Second Series *December 15, 1931* *Vol. 38, No. 12*

THE

PHYSICAL REVIEW

THE GRATING CONSTANT OF CALCITE CRYSTALS

By J. A. Bearden

Department of Physics, Johns Hopkins University

(Received November 7, 1931)

Abstract

The precise methods of measuring x-ray wave-lengths, now in use, raise two important questions concerning the crystal grating used. First, what variation in the grating constant is to be expected for crystals grown under different conditions? Second, what is the most accurate value of the grating constant? Since calcite crystals are the most used crystals in x-ray spectroscopy the present work was undertaken to answer as well as possible the above questions for this crystal. The variations in the grating constants of six calcite crystals from four sources (Iceland, Montana, Argentina, and Spain) have been determined by measuring the angle of diffraction for the molybdenum $K\alpha_1$ line in the fourth order. A high precision two crystal spectrometer was used for measuring the diffraction angles. The results are given in the table below. The density of these crystals was then carefully determined. Six to nine independent determinations were made at a temperature of 20.00 ±0.01°C. The averages of these values are given for a temperature of 20.00°C, in the fourth column of the table. The probable error determined by the method of least squares is given in the fifth column. The mass of the crystals used in determining the density is given in the sixth column. Considering the density measurements of DeFoe and Compton the writer gives the density ρ in g/cm^{-3} at 20°C as $\rho=2.71030\pm0.00003$. The crystals were then chemically analyzed. The results showed that all samples contained about 0.01 percent ferrous oxide, 0.01 percent manganous oxide, and 99.98 percent calcium carbonate. The angle between the cleavage faces of the calcite crystals was determined by three methods. X-rays were used for determining the angle in the first two methods and an optical method for the third. The results for 20°C were $\alpha=105°\ 3'\ 29''$ or $\beta=101°\ 54'\ 4''$, where α is the interior obtuse dihedral angle, and β the angle between the edges of the crystal. The grating constant of the crystal can be calculated from the equation $d=(nM/\rho N\phi)^{1/3}=3.02816$A at 20°C, $=3.002810$A at 18°C. The values of the constants used were, $n=1/2$, $M=100.078$, $\rho=2.71030$, $N=6.0669\times10^{23}$, $\phi=1.09594$.

Origin	Diffraction angle θ	Difference from mean	Density g/cm^{-3}	Probable Error	Mass of crystals g
Iceland	37° 51′ 34.0″	−0.4″	2.7104	±0.000021	12.9764
Iceland	27° 51′ 34.0″	−0.4″	2.71035	±0.000015	15.5780
Montana	27° 51′ 34.6″	+0.2″	2.7102	±0.000081	7.1467
Montana	27° 51′ 34.7″	+0.3″	2.7102	±0.000024	14.8650
Argentina	27° 51′ 34.7″	+0.3″	2.7102	±0.000042	11.0769
Spain	27° 51′ 34.4″	0.0″	2.7102	±0.000036	13.0083
Mean	27° 51′ 34.4″		2.71026		

INTRODUCTION

IT IS now possible to measure the diffraction angles of certain x-ray lines to one part in 400,000, or better, by using a double crytal spectrometer[1,2] or a high precision photographic spectrometer.[3] Thus, it is essential to know more about the grating constant of the crystals used. This is especially true if the results obtained by different observers are to be compared. Since calcite crystals are the most used crystals in x-ray spectroscopy, the present work has been undertaken to remove as far as possible any existing uncertainty in the use of this crystal as an x-ray grating. This report may be divided into the following six divisions: (1) X-ray comparison of the grating constant of calcite. (II) Chemical analysis of samples used. (III) Density of calcite. (IV) A determination of the angle between the cleavage faces of calcite. (V) Calculation of the grating constant from chemical data. (VI) Discussion of results.

