INDEX OF REFRACTION OF CALCITE FOR X-RAYS

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Abstract

Index of refraction of calcite for MoKα_1 rays.—Previous work has indicated that in the case of first order reflection from calcite the bending due to refraction is only 3″. As suggested by Bergen Davis, however, the effect can be greatly increased by using a wedge shaped crystal with a surface ground and polished so as to make an angle φ with the cleavage planes slightly less than the angle of reflection. The first crystal was ground with φ equal to 5°48.3′ so that rays which entered at an angle of 12.5° with the surface, after first order reflection left making an angle of 54′ with the surface. The refraction bending was 29″. A second crystal was ground with $\varphi = 6°21.5'$ so that the glancing angle was only 21′ and the refraction bending was 64″. The lack of symmetry due to the refraction bending at one surface was determined either by rotating the crystal about a horizontal axis perpendicular to the crystal planes or by using two halves of a split crystal, one ground and the other with natural cleavage, placed one over the other so as to get reflection from each in turn. The mean result is $\mu = 1 - (2.03 \pm .1) \times 10^{-6}$. This agrees well with the value given by the Lorentz dispersion formula, $1 - 1.91 \times 10^{-6}$.

Wave-length of MoKα_1 corrected for refraction.—The correction is .017 per cent for first order reflection by calcite. Special measurements gave the corrected wave-length as .70772A (assuming $d = 3.028 \times 10^{-8}$), in good agreement with Duane's value.

SINCE the discovery of x-rays the question of their refraction has been of considerable interest to the physicist. Roentgen and others were satisfied that x-rays passed through matter without being refracted. This was explained on the assumption that the atoms contained no electrons whose natural frequencies were near those of x-rays a view in harmony with the earlier pulse theory of x-radiation. The above assumption is now known to be untenable.

Chapman[1] made the first effort to measure with any degree of precision the index of refraction of a substance for x-rays. He used a prism of ethyl bromide and concluded that the index differed from unity by less than 3×10^{-4}. Later Barkla[2] used two prisms of potassium bromide and showed that the index differed from unity by less than 5×10^{-6}. Webster and Clark[3] concluded from theoretical considerations that the maximum refractive effect of a resonance frequency was limited to a narrow band of the spectrum. Their results, using a rhodium prism, showed that the

[1] Chapman, Proc. Camb. Phil. Soc. (1912) p. 574
[2] C. G. Barkla, Phil. Mag. **31**, 257 (1916)
[3] D. L. Webster and H. Clark, Phys. Rev. **8**, 528 (1916)

index must differ from unity by less than 2×10^{-4} over quite a range of the spectrum.

Stenstrom[4] first noticed deviations from Bragg's relation, $n\lambda=2\,d\sin\theta$, and attributed them to the refractive effect. His method of measurement involved the determination of the relative displacement of the different orders of a characteristic radiation when reflected from the crystal to be tested. He gives values for the index of refraction of sugar crystals and of calcium sulphate for wave-lengths near 3 A. In the case of calcite, the displacements were very small when compared with the magnitude of the possible errors, so no actual value was obtained for the index. Darwin[5] seems to have been the first to point out that Bragg's relation cannot be strictly true and to give the relation between θ, the observed glancing angle, and θ_1 the glancing angle given by Bragg's relation as

$$\theta-\theta_1=\delta\,\mathrm{cosec}\,\theta\sec\theta$$

where $1-\delta$ is the index of refraction of the crystal for the x-rays. Duane and Patterson[6] and Siegbahn[7] have found that wave-lengths determined by Bragg's law differ slightly for different orders.

If a substance has a refractive index less than unity it is possible to determine its value by means of total reflection. A. H. Compton[8] has in this way obtained values for glass, silver and lacquer which show a remarkably close agreement with those predicted by the Lorentz equation. Davis and Terrill[9] determined the index of calcite both by Stenstrom's method and the total reflection method. By the first method they obtain a value of 3×10^{-6} for δ but the error limits were such as to make this result very uncertain. The value found by total reflection is $1.7\pm.5\times10^{-6}$.

The purpose of the present work was to determine the index of some calcite crystals with a much higher degree of precision than has been obtained heretofore, using two independent methods.

