

X-Ray Diffraction with Calcite in Several Orders of Reflection

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Theoretical and experimental values of the four properties of reflection (width of the $(n, -n)$ rocking curve, percent reflection, coefficient of reflection and a factor determined by the shape of the $(n, -n)$ curve) of calcite crystals have been compared throughout the wave-length ranges $0.71 < \lambda < 5.83\text{\AA}$ in first order, $0.71 < \lambda < 2.75\text{\AA}$ in second order, and with wave-lengths 0.71 and 1.54\text{\AA} in third order and 0.71\text{\AA} in fourth and fifth orders. The Darwin-Ewald-Prins theory was evaluated with an at-

tempt to correct (1) for the effects of the thermal motions of the atoms in the crystal and (2) for the variation of the atomic structure factor of calcium in the wave-length region of anomalous dispersion. Excellent qualitative agreement is found but general quantitative agreement is not found. The concept of mosaic structure in the crystal lattice is not entirely sufficient to account for the discrepancies.

I. INTRODUCTION

OF fundamental importance in x-ray spectroscopy is our knowledge of crystalline diffraction. Recent researches with the double spectrometer have been concentrating on the contours of x-ray emission lines and absorption limits. The true widths of these lines and limits are relatively large but not so large that the perturbations in the observed contours due to the diffraction patterns of the crystals can be neglected. The width contribution of the crystal effects (with "perfect" calcite crystals) is of the order of 20 to 35 percent^{1, 2} of the observed $(1, +1)$ width of the $K\alpha_1$ emission lines; whereas the random observational error in recording these line contours is of the order of 1 percent.^{2, 3} If the data of these researches are to have quantitative value we must have information about the shapes of the crystal diffraction patterns.

The importance of crystalline diffraction in its own right, in addition to its applications in x-ray spectroscopy, demands as much pertinent information as possible.

No direct experimental approach to this information is known. The Darwin-Ewald-Prins theory⁴ of crystalline diffraction predicts certain pattern shapes but these shapes cannot as yet be checked experimentally. The best we are

able to do is to take advantage of the zero dispersion of the double spectrometer in the so-called parallel positions and compare the theoretical and experimental values of the reflectivities (the $(n, -n)$ width, percent reflection, coefficient of reflection and the shape factor of the $(n, -n)$ curve) for these special positions of the crystals. If the theoretical and experimental values agree we have a check on the widths, heights and areas of the theoretical diffraction patterns. It should be noted, however, that this check is concerned with the resultant pattern of the two crystals in the $(n, -n)$ positions and actually gives but little direct information about the shapes of the single crystal patterns or of the patterns in the $(n, +n)$ positions. Our interest in the present paper is in the possibility of verifying in this more or less indirect manner the theory which predicts single crystal pattern shapes and from which theory the $(n, +n)$ pattern shapes can be determined.

The comparison mentioned above has been made previously^{5, 6} with calcite crystals⁷ in first order reflection throughout the wave-length range 0.21 to 4.94\text{\AA}. The work of the present paper extends this comparison in first order to 5.83\text{\AA} and includes the range of 0.71 to 2.75\text{\AA} in second order, 0.71 to 1.54\text{\AA} in third order, and

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¹ L. G. Parratt, *Phys. Rev.* **46**, 749 (1934).

² L. G. Parratt, *Rev. Sci. Inst.* **6**, 387 (1935).

³ J. A. Bearden and C. H. Shaw, *Phys. Rev.* **48**, 18 (1935).

⁴ C. G. Darwin, *Phil. Mag.* **27**, 315, 675 (1914); P. P. Ewald, *Physik. Zeits.* **26**, 29 (1925); J. A. Prins, *Zeits. f. Physik* **63**, 477 (1930); see also M. Kohler, *Ann. d. Physik* **18**, 265 (1933).

⁵ S. K. Allison, *Phys. Rev.* **41**, 1 (1932).

⁶ L. G. Parratt, *Phys. Rev.* **41**, 561 (1932).

⁷ M. Renninger, *Zeits. f. Krist.* **89**, 344 (1934) has made this comparison at one wave-length, 1.54\text{\AA}, in first-order reflection with NaCl crystals. He finds experimental reflectivities, using small sections of the crystal area, which are in good qualitative agreement with the reflectivities calculated from the Darwin-Ewald-Prins theory. *Naturwiss.* **21**, 334 (1934).

0.71Å in fourth and fifth orders of reflection. The previous calculations have been refined in the sense that (1) an attempt has been made to determine the order of magnitude of the effects of the temperature motions of the atoms in the crystal and (2) a correction in the atomic structure factor of calcium has been made in the wave-length region of anomalous dispersion.⁸

As previously discussed,^{5, 6} a most important factor in the theory is the absorption of the x-rays in the crystals; and the greater the range of values of the absorption coefficient (determined by the wave-length) the more significant is this comparison. The linear absorption coefficients of calcite are about 23, 1008 and 1390 at

the wave-lengths of 0.71, 2.75 and 5.83Å, respectively. The Ca *K* absorption limit of calcite is at 3.06Å.