I. X-RAY COMPARISON OF THE GRATING CONSTANT OF CALCITE

A comparison of the grating constant of different samples can be precisely made by measuring the diffraction angle of a given x-ray line for each sample.[2] In order to obtain the maximum precision in the comparison, several considerations are necessary. A large angle of diffraction is desired which could be secured by using either a long wave-length or a high order of diffraction. The latter was chosen because in using a high order of a shorter wave-length one has a much greater penetration of the rays into the crystal, and consequently a more reliable estimate of the variation in the grating constant. The method of measuring the diffraction angle must be such that a lack of perfect adjustment of each sample would make a minimum variation in the diffraction angle. A two crystal spectrometer has been used for the measurements because when properly adjusted it fulfills all the necessary conditions for a precise comparison.

The two crystal spectrometer used was a high precision type made by the Societe Genevoise.* The second crystal of this instrument is on the main axis of the spectrometer[1] thus permitting the angle through which this crystal is rotated to be measured very precisely. The graduated circle was calibrated by using a plane mirror on the axis of the spectrometer which reflected the images of two distant filaments into a telescope. As this calibration showed no error greater than 0.6″, which was the limit of resolution of the telescope used, another method was employed to obtain the absolute diffracting angle for one crystal.

A modified Michelson interferometer[4] was attached to the base of the in-

---

[1] A. H. Compton, Phys. Rev. **37**, 1694 (1931)A; Rev. Sci. Inst. **2**, 365 (1931).

[2] J. A. Bearden, Phys. Rev. **38**, 1389 (1931).

[3] The most precise photographic spectrometers in use are probably those used by Siegbahn and his collaborators.

* The author wishes to express his appreciation to Mr. Alfred L. Loomis of Tuxedo, New York, who so kindly furnished the necessary funds for the purchase of this instrument.

[4] J. A. Bearden, Phys. Rev. **37**, 1217 (1931).

strument and at the height of the crystal tables. This was used to adjust a three point support parallel to and on the axis of the spectrometer. A telescope with a Gauss eyepiece was placed perpendicular to the axis of the spectrometer. A crystal was then placed against the three points and held in place by three light springs. Thence by using the telescope, the cleavage plane of the crystal could be adjusted parallel to the axis of the spectrometer. The interferometer was used to place the part of the crystal which actually diffracted the x-rays on the axis of the spectrometer. The first crystal was then adjusted to diffract the molybdenum $K\alpha_1$ line over the axis of the spectrometer. It was then adjusted parallel to the second crystal by making the width of the rocking curve a minimum.

The slits, one near the x-ray tube and the other in front of the ionization chamber, were placed on a horizontal line perpendicular to the axis of the spectrometer to within 0.1 mm. As is well known, the height of these slits affects the width and angular position of a diffracted line. For a uniformly illuminated source and slits of equal height the correction may be written

$$d\theta''_{\text{eff}} = 0.204\frac{a^2}{L^2}\tan\theta$$

where a is the height of the slit and L their separation. This equation was tested for four slit heights from 0.5 mm to 3.0 mm, and a separation of 52 cm.

The measured angles have been reduced to 18° C by using the equation[5]

$$d\theta = -1.04(t - 18°\text{C})\tan\theta \times 10^{-5}$$
$$\text{or } d\theta'' = -2.15(t - 18°\text{C})\tan\theta$$

where t is the temperature of the crystal at the time of the measurement of the diffracting angle θ.

The diffraction angle for one crystal was then very carefully measured in three different positions on the graduated circle (120° apart). The maximum variation observed was 0.4″ and an average variation slightly less than 0.2″. The average angle was accepted as the absolute diffraction angle for this crystal, and all other results have been obtained relative to this crystal. I do not believe the diffraction angle for this crystal is in error by more than 0.2″ and is probably less.

Some very clear and perfect samples of calcite crystals from Montana, Argentina, Spain, and Iceland have been obtained. (These samples will now be referred to by the first letter of each.) Slabs about 10 mm thick have been carefully cleaved from these samples. Some surfaces were obtained which were almost free from "steps," and the others showed only a few small "steps." Adjacent pairs were selected and the width of the rocking curves measured. The widths varied from 5.5″ to 7″. It was also found that pairs selected even from crystals of different origin gave the same rocking curve widths as adjacent pairs from the same crystal. Only one large I crystal (12×

---

[5] The value of the expansion coefficient α was misprinted as 1.09×10^{-5} in the Phys. Rev. **38**, 1390 (1931). The value actually used was $\alpha = 1.04\times10^{-5}$.