Spectrometer

The spectrometer used in this investigation was the one used by Davis and Terrill in their measurements,[10] with the added advantage that an optical lever was used to check all calibrations. To calibrate the worm

[4] Strenstrom, dissertation, Lund (1919)
[5] C. G. Darwin, Phil. Mag. **27**, 318 (1914)
[6] Duane and Patterson, Phys. Rev. **16**, 532 (1920)
[7] M. Siegbahn, Comptes Rendus (1920) p. 1350; idem (1922), p. 745.
[8] A. H. Compton, Bull, Nat. Research Coun. No. 20, p. 48 (1922); Phil. Mag. **45**, 1121 (1923)
[9] Bergen Davis and H. M. Terrill, Nat. Acad. Sci. **8**, 357 (1922)
[10] H. M. Terrill, J. Opt. Soc. Amer. (May 1922)

gear by which the crystal table was slowly rotated, a millimeter scale was reflected from a plane mirror on the crystal table back over a path of about 110 feet into a three inch telescope. A deviation of one second in three hundred, the scope of a single calibration, could be detected. The least count on the worm gear read to 3 seconds and could be estimated to half seconds. The complete calibration showed that the worm gear was slightly eccentric. Although a complete revolution of the worm introduced an error of less than one part in 7000, equal fractions of a revolution of the worm, taken at different angular positions, revolved the crystal through slightly different angles. Tables II and III have been corrected for this eccentricity. The error due to this, however, turned out to be only a small part of the total possible error due to the screw, since in most of the work it so happened that either the worm was turned for each setting through a whole number of revolutions or else the error was cancelled by turning the worm first in one direction and then in the opposite direction.

I. Wedge Method

If we assume that x-rays are propagated as electromagnetic waves and that the Lorentz equation holds approximately, we are to expect refraction to cause a displacement of the Mo $K\alpha_1$ first order line when reflected from calcite, of only about three seconds of arc when the glancing angle is about $6° 42' 43''$. The effect may be considerably increased, however, by adopting a method suggested by Prof. Bergen Davis. A clear calcite crystal was ground and polished to an optical surface on the (100) face, so as to make an angle φ of $5° 48' 20'' \pm 20''$ with the cleavage planes of the crystal, thus presenting a wedge-like appearance. The crystal was mounted on the spectrometer table and also on the end of a horizontal axle which enabled it to be rotated 180° about a horizontal axis so that either the thin edge AD of the crystal or the thick edge BC could be placed nearest the source of x-rays (Fig. 1). In the first position, called the obtuse position, the radiation from the direction P_1T makes an angle $(\theta_1+\varphi)$ with the polished surface AB (where θ_1 is the Bragg angle for the MoKα_1 radiation used and φ is the angle BAO of the polished face with the crystal planes), and is reflected in the direction OSQ_1', making an angle $r=\theta_1-\varphi$ with the polished surface. Since the angle r in this case is less than one degree, the refraction at the surface is not negligible as is the case at T where the angle of incidence is over 12°, so the emerging ray SQ_1 makes an angle i with AB which is greater than r. We shall call the difference γ so that $i=r+\gamma$.

Now suppose the crystal rotated 180° about an axis XX' which is exactly perpendicular to the crystal planes. This is equivalent to supposing the rays come from the right instead of the left. Evidently the rays must strike the surface AB in the direction Q_1S in order to be reflected. But this direction makes an angle $\theta_1+\gamma$ with the cleavage planes whereas the incident rays actually make the angle θ_1, the same as in the first position. Hence the crystal must be turned about a vertical axis so as to increase the angle of incidence by γ. By measuring this angle of turning, we measure γ.

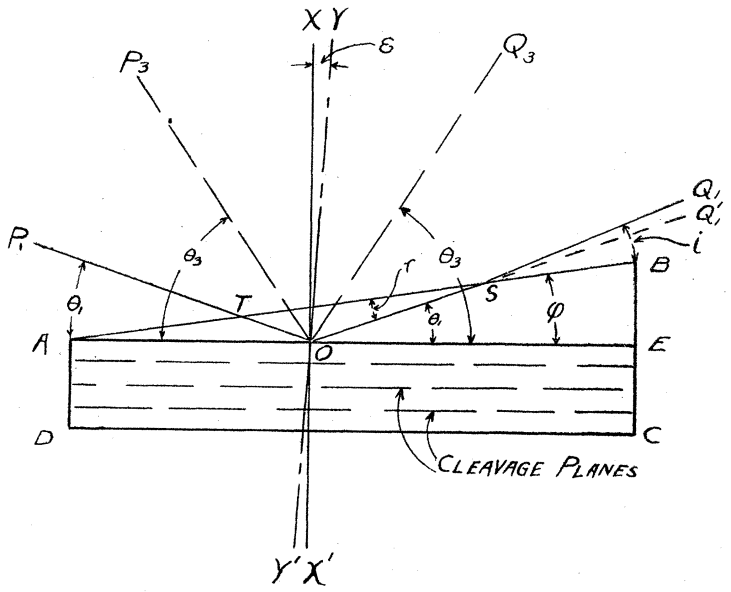

Fig. 1. Paths of rays in wedge method.