The wave-length and the Bragg angle are the fundamental variables in the study of crystal reflectivities. These two variables are of course not unrelated but the significance of the comparison of the calculated and observed reflectivities in several orders of reflection lies in the variance of the Bragg angle with a given wave-length.

II. THEORETICAL CALCULATIONS

The expression for the theoretical diffraction pattern of a single perfect crystal is

$$F(l) = \frac{1}{2} \left| \frac{(D+iB)\delta^{-1}}{l-i\beta\delta^{-1} \pm \{(l-i\beta\delta^{-1})^2 - [(D+iB)\delta^{-1}]^2\}^{\frac{1}{2}}} \right|^2 + \frac{1}{2} \left| \frac{(D+iB)\delta^{-1} |\cos 2\theta_0|}{l-i\beta\delta^{-1} \pm \{(l-i\beta\delta^{-1})^2 - [(D+iB)\delta^{-1} |\cos 2\theta_0|]^2\}^{\frac{1}{2}}} \right|^2. \quad (1)$$

This equation and its development are discussed in detail in Chapter VI of *X-Rays in Theory and Experiment* by Compton and Allison.⁹ The notation in Eq. (1) is the same as that used by Compton and Allison except $I'(l)$ is replaced by $F(l)$. In determining the reflectivities from the second crystal the function $\Phi(k)$ is used as defined in reference 6. $\Phi(k)$ is the expression for the theoretical ($n, -n$) diffraction pattern obtained by rotating the second crystal.

We have calculated the theoretical values of the coefficient of reflection, the percent reflection, the width of the ($n, -n$) curve and a factor which is determined by the shape of the ($n, -n$) curve. The expressions for the first three properties are derived in terms of Eq. (1) in reference 6 and in Chapter IX of reference 9; the shape factor is defined in the present paper. The simplification, recently published by one of us,¹⁰ in handling Eq. (1) has made calculation con-

siderably easier and eliminated some of the laborious graphical integrations employed in the earlier evaluations. Another short-cut in the integrations is afforded by the fact that

$$\int_{-\infty}^{\infty} \Phi_{\sigma}(k) dk \equiv \left[\int_{-\infty}^{\infty} F_{\sigma}(l) dl \right]^2 \quad (2)$$

as derived on page 725 of reference 9. A similar identity can be written for the π -polarized components.

The constants involved in the calculations were determined as previously described^{6, 9} with the following exceptions:

(1) The wave-mechanical method of Hönl¹¹ was used in calculating the refractive index of calcite at wave-lengths greater than those employed in Larsson's measurements.¹²

(2) The values of the structure factors used were taken from the tables of Pauling and Sherman¹³ and of James and Brindley¹⁴ and are given in Tables IA and IB. The calcium structure

⁸ It should be pointed out that the effects of anomalous dispersion were otherwise incorporated in the earlier calculations by the use of experimental values of the refractive index and of the absorption coefficient.

⁹ A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., 1935).

¹⁰ F. Miller, Jr., *Phys. Rev.* **47**, 209 (1935).

¹¹ H. Hönl, *Zeits. f. Physik* **84**, 1 (1933).

¹² A. Larsson, *Inaugural-Dissertation*, Uppsala (1929).

¹³ L. Pauling and J. Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

¹⁴ R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

TABLE IA. Structure factors of calcium, carbon and oxygen in five orders of reflection as used in the calculations.

	ATOM	f_j	$f_j(2\theta_0)/f_j(0)$
First Order	carbon	3.90	0.650
	oxygen	6.20	0.775
Second Order	carbon	2.25	0.375
	oxygen	3.77	0.471
Third Order	calcium	8.32	0.416
	carbon	1.67	0.278
	oxygen	2.21	0.276
Fourth Order	calcium	7.57	0.379
	carbon	1.53	0.255
	oxygen	1.70	0.212
Fifth Order	calcium	6.64	0.332
	carbon	1.40	0.233
	oxygen	1.53	0.191

TABLE IB. Structure factors of calcium at different wavelengths in first and second orders of reflection as used in the calculations.

WAVE-LENGTH (Å)	FIRST ORDER		SECOND ORDER	
	f_{Ca}	$f_{Ca(2\theta_0)}/f_{Ca(0)}$	f_{Ca}	$f_{Ca(2\theta_0)}/f_{Ca(0)}$
0.71	15.30	0.765	10.55	0.528
1.54	15.30	0.765	10.55	0.528
2.14			10.55	0.528
2.75	13.80	0.745	9.05	0.489
3.11	11.30	0.705		
4.28	13.54	0.742		
5.00	13.60	0.743		
5.36	13.67	0.744		
5.83	13.77	0.745		

factor varies in the region of anomalous dispersion and the subsequent corrections (decrements) to the values 15.3 and 10.55 in the first and second orders of reflection have been estimated from an extrapolation with atomic number of the theoretical values given by Hönl¹⁵ for Fe (26). Glocker and Schäfer¹⁶ give experimental values for Fe (26) which are in excellent agreement with Hönl's calculations.¹⁷ The decrement in the structure factor is taken as independent of the scattering angle and is present in both the numerator and the denominator of the ratio $f_{Ca}(2\theta_0)/f_{Ca}(0)$ as given in Table IB.