8×3 cm) was available, so two samples were cleaved from it in order to see how well the various observations would check. Two *M* samples were cleaved from different crystals but from the same region.

The grating constants of these crystals were compared by using the molybdenum $K\alpha_1$ line and the fourth order of diffraction. That is, $(1, +4)$, $(1, -4)$ in Allison's notation. Fig. 1 shows typical data forming one set of measurements. The curves were taken in the order of the small numerals so that any errors due to a slow change in the adjustment of the apparatus would be eliminated. Two such sets of measurements were made on each crystal in the order I_1, I_2, M_1, M_2, A, and S. Then two more sets in the order S, A, M_2, M_1, I_2, I_1. The results are given in Table I. The angles have been reduced to 18° C and corrected for the height of the slit. They have also been slightly corrected for the small error in the graduated circle. Since in each case the measurements have been made on the same part of the graduated circle, I believe the relative values are not in error by more than 0.1″. Thus, there is a real dif-

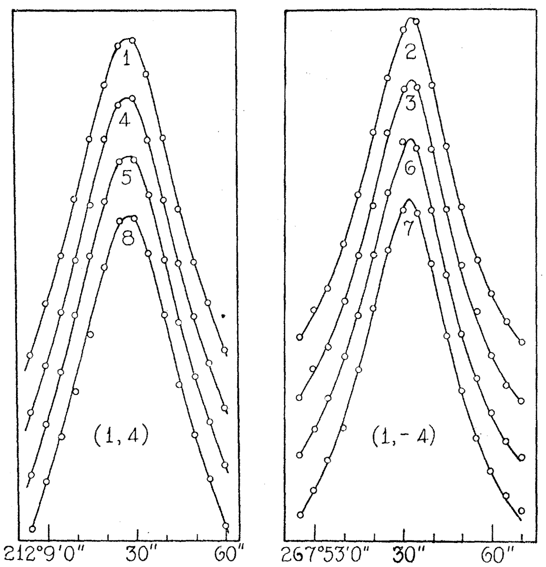

Fig. 1. One set of diffraction curves for (1, 4) and (1, −4) orders. The curves were taken in the order of the numerals.

TABLE I.

Origin	Diffraction angle	Difference from mean
Iceland	27° 51′ 34.0″	−0.4″
Iceland	27° 51′ 34.0″	−0.4″
Montana	27° 51′ 34.6″	+0.2″
Montana	27° 51′ 34.7″	+0.3″
Argentina	27° 51′ 34.7″	+0.3″
Spain	27° 51′ 34.4″	0.0″
Mean	27° 51′ 34.4″	0.26″

ference in the grating constant of the various crystals. However, the maximum difference is only one part in 145,000, and the maximum difference from the average is about 1 part in 250,000. If one only considers the M_1, M_2, A, and S crystals the maximum variation from the average is about one part in 500,000. These variations are so small that the differences in x-ray wavelengths reported by some observers must be due to the method used, and not to a variation in the grating constant of the crystals. A redetermination of a series of x-ray lines from 0.5A to 2.25A will be given in this Journal in a few weeks.

II. A Chemical Analysis of Crystals

After the above x-ray data had been secured, two samples were cut from each crystal near the point on the surface that had been used for diffracting the x-rays. Then samples, one from each crystal, were carefully analyzed for the writer by Dr. W. B. D. Penniman and Dr. A. L. Browne. The results are given in Table II. Thus, chemically there appears to be very little difference between the various samples. These samples were selected because of their optical clearness and perfection, so that one might expect them to be almost chemically pure. It is well known that colored calcite may contain several percent of some impurity. However in x-ray work it is the general practice to select the best samples available, so that the above results are probably a fair estimate of the chemical purity of the crystals normally used.

Table II.