Now suppose the horizontal axis is not exactly perpendicular to the crystal planes but has a direction YY' making a horizontal angle ϵ with the perpendicular to the planes XX'. After a rotation of exactly 180° about this axis the angle between the incident x-rays and the crystal planes is not θ_1 but $\theta_1-2\epsilon$, and to get reflection the crystal must be turned so as to increase the angle of incidence by $2\epsilon+\gamma$. The value of 2ϵ may be determined however by use of the third order reflection P_3OQ_3. Here the angles are so large that the refraction is negligible; therefore after rotation through 180° the angle which the crystal must be turned through to give reflection is equal to 2ϵ.

The actual procedure was to mount the crystal as shown in Fig. 1 for obtuse reflection and so orient it as to reflect the third order of $K\alpha_1$. The

angular reading was called B_3'. Then the crystal was turned so as to reflect the first order $K\alpha_1$, the reading being called B_1'. After rotation through 180° about the horizontal axis, corresponding readings B_1 and B_3 were taken. Evidently $B_3-B_3'=2\epsilon$ and $B_1-B_1'=2\epsilon+\gamma$. Hence

$$\gamma=(B_1-B_1')-(B_3-B_3')=i-r. \tag{1}$$

The index of refraction is given by

$$\mu=\frac{\cos i}{\cos r}=\frac{\cos(r+\gamma)}{\cos r}=1-\delta \tag{2}$$

where $r=\theta_1-\varphi$. Since $\cos(r+\gamma)=\cos i\cos\epsilon-\sin r\sin\epsilon=\cos r-\epsilon\sin r$, evidently

$$\delta=\gamma\tan r=[(B_1'-B_1)-(B_3'-B_3)]\tan(\theta_1-\varphi), \tag{3}$$

and it is unnecessary to determine r with greater precision than γ can be measured.

We have assumed that refraction for angles 12° and greater is negligible. After the index has been approximately determined, however, the various readings can be corrected for the refraction and still more accurate values obtained. In Table I are given the refractive effects for the various orders computed by using the mean values of δ obtained from the results of both methods given below.

TABLE I

Refractive effect computed for various orders of reflection.

Order	Angle of incidence	Refractive effect $\gamma=(i-r)$
1st acute	54′ 51″	28.0″
2nd "	7° 42′ 47″	3.0″
3rd "	14° 43′ 15″	1.6″
1st obtuse	12° 31′ 03″	1.9″
2nd "	19° 19′ 27″	1.2″
3rd "	26° 19′ 55″	.8″

PROCEDURE

The x-rays were rendered practically parallel by means of two narrow slits 28 cm apart between lead blocks adjustable by micrometer screws. By using slits only .02 mm wide at the first order, a beam parallel within 30″ was obtained. The tube carried about 1.5 kw so that the peaks of the curves from which the line positions were determined with reference to the direction of the incident x-rays were very sharp; at half maximum the width of the curves from which $K\alpha_1$ first order was located were less than 1.5′ of arc. The crystal was mounted on the spectrometer table and so oriented as to reflect the third order of $K\alpha_1$ in the position of obtuse

incidence; then having determined the angular direction B_3' of this line (OQ_3 Fig. 1), the crystal was turned by means of the worm gear into position to reflect first order $K\alpha_1$ and the angular direction B_1' of this line SQ_1 determined. The crystal was next rotated through 180° about the horizontal axis YY', then rotated around the vertical axis a few minutes of arc γ until first order of $K\alpha_1$ in the position of acute incidence was reflected, and reading B_1 taken. Finally the crystal was rotated so as to reflect $K\alpha_1$ third order acute incidence and reading B_3 made. The first four columns of Table II give the result of a number of determinations. Similar readings made for the second order are denoted by B_2 and B_2'.

TABLE II

Readings made with wedge of 5° 48′ 20″.