¹⁵ H. Hönl, Ann. d. Physik **18**, 625 (1933).

¹⁶ R. Glocker and K. Schäfer, Naturwiss. **21**, 559 (1933). See also K. Schäfer, Zeits. f. Physik **86**, 739 (1933).

¹⁷ Experimental determinations of the structure factor decrements due to anomalous dispersion are not entirely in accord with the predictions of Hönl's theory. See reference 9, pp. 298-304, Lameris and Prins, Physica **1**, 881 (1934), and W. P. Jesse and S. K. Allison, Bull. Am. Phys. Soc. **10**, (7), 1935, Abstract 58. However, for the purposes of the present calculations, more accurate decrements than are used in the values of Table IB would be of no advantage.

(3) The effect of the thermal vibrations of the atoms in the crystal is to decrease the structure factor values. Presumably for calcite the temperature correction in the structure factors for first order reflection is small. In the case of second and higher orders, however, due to the increased values of $\sin^2 \theta/\lambda^2$, the corrections are much larger and cannot be neglected. Although the complexity of an adequate temperature correction for calcite forbids its execution at the present time, it nevertheless is possible to investigate the tendency and the order of magnitude of such a correction. A very rough idea of the temperature effect is obtained as follows: The structure factor correction, due to Debye and to Waller,¹⁸

$$f_T = f_0 e^{-M}, \quad (3a)$$

$$\text{where } M = \frac{6h^2}{mk\Theta} \left(\frac{\phi(x)}{x} + \frac{1}{4} \right) \frac{\sin^2 \theta}{\lambda^2}, \quad (3b)$$

applies to a crystal having a simple cubic lattice of only one atomic species. Calcite is a more complex crystal but no general correction has been developed applicable to such complex crystals. In Eq. (3b), h is Planck's constant, m is the mass of the atom, k is Boltzmann's constant, Θ is the characteristic temperature of the crystal, $x = \Theta/T$, where T is the temperature of the crystal (290°K) at which the reflectivities are measured, and $\phi(x)$ is a function whose values are given by Debye.¹⁶ For m we shall take the mean mass of the atoms of CaCO_3 , 3.30×10^{-23} gram. The value of Θ may be determined from the equation¹⁹

$$\Theta = (A'T_m V'^{2/3}/AT_m' V'^{2/3})^{1/2} \Theta', \quad (4)$$

where A , T_m and V are the atomic weight, melting point temperature and specific volume of calcite, and the primed quantities refer to a crystal (such as NaF) whose characteristic temperature is known. Or Θ may be roughly estimated from the relation between crystal hardness and characteristic temperature since the relative hardness of calcite is known. In the

¹⁸ P. Debye, Ann. d. Physik **43**, 49 (1914); I. Waller, Ann. d. Physik **79**, 261 (1926), **83**, 154 (1927), Zeits. f. Physik **51**, 213 (1928); A. H. Compton and S. K. Allison, reference 9, pp. 435-444.

¹⁹ J. J. Shonka, Phys. Rev. **43**, 947 (1933).

TABLE II. Correction factors for thermal agitation of the atoms in calcite in various orders of reflection as used in the present calculations. The quantity M is defined in Eq. (3). (These values can have only qualitative meaning in view of the assumptions involved.)

	FIRST ORDER	SECOND ORDER	THIRD ORDER	FOURTH ORDER	FIFTH ORDER
M	0.036	0.144	0.324	0.576	0.897
e^{-M}	0.965	0.867	0.724	0.564	0.408

present work Θ is taken as 360°K. Substituting these values in Eq. (3) gives the temperature corrections listed in Table II. This correction is incorporated in the calculations by simply multiplying the D and B values²⁰ by the appropriate ratio in Table II.

The other constants requisite to evaluating Eq. (1) are listed in Table III. Two sets of D and B values are given: Subscript 1 refers to values in which no correction for anomalous dispersion in the atomic structure factor of

²⁰ The quantities D and B , constants for a given wavelength and order of reflection, are defined in Eq. (6.46) of reference 9. In evaluating these quantities care must be taken in regard to the phase relations of the rays scattered from the respective atoms.

TABLE III. Constants used in evaluating Eq. (1) for calcite in various orders of reflection. The subscripts on the D and B values refer (1) to uncorrected and (2) to corrected values as discussed in the text. μ_l = linear absorption coefficient; δ = deviation of refractive index from unity; β = absorptive index $\equiv \mu_l \lambda / 4\pi$.