Origin	Silica	Alumina	Ferrous oxide	Manganous oxide	Magnesium oxide	Calcium carbonate
Iceland	absent	absent	0.007	0.008	absent	99.98%
Iceland	absent	absent	0.006	0.007	absent	99.98
Montana	absent	absent	0.005	0.011	absent	99.97
Montana	absent	absent	0.006	0.011	absent	99.97
Argentina	absent	absent	0.006	0.010	absent	99.98
Spain	0.004	absent	0.007	0.006	absent	99.98

III. Density of the Crystals

The other pieces of calcite which were cut from each crystal above, were prepared for determining the density. Five of the crystals were finely ground and all surface flaws due to cleaving the crystal were removed. The edges were rounded off so there would be no possibility of occlusion of air on the surface. Four of these crystals were used in this condition and the fifth was polished with rouge. The sixth crystal was left unground. The masses of the crystals were determined by weighing in air with calibrated weights and correcting for the buoyancy of the air. The crystals were then weighed in kerosene at a temperature of 20° ±0.01° C. The density of the kerosene can be determined very accurately and thus the density of the crystals. Corrections were, of course, made for the weight of the rough gold plated copper supporting wire and surface tension. From 6 to 9 independent measurements have been made on each crystal. In Table III the results, with the probable errors for each crystal, are given for a temperature of 20° C. The probable error was calculated according to least squares method as was used by Birge.[6] The best previous determinations of the density of calcite crystals were made by De Foe and Compton.[7] Their results are given in Table IV. They give as a probable error for each sample ± 0.0001 g/cm^{-3}. The variations in Table IV are much greater than those in Table III. This may be due to a fortuitous selection of crystals used in the present experiment. However if this were true, one would hardly expect the mean value for the two sets of crystals to agree so closely.

TABLE III.

Origin	Density-g/cm 20°C	Probable error	Mass of crystal -g
Iceland	2.7104	±0.00002	12.9764
Iceland	2.71035	±0.00002	15.5780
Montana	2.7102	±0.00008	7.1467
Montana	2.7102	±0.00002	14.8650
Argentina	2.7102	±0.00004	11.0769
Spain	2.7102	±0.00004	13.0083
Mean	2.71026		

TABLE IV.

Origin	Density at 20°C g/cm^{-3}
Missouri	2.7106
U.S.A.	2.7102
Iceland	2.7103
Iceland	1/2 (2.7090)
Unknown	2.7101
Unknown	2.7103
Mean	2.7102

The second Iceland crystal in Table IV differs so much from the others that I believe the crystal must have been imperfect and should be given zero weight instead of 1/2. Thus, the mean would have been 2.71034. Taking this result into consideration with the present results of Table III, the writer believes that the most probable value of the density ρ is

$$\rho = 2.71030 \pm 0.00003 \text{ g/cm}^{-3} \text{ at } 20^{\circ}\text{C}.$$

This probable error given assumes that the variations from this value were experimental errors. The maximum variation would be 0.0003 g/cm^{-3} for De Foe's and Compton's[7] results, and 0.0001 for the present results.

---

[6] R. T. Birge, Phys. Rev. Supplement **1,** 1 (1929).

[7] O. K. DeFoe and A. H. Compton, Phys. Rev. **25,** 618 (1925).

IV. A Determination of the Angle Between the Cleavage Faces of Calcite

Since the angle between the cleavage faces of a crystal enter into the calculation of the grating constant, it is important to know this angle as precisely as possible. This angle can be measured with high precision by using a two crystal spectrometer as described above. It has also been reported[8] that this angle varies slightly for different crystals.

In the first measurements crystals from 4 to 6 mm square and 10 to 20 mm long were used. The cleavage planes were aligned parallel to the spectrometer axis. The crystals were placed so that the molybdenum $K\alpha_1$ line could be reflected from two faces by simply rotating the crystal through the angle α where α is the angle between the planes of the crystal. Since the results obtained by this method differed from those of previous investigators two other methods were used.