B_1	B_1'	$(B_3'-B_3)$	γ_3	$(B_2'-B_2)$	γ_2
114° 58′ 46″	115° 08′ 31.1″	10′ 10.8″	25.7″	10′ 05.8″	20.7″
114° 58′ 41″	115° 08′ 30.1″	10′ 12.8″	23.7″	10′ 15.8″	26.7″
114° 58′ 38″	115° 08′ 28.1″	10′ 19.8″	29.7″	10′ 17.8″	27.7″
114° 58′ 41″	115° 08′ 19.1″	10′ 07.8″	29.7″	10′ 12.8″	34.7″
114° 58′ 28″	115° 08′ 08.1″	10′ 13.8″	33.7″	10′ 06.8″	26.7″
114° 57′ 39″	115° 07′ 13.1″	10′ 04.8″	30.7″	10′ 05.8″	31.7″
114° 57′ 29″	115° 07′ 14.1″	10′ 15.8″	30.7″	10′ 14.8″	29.7″
		Averages	29.1″		28.3″

Final average 28.7″

All readings in the above table have been corrected for eccentricity of the worm gear and all except B_1 have been corrected for refraction in accordance with Table I. From equation (1) γ is known and μ is determined from equation (2). The fifth column of Table II gives a value for γ exactly analogous to column three, using the corrected readings for the second order reflections. Since the B's in columns three and five have all been corrected for refractive effects it is clear that we should have

$$(B_3'-B_3)=(B_2'-B_2)=2\epsilon.$$

The differences between columns 3 and 5 are not much greater than the errors of experimentation. This is likewise true of columns 4 and 6. The average of γ_3 and γ_2 was used in the final determination of the mean index by this method which gave

$$\delta=(2.21\pm.16)\times10^{-6}.$$

II. DIFFERENTIAL WEDGE METHOD

In this method the crystal is rotated through only a small angle and less than a complete revolution of the worm gear (10′ of arc) is used. The ionization chamber is not moved and the collimating slits are not

changed during a determination. This was accomplished by having only the upper half of the crystal ground and polished to the desired angle, leaving the lower half a natural crystal.

In Fig. 2, let the lower half of the compound crystal $A'B'CD$ present cleavage faces only while the upper half $ABCD$ has one ground and polished face AB making an angle $6°21'30''\pm20''$ with the cleavage planes. In order to do this polishing the crystal must be split in half, but we will suppose the two halves are cemented together again so that cleavage planes of each are accurately parallel. Then readings taken by reflecting first from the lower half and then from the upper half should differ by the angle between SQ and SQ' which as in Fig. 1 is equal to $i-r=\gamma$, and from this and $(\theta_1-\varphi)$, μ and δ can be immediately determined. If, however, the crystal planes of $A'B'C'D'$ make an angle ψ with those of $ABCD$ the difference in readings will be $\psi+\gamma$ and ψ must be determined either by use of second and third order or by reflection from the back surfaces CD and $C'D'$, assuming these are parallel to the respective front cleavage planes.

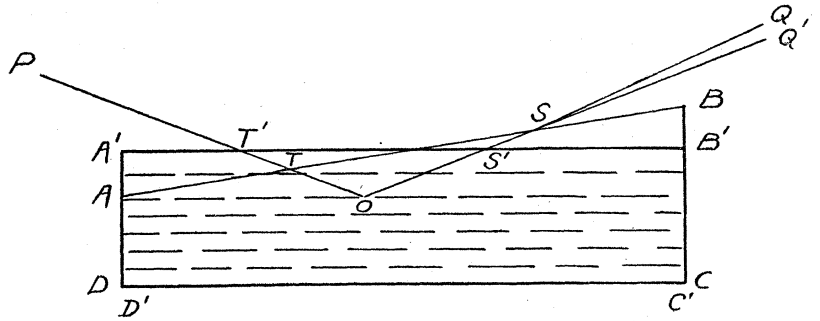

Fig. 2. Paths of rays in differential wedge method.

Procedure

The compound crystal was mounted on the table so as to reflect from either of the two cleavage surfaces CD or $C'D'$. The positions of $K\alpha_1$ third order for the upper and the lower half respectively were determined. This difference B_3-B_3' determines the angle ψ, the lack of parallelism between the (100) planes of the upper and lower halves. The crystal is now moved across the table a distance equal to its thickness. Reflection may now take place from either half face AB or $A'B'$ (Fig. 2). The angular position B_1' of the crystal when reflecting $K\alpha_1$ first order from the split half $A'B'$, the upper half being covered, is determined. The crystal is rotated a few minutes of arc and its position B_1 when reflecting the same line first order from the ground-polished face AB, is

determined. Table III gives the five separate sets of readings. All the readings have been corrected for the eccentricity of the worm gear and B_1' has been corrected for refraction. Since φ in this case is larger than in the first case, the glancing angle i is less and the value of γ is greater.