WAVE-LENGTH (Å)	GLANCING ANGLE	μ_l	$\delta \times 10^6$	$\beta \times 10^6$	ANGULAR UNIT (radians $\times 10^6$)	$D_1 \times 10^6$	$B_1 \times 10^6$	$D_2 \times 10^6$	$B_2 \times 10^6$
<i>First Order</i>									
0.71	6° 43'	23.4	1.82	0.0132	15.67	0.938	0.0097	0.905	0.00936
1.54	14° 42'	208.	8.80	0.254	35.85	4.457	0.185	4.30	0.1785
2.75	26° 55'	1008.	26.7	2.20	66.15	13.32	1.601	12.62	1.499
3.11	30° 56'	265.	32.6	0.657	73.91	15.77	0.348	14.55	0.317
4.28	45° 00'	617.	65.5	2.10	130.0	31.80	1.08	29.94	1.02
5.00	55° 32'	920.	88.5	3.65	189.7	44.38	1.86	42.02	1.76
5.36	62° 20'	1100.	102.0	4.69	248.0	51.02	2.37	48.40	2.24
5.83	74° 18'	1390.	121.0	6.44	464.5	60.22	3.25	57.00	3.07
<i>Second Order</i>									
0.71	13° 30'	23.4	1.82	0.0132	8.018	0.334	0.00645	0.289	0.00559
1.54	30° 30'	208.	8.80	0.254	20.12	1.602	0.1203	1.388	0.1042
2.14	45° 00'	446.	17.0	0.760	34.00	2.96	0.410	2.56	0.355
2.75	65° 14'	1008.	26.7	2.20	70.19	4.43	1.035	3.49	0.831
<i>Third Order</i>									
0.71	20° 34'	23.4	1.82	0.0132	5.545	0.448	0.00523	0.325	0.00379
1.54	49° 34'	208.	8.80	0.254	17.83	2.156	0.0987	1.562	0.0715
<i>Fourth Order</i>									
0.71	28° 00'	23.4	1.82	0.0132	4.404	0.522	0.00486	0.294	0.00274
<i>Fifth Order</i>									
0.71	35° 55'	23.4	1.82	0.0132	3.839	0.372	0.00418	0.152	0.00171

calcium and no correction for thermal agitations have been applied to any of the structure factors; subscript 2 refers to values in which both of these corrections have been made as discussed above. The corrected and the uncorrected D and B values are listed to indicate the magnitudes of the effects of these corrections, and the theoretical reflectivities using both sets of D and B values in the calculations are given in Table IV to indicate the sensitivity of the reflectivities to changes in D and B .

III. EXPERIMENTAL PART

The double spectrometer and accessory apparatus have been described in previous reports.²¹ With large glancing angles the horizontal divergence of the incident x-ray beam was limited by the size (approximately 1.5 mm) of the focal-spot of the target and by the collimating action of the crystals; with small glancing angles a Seeman slit at the first crystal was used to limit

²¹ L. G. Parratt, Phys. Rev. **41**, 553 (1932); Rev. Sci. Inst. **5**, 395 (1934).

TABLE IV. *Calculated and observed* values of reflectivities of calcite in various orders of reflection.* The (1) and (2) calculated values are obtained with the D_1B_1 and D_2B_2 values, respectively, in Table III.

WAVE-LENGTH (A)	FULL WIDTH AT HALF-MAX. (seconds of arc)			PERCENT REFLECTION			COEFFICIENT OF REFLECTION ($\times 10^6$ radians)			SHAPE FACTOR $s=R/wP$ (l units)	
	CALCULATED (1)	CALCULATED (2)	OBSERVED	CALCULATED (1)	CALCULATED (2)	OBSERVED	CALCULATED (1)	CALCULATED (2)	OBSERVED	CALC. (2)	OBS.
<i>First Order</i>											
0.71	4.60	4.51	5.2	77.0	75.5	66.0	2.03	1.98	2.40	1.20	1.43
1.54	9.90	9.64	10.0	69.2	66.4	65.0	3.82	3.87	3.90	1.25	1.24
2.75	17.2	16.6	16.8	49.1	47.1	45.0	4.79	4.78	4.60	1.27	1.26
3.11	17.4	16.0	16.9	69.1	67.4	60.0	6.80	6.43	5.95	1.23	1.21
4.15	—	—	35.0	—	—	60.0	—	—	12.00	—	1.18
4.28	36.5	34.7	—	68.6	66.3	—	14.5	13.7	—	1.22	—
5.00	49.5	47.5	51.0	60.8	58.6	48.0	17.1	16.5	13.9	1.22	1.18
5.36	62.4	59.8	64.0	59.9	57.8	43.0	21.7	21.0	15.3	1.25	1.15
5.83	130.7	123.5	127.0	59.6	56.7	44.0	44.1	41.9	30.3	1.24	1.11
<i>Second Order</i>											
0.71	—	0.70	1.1	69.7	—	49.0	0.286	—	0.37	1.22	1.41
1.54	—	1.62	1.9	43.7	—	44.0	0.466	—	0.56	1.36	1.38
2.14	—	3.44	—	38.9	—	—	0.796	—	—	1.23	—
2.75	—	7.67	5.5	16.1	—	24.0	0.826	—	0.89	1.38	1.39
<i>Third Order</i>											
0.71	—	0.50	1.1	68.9	—	49.0	0.206	—	0.34	1.22	1.30
1.54	—	1.99	2.0	47.4	—	48.0	0.570	—	0.63	1.25	1.35
<i>Fourth Order</i>											
0.71	—	0.35	0.7	63.9	—	40.0	—	—	0.138	0.20	1.29
<i>Fifth Order</i>											
0.71	—	0.18	0.7	56.6	—	30.0	—	—	0.061	0.14	1.26