In the second method, crystals about 1 mm × 1 mm × 10 mm were mounted parallel to and on the axis of the double crystal spectrometer. The first crystal was adjusted to diffract the silver $K\alpha_1$ line over the axis of the spectrometer. The small crystal was then rotated until it diffracted this line into the ionization chamber. Thus, when the crystal was rotated through an angle α or $180° - \alpha$ the same line was again diffracted into the ionization chamber.

In the last method, the crystals used in the first method were spluttered with gold and adjusted on the spectrometer as above. Optically the angles were determined by using the telescope with a Gauss eyepiece. The results of the three methods are given in Table V in terms of the interior obtuse dihedral angle α. The angles were measured at 25° C to 26° C and reduced to 20° C by using the known expansion coefficients parallel to and perpendicular to the axis of the crystal. This correction can be calculated in terms of the angle β between the edges of the crystal β and α are connected by the trigonometric relation

TABLE V.

Origin	1st method α	2nd method α	3rd method α
Iceland	105° 3′ 28″	105° 3′ 30″	105° 3′ 35″
Montana	105° 3′ 31″	105° 3′ 31″	105° 3′ 20″
Argentina	105° 3′ 29″	105° 3′ 27″	105° 3′ 25″
Spain	105° 3′ 30″	105° 3′ 28″	105° 3′ 25″

$$\cos\frac{\beta}{2} = \left(2\sin\frac{\alpha}{2}\right)^{-1/2}$$

The correction is then

$$\frac{d\beta}{dt} = 2\tan\frac{\beta}{2}\left(1 - \frac{3}{4}\sin^2\frac{\beta}{2}\right)(\alpha_1 - \alpha_{11})$$

---

[8] H. N. Beets, Phys. Rev. 25, 621 (1925).

by using the values $\alpha_{\perp} = -0.0000056$ deg.$^{-1}$C and $\alpha_{\parallel} = 0.000025$ deg.$^{-1}$C. one obtains $d\beta/dt = -3.1''$ per degree C.

The weighted mean of methods one and two gives

$$\alpha = 105^\circ\ 3'\ 29''$$

$$\beta = 101^\circ\ 54'\ 4''.$$

The value of α differs by about 90 seconds from the value obtained by Beets.[8] The present results also show very little, if any, variation in the angle α for different samples. The writer is unable to explain the difference but feels that the above experiments are conclusive.

V. Calculation of the Grating Constant *d*

From fundamental considerations of crystal structure it can be shown that the grating space of a rhombohedral crystal is given by

$$d = \left(\frac{nM}{N\phi}\right)^{1/3}$$

where n is the number of molecules in each elementary rhombohedron, M the molecular weight of the crystal, N is Avogadro's number, ρ the density of the crystal, and ϕ is the volume of a rhombohedron, the perpendicular distance between whose opposite faces is unity. It can also be shown that

$$\phi = \frac{(1 + \cos\beta)^2}{(1 + 2\cos\beta)\sin\beta}$$

where β is the same as in the last section. ϕ thus becomes

$$\phi = 1.09594 \pm 0.00001.$$

For a calcite crystal $n = \frac{1}{2}$.[9] Birge[6] gives for the molecular weight of calcite $M = 100.078 \pm 0.005$. The density as determined above is, $\rho = 2.71030 \pm 0.00003$. Avogadro's number can be most accurately determined from the relation

$$N = \frac{FC}{e}$$

where F is the Faraday constant, C the velocity of light, and e the charge on the electron. Birge[6] gives $FC = 2.8987 \pm 0.0002 \times 10^{14}$ Abs. e.s.u. and $e = 4.770 \pm 0.005 \times 10^{-10}$ e.s.u. From Millikan's experiments Birge obtained a value of $e = 4.768 \times 10^{-10}$ e.s.u. and in consideration of Wadlun's[10] grating wavelength measurements of x-ray spectra which gave $e = 4.774 \times 10^{-10}$ e.s.u. raised Millikan's value to 4.770×10^{-10} e.s.u. More recent grating measurements by the writer[11] have shown that e, from such experiments, is 4.806×10^{-10} e.s.u. It appears to the writer to be out of the question to average this

---

[9] W. H. Bragg and W. L. Bragg, X-rays and crystal structure.