TABLE III

Readings made with differential wedge of 6° 21′ 30″.

B_1	B_1'	(B_3-B_3')	γ
66° 02′ 06.5″	65° 53′ 34.5″	7′ 32″	1′ 00″
66° 02′ 07.5″	65° 53′ 28.5″	7′ 34″	1′ 05″
66° 02′ 24.0″	65° 53′ 44.0″	7′ 34″	1′ 06″
66° 02′ 01.0″	65° 53′ 21.0″	7′ 33″	1′ 07″
66° 02′ 02.5″	65° 53′ 30.5″	7′ 32″	1′ 00″
		Average	1′ 03.6″

The method of computation of μ and δ is the same as for the first method.

The average deviations in Table III are of the same order as those in Table II.

Since the angle of incidence is smaller with this wedge than with the wedge used in Method I, the peaks of the curves are broader and consequently the determination of the position is less accurate in II than in I. In the second method the line reflected from the polished face could not be located by a single trial closer than 4 or 5 seconds. This broadening of the peak of the line accounts for the deviations in table III. From the curves the lines with wedge I could be located to within 2 or 3 seconds since the peaks of the curves were sharp. The deviations in Table II are chiefly due to the fact that the crystal had to be rotated over larger angles and many other adjustments made that were avoided in method II. Since the average absolute deviations are about the same for the two methods and since the refractive effect is over twice as great in II as in I the results from method II are weighed twice as much as those from method I.

The average deviation in each method is near 3″. The number of determinations is too small to warrant the use of the probability law to establish the precision. Instead a value of 2″ is chosen as best representing the precision of the final results.

The final value is expressed in terms of δ instead of μ.

From method I, $\delta = (2.21 \pm .16) \times 10^{-6}$;

From method II, $\delta = (1.94 \pm .06) \times 10^{-6}$.

Final mean, $\delta = (2.03 \pm .09) \times 10^{-6}$.

This value for δ agrees very well with that given by the Lorentz equation for refraction which in the simplified form required by this case may be written

$$\delta = Ne^2/2\pi m\nu^2 = 1.91\times 10^{-6}\ .$$

The critical frequencies of the calcite are too far removed from the frequency of the incident radiation to show any of the effects of resonance involved in the development of the Lorentz dispersion formula.

Correction of Wave-Length for Refraction

The value of θ, the angle made by the external incident beam and the surface, was determined for Mo $K\alpha_1$ reflected from a split crystal. First the radiation was reflected to the right and the angular position of the crystal was recorded. Then the crystal was rotated around the vertical axis of the spectrometer through $(180°-2\theta)$ so that the energy was reflected to the left. The angle $(180°-2\theta)$ was determined by means of the optical lever and the worm gear described above. The average of the two positions gives the zero of the crystal and the value of θ. From this value and the value of δ given above, the magnitude of θ_1, the true angle between the internal incident beam and the planes, was computed by the equation

$$\sin\theta_1 = \sin\theta - \delta\tan\theta\cos\theta.$$

Using the first orders of $K\alpha_1$, the value of θ comes out 6° 42′ 44″. When all three orders are properly weighted, the average value is 6° 42′ 43.3″. This value of θ when substituted in above equation gives $\theta_1 =$ 6° 42′ 39.8″$\pm$.5″. If we assume a value for d of 3.0280×10^{-8} cm for calcite and compute γ from Bragg's relation we get for Mo $K\alpha_1$

$$\gamma\ (\text{in calcite}) = .707718 \pm 15\ \text{A.}$$

Due to refraction, the value in air will be slightly less and is given by

$$\gamma\ (\text{in air}) = \gamma\ (\text{in calcite})\times(1-\delta) = .707717 \pm 15\ \text{A.}$$

If we allow for refraction this agrees very well with Duane's value .70783$\pm$8 A.

The writer wishes to express his indebtedness to Professor Bergen Davis who suggested the problem and gave many valuable suggestions during the experimental work, and to other members of the Physics Department of Columbia University for their interest and assistance throughout the investigation.

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