* The experimental data in this table (the only complete set of consistent data with calcite crystals, consistent in the sense that just one pair of crystals was used) were obtained with crystals A_4B_4 . Data with other calcite crystals are given by S. K. Allison, Phys. Rev. **41**, 1 (1932); L. G. Parratt, Phys. Rev. **41**, 561 (1932); Rev. Sci. Inst. **5**, 395 (1934); **6**, 387 (1935); S. K. Allison and J. H. Williams, Phys. Rev. **35**, 1476 (1930); F. K. Richtmyer and S. W. Barnes, Rev. Sci. Inst. **5**, 351 (1934); J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

the area irradiated on the crystal. The maximum vertical divergence with respect to the central ray was 5×10^{-3} radian. The crystals had been tested and found to have uniform reflectivity over their surfaces. The second crystal only was rotated in recording the curves.

The calcite crystals²² used (crystals A_4B_4 of reference 2) had been etched for 7 seconds with 0.7N HCl in accord with the method described by Manning.²³ Since in the earlier first order work⁶ in the wave-length range $1.54 < \lambda < 4.94$ A the crystals used (crystals IIA–IIB) were not “spectrometrically perfect,”²⁴ this range of wave-lengths was re-examined with the present crys-

tals, A_4B_4 , which do show “spectrometric perfection.”

The radiations used are the $U_{MIII} O_I$, Ag $L\alpha_{1,2}$, Mo $L\beta_3$, S $K\alpha_{1,2}$ and Au $M\alpha_{1,2}$ lines in first order, the $K\alpha_{1,2}$ lines of Mo, Cu and Ti in both first and second orders, the $K\alpha_{1,2}$ lines of Mo and Cu in third order and the $K\alpha_{1,2}$ lines of Mo in fourth and fifth orders. The x-ray tube voltage was at all times maintained lower than that voltage which would excite continuous radiation of half the wave-length being studied.

After all the data had been recorded the crystals were again studied with 0.71A radiation in second order to detect any possible change in their reflecting properties. The percent reflection was found to have decreased from 49 to 45 and the width of the (2, -2) curve to have increased from 1.1 to 1.25 seconds of arc. These differences are slightly greater than the observational errors. Several investigators have reported no change

²² The authors are indebted to Professor J. A. Bearden of Johns Hopkins University for supplying these crystals.

²³ K. V. Manning, Rev. Sci. Inst. **5**, 316 (1934).

²⁴ The term “spectrometric perfection” is defined in reference 2 in terms of high percent reflections and/or narrow widths of the curves of, say, Mo $K\alpha_1$, in both the (1, -1) and the (1, +1) positions.

with time in the reflecting properties of cleavage surfaces of calcite crystals but no such test has previously been made of etched surfaces. It is reasonable that any tendency toward deterioration would be enhanced in the case of an etched surface because of the much greater exposed area. The present crystals, A_4B_4 , were preserved in a vacuum during intervals of time of a few days or more when data were not being recorded and the present test of such a possible time change is not conclusive.

IV. RESULTS

The calculated and experimental values of the reflectivities are given in Table IV and compared graphically in Figs. 1-6. The theoretical values plotted in the figures are the corrected values obtained by using D_2 and B_2 of Table III. The sharp rise in the values of first-order widths and reflection coefficients at glancing angles of about 60° is due to the rapid increase in the unit of angular measure,

$$\text{angular unit} = \delta \sec \theta_0 \csc \theta_0. \quad (5)$$

An alternative method of plotting in terms of l units rather than radian units eliminates this trigonometric effect and shows to better advantage the crystal reflectivities. The l unit is defined as

$$l \equiv \delta^{-1}(\psi - \theta_0) \sin \theta_0 \cos \theta_0 - 1 \quad (6)$$

and represents the fractional deviation of the

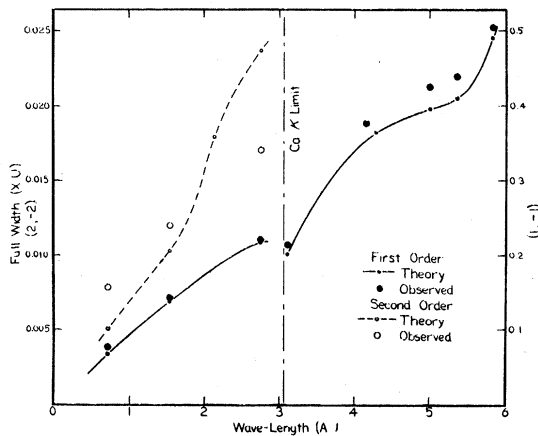


FIG. 1. Comparison of the observed and calculated full widths, w (in X units) at half-maximum intensity of the $(1, -1)$ and $(2, -2)$ rocking curves of calcite crystals A_4B_4 at different wave-lengths.

glancing angle from the corrected Bragg angle. (θ_0 is the Bragg angle not corrected for refraction.) Unit deviation is given by Eq. (5). Fig. 4 is a plot of the $(1, -1)$ width in l units as a function of the wave-length. The $(n, -n)$ width in l units from the width in seconds of arc is obtained from the relation

$$W \text{ (in } l \text{ units)} = 4.85 \times 10^{-6} \frac{W \text{ (in seconds of arc)}}{\text{angular unit}}. \quad (7)$$

Values of the angular unit, Eq. (5), are listed in Table III.

