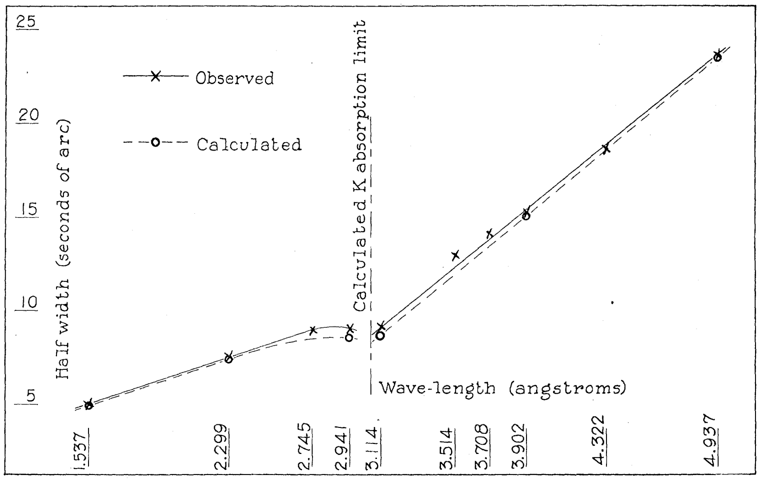

Fig. 4. Comparison of the observed and calculated half-width at half-maximum intensity ($W_{1/2}$) of the rocking curves obtained with the double-crystal spectrometer in the (1, −1) position. The differences are near the limit of experimental error. *Note added in proof:* "Calculated *K* absorption limit" should read "Calcium *K* absorption limit."

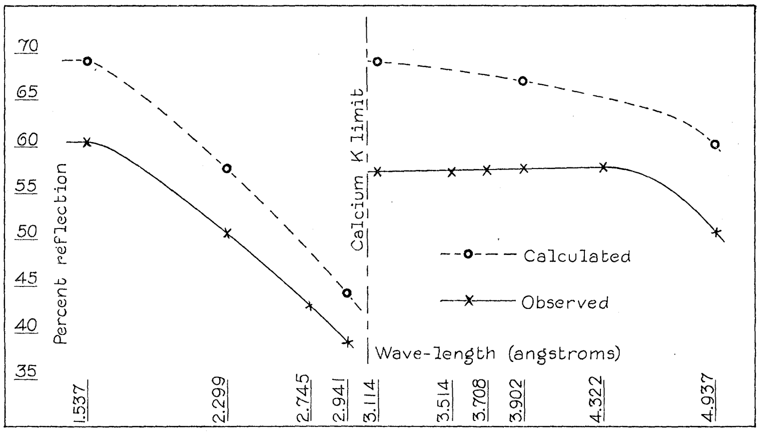

Fig. 5. Comparison of the observed and calculated percent reflection (P) of the rocking curves obtained with the double-crystal spectrometer in the (1, −1) position.

extend to this wave-length. Also there is reason to believe that the absorption coefficient is least reliable at this long wave-length.

In developing the equations on which the calculations are based, we considered reflection from a perfect crystal; and in the experimental measurements a real crystal is used. The differences between a real and a perfect crystal, for practical purposes, are present in the distortion of the grating planes, or the mosaic structure, and in the temperature motion of the atoms. In view of the excellent agreement in the width of the lines, Fig. 4, the mosaic structure in the specimens of calcite used in these experiments may be considered to be very small. A correction for temperature motion of the atoms in a calcite crystal is difficult to carry out, and has not been attempted in this paper. In general, the effect of raising the temperature of the crystal is to lower the values of percent reflection and coefficient of reflection leaving unaltered the width of the pattern, and it seems possible that such a correction for temperature would give very satisfactory agreement between theory and experiment with specimens of calcite in which the mosaic structure is a minimum.

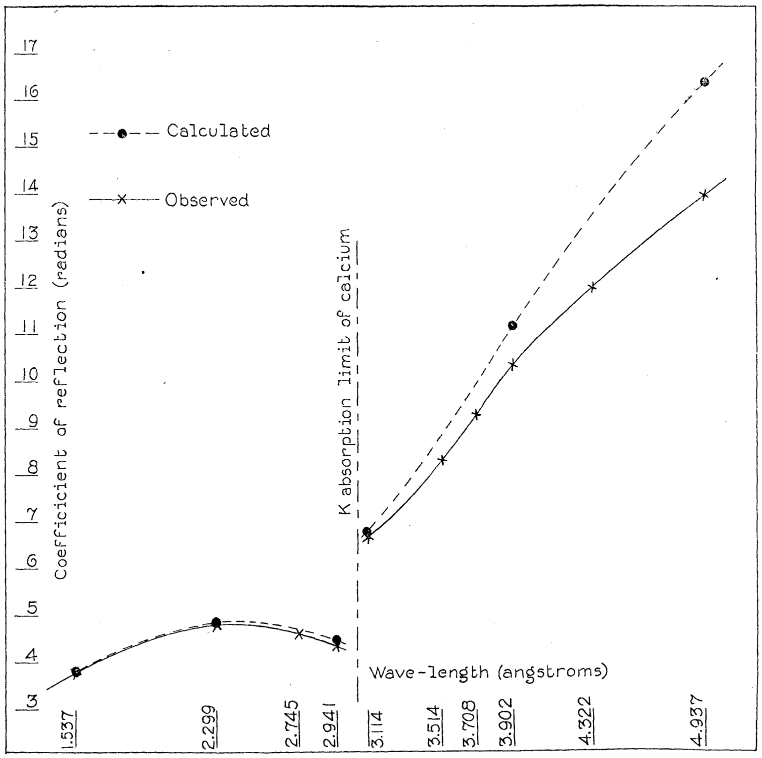

Fig. 6. Comparison of the observed and calculated coefficient of reflection ([illegible]) from the second crystal of the spectrometer. The differences for wave-lengths less than 3.902 A are within experimental error.

It is a pleasure to acknowledge the many essential suggestions and the constantly helpful advice and criticism which Professor S. K. Allison has offered in the course of this work.

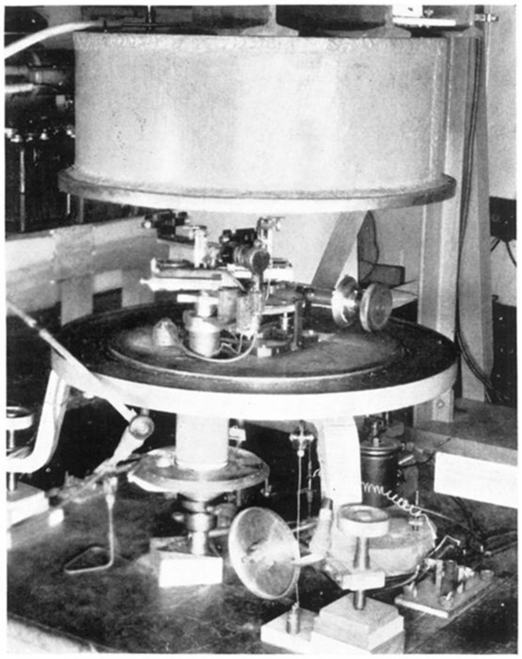

Fig. 3. Photograph of the double-crystal vacuum spectrometer.