[10] A. P. R. Wadlung, Phys. Rev. **32,** 841 (1928).

[11] J. A. Bearden, Phys. Rev. **37,** 1210 (1931).

result with that of Millikan's. The difference of such an average from the results of either experiment would be many times the experimental error of either. The writer thus believes it is preferable to retain Millikan's value

$$e = 4.768 \pm 0.005 \times 10^{-10} \text{ e.s.u.}$$

until the magnitude of the mosaic structure can be determined and the validity of the grating formula established for x-ray wave-lengths. From this value of e one obtains

$$N = 6.0669 \times 10^{23} \text{ molecules/mole.}$$

The value of d is then calculated to be

$$d = 3.02816\text{A at } 20°\text{C}$$

$$d = 3.02810\text{A at } 18°\text{C}.$$

The probable error is ± 0.001, which is almost entirely due to the probable error in e. This value is about one part in 3000 lower than the value adopted by Siegbahn.[12]

In order to calculate the true wave-length of an x-ray line with the true grating constant as determined above, the complete Bragg law

$$n\lambda = 2d\left(1 - \frac{1-\mu}{\sin^2\theta}\right)\sin\theta$$

must be used where λ is the true wave-length, d the true grating space, μ the index of refraction, and θ the diffraction angle for the n-th order. If we use the value $(1-\mu)/\lambda^2 = 3.69 \times 10^{-6}$ the above equation becomes

$$\begin{aligned} n\lambda &= 2d\left(1 - \frac{135 \times 10^{-6}}{n^2}\right)\sin\theta \\ &= 2d_n \sin\theta \end{aligned}$$

where d_n is the effective grating constant for the n-th order. With the true grating constant $d = 3.02810$, the calculated values of d_n and log $2d_n$ are given in Table VI.

TABLE VI.

$d_1 = 3.02769$A	$\log 2d_1 = 0.7821415$
$d_2 = 3.02799$	$\log 2d_2 = 0.7821752$
$d_3 = 3.02805$	$\log 2d_3 = 0.7821937$
$d_4 = 3.02807$	$\log 2d_4 = 0.7821966$
$d_5 = 3.02808$	$\log 2d_5 = 0.7821980$
. . . . .	. . . .
$d_\infty = 3.02810$	$\log 2d_\infty = 0.7822002$

VI. DISCUSSION

Attention should be called to some of the results in the present experiment. Chemically all the samples seemed to be very similar and almost pure

---

[12] M. Siegbahn, Spectroskopie der Roentgenstrahlen.

calcium carbonate. In the calculation of the grating constant the effect of the slight impurities was neglected. In the x-ray comparison of the samples the variations in the diffraction angles were small, but the angles I_1 and I_2 were definitely smaller than the others. This would suggest a smaller crystal density. On the contrary the densities of I_1 and I_2 were the largest in the group. This indicates that a difference in density does not reflect itself as a corresponding change in the grating constant of the crystal. Consequently the measured density may not be the real density of the crystal lattice which is responsible for the diffraction of the x-rays.

It has been pointed out[2] that the absolute value of the diffraction angle for the molybdenum $K\alpha_1$ line, obtained by the writer, differs by about 1.4″ from the precision measurement reported by Compton.[1] This difference is about five times the apparent probable error of either experiment. However, the writer has recalculated the correction for the height of the slits in Compton's experiment and finds a value $d\theta_{\text{eff}} = -0.6''$ instead of $-2.2''$ as used by him. Thus his diffraction angle would be increased to 27° 51′ 34.6″ which agrees, within the experimental error, with the present results.

The difference between the writer's ruled grating wave-length measurements[11] and the corresponding crystal results now is 0.25 percent instead of 0.22 percent as previously given. Such a great difference must be due to a failure of the ruled grating diffraction equation to be valid for the x-ray region. The boundary conditions are probably not the same for optical wavelengths and x-rays and might thus alter the position of the diffraction maxima. A careful analysis of the diffraction theory for x-ray wave-lengths and for the conditions under which x-ray spectra are obtained is badly needed in order to settle the questions raised by such experimental differences.