The intensity of the π -polarized component of the radiation is zero when the Bragg angle is 45° ; and the π -intensities are equal to those of the σ -polarized components at angles of 0° and 90° . This effect of the relative intensities of the two components of polarization accounts for some of the curious variations in the reflectivities.

In Fig. 5 are shown the reflectivities, calculated and observed, at the wave-length of 0.71\AA in five orders of reflection. In general, the good agreement in the higher orders of reflection (especially 1.54\AA) may be evidence that the order of magnitude of the temperature correction (which increases rapidly in relative effect with the order of reflection, as is seen in Table II) is about right.

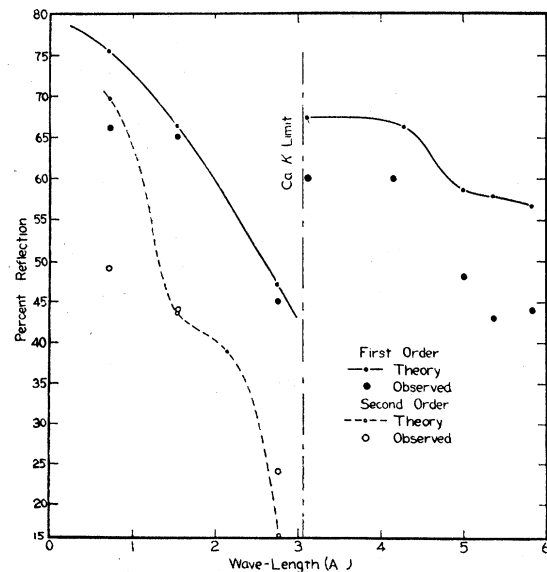


FIG. 2. Comparison of the observed and calculated percent reflections, P , of calcite crystals A_4B_4 in first and second orders at different wave-lengths.

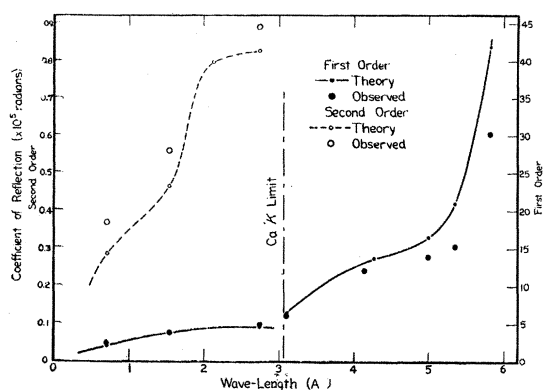


FIG. 3. Comparison of the observed and calculated coefficients of reflection, R , of calcite crystals A_4B_4 in first and second orders at different wave-lengths.

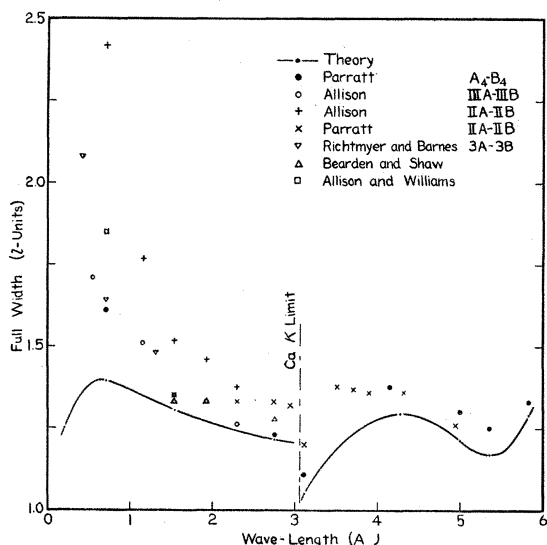


FIG. 4. The variations in the $(1, -1)$ widths of different pairs of calcite crystals is shown to better advantage when the widths are expressed in l -units. In the figure are included data with several pairs of calcites which have been used in studies of x-ray line widths by the investigators indicated in the legend. References are given at the bottom of Table IV.

The coefficient of reflection R may be defined as

$$R \equiv \frac{\text{area under the } (n, -n) \text{ curve}}{\text{intensity incident upon the second crystal}} \quad (8a)$$

In view of this definition, the comparison of the calculated and observed values of R , shown in Fig. 3, is effectively a comparison of the areas under the $(n, -n)$ diffraction patterns. The widths and heights of the patterns have already been compared, Figs. 1 and 2, respectively, and

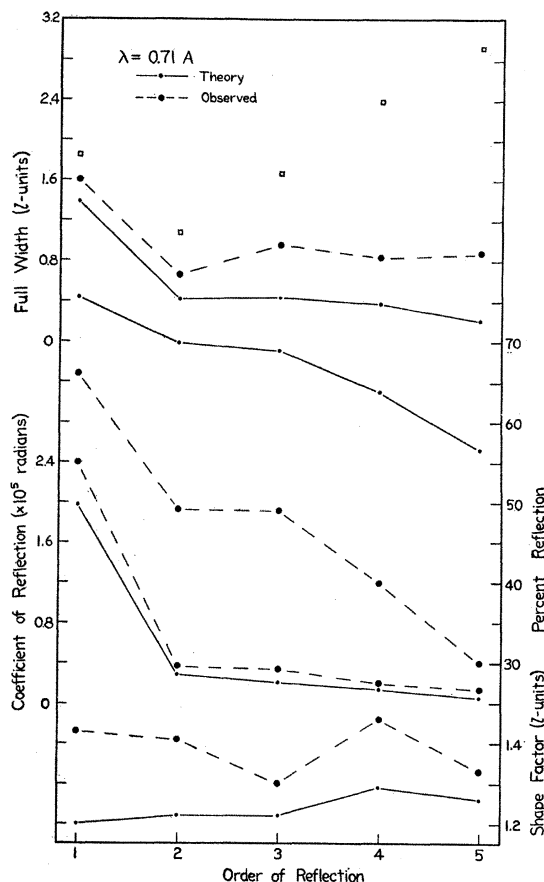


FIG. 5. Comparison of the observed and calculated values of the four reflectivities of calcite crystals A_4B_4 in five orders of reflection at the wave-length $0.71A$. The widths of the $(n, -n)$ curves with the calcites studied by Allison and Williams are represented by the open squares.

we are now interested in gleaned what information we can about the *shapes* of the $(n, -n)$ patterns. The coefficient of reflection may also be written, again from definitions, as

$$R \equiv swP, \quad (8b)$$

where w is the $(n, -n)$ width, P is the percent reflection and s is a factor determined by the shape of the curve. That the $(1, -1)$ shape varies with wave-length we already know,²⁵ but we wish also to refer to the possible difference in the calculated and observed shapes at the same wave-length. All the $(n, -n)$ shapes involved are symmetrical about the maximum ordinate. Eq. (8b) may be written with the

²⁵ L. G. Parratt, Rev. Sci. Inst. 5, 395 (1934), Fig. 6.

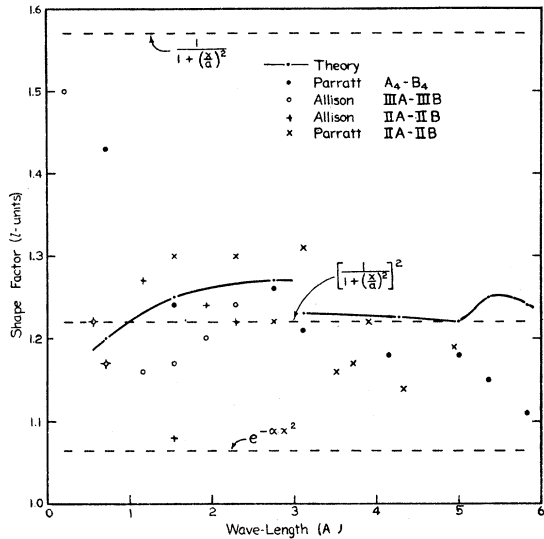


FIG. 6. The shape factor, s (defined as the ratio R/wP) at different wave-lengths in first order with several pairs of calcite crystals as indicated in the legend. The shape factors for the Gauss error function, for the classical function and for the square of the classical function are drawn in the figure as dashed lines.

calculated values of R , w and P , then again with the observed values, and a comparison made of the two values of s so obtained. This comparison of the shape factors is made in Fig. 6. The factor s does not uniquely determine the shape of the curve but it is nonetheless a convenient and very sensitive factor—almost too sensitive as judged from the scattering of the experimental points in the figure. Reference values for use in interpreting the figure are

afforded by a few well-known curves: For a triangle, $s=1.00$; for a Gauss error curve, $s=1.06$; and for a classical (Hoyt) curve, $s=1.57$. The square of the classical curve was found by Allison²⁶ to agree very well with observed $(1, -1)$ curves; for such an expression, $s=1.22$. These type curves are represented in Fig. 6 by dotted horizontal lines. The shape factors of the curves of higher orders of reflection are given in Table IV but to avoid confusion are not included in Fig. 6. The curve suggested by Allison obviously gives the best general fit, but at the short wave-lengths the observed shape factors approach and, in some cases at least, exceed the factor of the classical curve.

V. CONCLUSIONS

We have before us now a more complete and rigorous test of the validity of the theory than has been made before. Refinements in the calculations have been attempted and the comparison of the theory with experiment has been extended both in wave-length and in the order of reflection. The crystals used in the experimental part are more nearly "perfect" (as indicated by the percent reflections which seems to be the most sensitive criterion) than any other calcites whose reflectivities have been studied. Many points relative to the agreements and disagreements shown in the figures could be mentioned but it is perhaps best to let the figures speak for them-

²⁶ In private communication (1932) with Professor S. K. Allison.

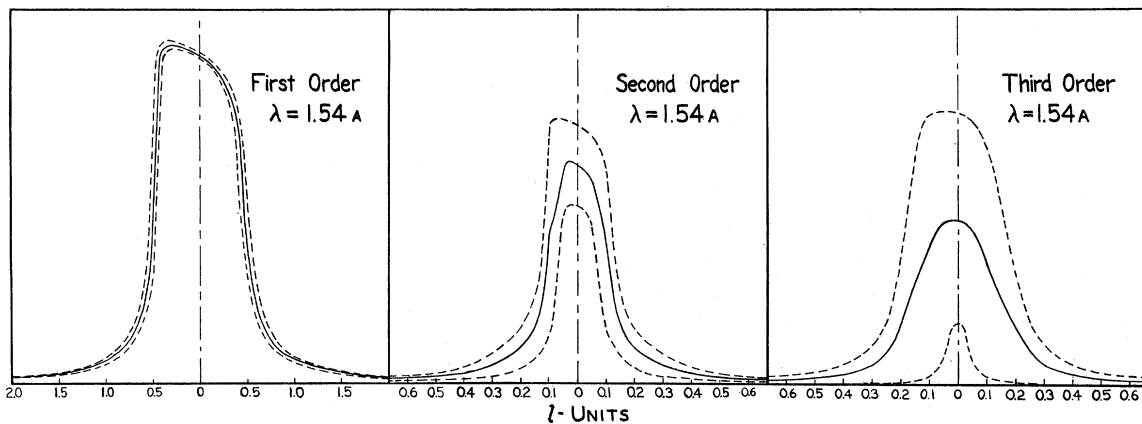


FIG. 7. Theoretical diffraction patterns from a single calcite crystal for the wave-length 1.54 Å in three orders of reflection. The solid curve is the sum of the two components of polarization, the dashed curves, with the assumption that the incident x-ray beam is completely unpolarized as indicated in Eq. (1).

selves. In general the discrepancies cannot be reconciled by changing the magnitude of the temperature correction nor by ascribing to the crystals the usual mosaic structure. There seems to be some inherent inadequacy in the theory in accounting quantitatively for all four reflectivities, particularly at the short wave-lengths in first-order and the long wave-lengths in second-order reflections. However, the qualitative agreement throughout is remarkably good considering the difficulties and assumptions involved in evaluating the theoretical reflectivities.

The corrected theoretical values make more obvious the conclusion that, with certain wave-lengths in certain orders of reflection, all calcite crystals reported to date show evidences of some mosaic structure, but that at other wave-lengths the evidence is not present.

Information about the complete shape of the

single crystal diffraction pattern is the primary objective of these researches. The shapes of the single crystal theoretical patterns of the first order reflections are given in Fig. 2 of reference 2. The theoretical shapes are asymmetrical and vary somewhat with the order of reflection as indicated in the patterns for $\lambda=1.54\text{\AA}$ in Fig. 7. The patterns of Fig. 7 are calculated with the values of D_2 and B_2 , that is, corrected as discussed above; while the patterns of reference 2 were calculated with the D_1 and B_1 values. How much practical meaning can be attached to these predicted single crystal patterns cannot be definitely answered, but the surprisingly good general qualitative, and in many instances quantitative, agreement in the calculated and observed reflectivities lends significant support to the general validity of the theory.

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Fraunhofer's Spectrum in the Neighborhood of 96,000A

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The absorption of solar radiation by the atmospheres of the sun and the earth has been examined with high resolving power over the spectral region from 70,000A to 110,000A. This paper is concerned with a discussion of the spectrum in the vicinity of 96,000A. The strongest rotation-vibration band of the ozone molecule occupies this region and has been separated into lines. The structure of the molecule is discussed in the light of these new data.

DURING December, 1934 and January, 1935 the Fraunhofer spectrum was investigated with low resolving power over the range from 5μ to 21μ .¹ At this time, the limits and magnitudes of the great regions of absorption were defined and were assigned to the atmospheric molecules responsible for them. There are but three of the latter. Only the water, carbon dioxide, and ozone molecules exhibit changes of electric moment when executing transitions between vibrational states.

The present paper is concerned with the strong, symmetrical absorption band of the ozone molecule lying between 9μ and 10μ . We have analyzed it with high resolving power, thereby revealing

its essential nature. This band is the most intense in the entire infrared spectrum of ozone.² An idea of its strength may be obtained by examining the low resolving power curve of this region in the light of the knowledge that the earth's atmosphere contains the equivalent of merely three millimeters of the gas at atmospheric pressure, in the zenith direction.³

The same observing station was employed for the present as for the previous experiment, the physics laboratory at the University of Michigan campus, latitude $42^\circ 17'$. The measurements with which we are now concerned were made during the summer of 1935 so that a somewhat shorter

¹ A. Adel, V. M. Slipher and E. F. Barker, *Phys. Rev.* **47**, 580 (1935).

² Hettner, Pohlman and Schumacher, *Zeits. f. Physik* **91**, 372 (1934).

³ E. and V. H. Regener, *Physik. Zeits.* **35**, 788 (1934).