

A DETERMINATION OF THE ANGLE BETWEEN
THE CLEAVAGE FACES OF CALCITE
BY USE OF X-RAYS

BY HENRY NICHOLAS BEETS*

ABSTRACT

The dihedral angle was determined by measuring the angle through which the crystal must be turned to reflect the MoK α line, first from one cleavage face and then from the adjacent face. Of the six crystals studied, one gave imperfectly cleaved surfaces, one showed slightly rippled faces, the others gave for the mean dihedral angle $74^{\circ} 55'.0 \pm .2'$ in excellent agreement with optical determinations. This corresponds to an angle between the edges of the crystal of $\beta = 101^{\circ} 55.0 \pm .2'$. From the coefficients of thermal expansion the change of β with temperature is $d\beta/dt = -.051'$ per degree. The volume of a rhombohedron the distance between whose opposite faces is unity comes out $1.09630 \pm .00007$ at 20°C .

THE present investigation has for its object a measurement of the angles between the faces of calcite, which has been considered¹ one of the important sources of error in the determination of its grating space. The grating space of calcite can be calculated from the relation²

$$D = \left[\frac{1}{2} M / \rho N \varphi(\beta) \right]^{1/3} \quad (1)$$

where M is the molecular weight of calcite, ρ is its density, N is the number of molecules per mol, and $\varphi(\beta)$ is the volume of a rhombohedron the distance between whose opposite faces is unity and the angle between whose edges is β . From spherical trigonometry,

$$\varphi(\beta) = \frac{(1 + \cos \beta)^2}{(1 + 2 \cos \beta) \sin \beta}, \quad (2)$$

where

$$\cos \frac{1}{2}\beta = 1 / (2 \sin \frac{1}{2}\alpha), \quad (3)$$

and α is the interior obtuse dihedral angle of the crystal.

* Coffin Foundation Fellow.

¹ H. S. Uhler, Phys. Rev. **12**, 39 (1918).

² W. H. Bragg, Proc. Roy. Soc. A **89**, 468 (1914).

The following values of $180^\circ - \alpha$ are given by crystallographers from goniometric measurements

$180^\circ - \alpha$	Temperature	Observer
74° 56'	ordinary	Groth ³
74 55.5	10°C	Mitscherlich ⁴
74 54.93	20	Hastings ⁵ (calculated)
74 55.5	ordinary	Kuppfer ⁶
74 54.25	"	Breithaupt ⁶
74 55	"	Breithaupt ⁶
74 55.2	"	Roth ⁶
74 56	"	Koksharov ⁶
74 55	"	Dana ⁶
74 55	"	Zolton Toborffij ⁷
74 55	"	Zolton Toborffij ⁷
74 55	"	Malus ⁸

The mean of these values, assigning equal weights to each, is $74^\circ 55'.2$, with a probable difference from the mean for each determination of $\pm .3'$.

It was suggested by A. H. Compton that the angle be measured in a new way which might well be called the x-ray goniometric method, namely, that x-rays of a given wave-length be reflected from one cleavage face of the crystal and the crystal then be revolved till reflection of the same wave-length and order be obtained from the adjacent cleavage face. The angle through which the crystal is turned is then either the desired angle or its supplement.

METHOD AND APPARATUS

The method employed is similar to Bragg's third method of crystal analysis.⁹ The crystal is made to revolve while the ionization chamber stands still, its slit being wide open. The incident pencil of x-rays is made as fine as possible, one of the limiting slits being placed as close to the crystal as is conveniently possible.

The crystal is mounted on the spectrometer table by means of a holder which can be moved in accurately parallel grooves so that the crystal faces can be moved parallel to themselves without changing the angle made by the beam with the crystal face. The table is so placed that the x-ray beam passes through the prolongation of the axis of the table. The ionization chamber is placed at the calculated angle for the reflection of the wave-length used, in this case the $K\alpha$ line of molybdenum. The width of the chamber slit permits some latitude in the position of the chamber.

³ Groth, "Physikallische Kristallographie," (1905).

⁴ Mitscherlich, cf Liebisch, "Physikallische Kristallographie" (1891).

⁵ Hastings, Am. Jour. Sci. **35**, 68 (1888).

⁶ Quoted by Dana, "System of Mineralogy."

⁷ Zolton Toborffij, Zeits. f. Kristallographie **44**, 605 (1908).

⁸ H. Buttgenbach, "Constantes Geometrique des Mineraux," (1918).

⁹ Bragg, "X-Rays and Crystal Structure," 3d ed., p. 29.

The crystal is so mounted that its edge is parallel to the axis of rotation of the table and about 2 mm to one side of it, the prolongation of the axis lying in the face of the crystal. The crystal is gradually turned till the $K\alpha$ line is reflected into the ionization chamber. It was not found possible under the conditions of the experiment to resolve the $K\alpha_1$ and the $K\alpha_2$ lines, but fairly sharp peaks were obtained. The setting of the crystal at the peak is noted, and the crystal then rotated to the second position, that is, for reflection from the second face, the crystal being moved backward or forward parallel to itself if necessary.

In this investigation the distance between the slits collimating the primary beam was 15 cm, and their width 0.08 mm. The x-ray source was a molybdenum target Coolidge tube operated at 40 kv and 12 milliamp. The ionization chamber was filled with sulphur dioxide. A Compton quadrant electrometer with a sensitivity of 2000 mm per volt indicated the ionization current. The circle of the Geneva spectrometer could be read to seconds of arc with the aid of the reading microscopes.

Six crystals of varying size, each having fairly good cleavage faces, were measured. The angles obtained were corrected for any errors in the centering of the table by reading both sides of the table and taking the mean. The average temperature at which the readings were taken was 22°C. The values obtained are given in the following table.

Crystal	Size and description	Angle	Weight
1	2×2×1.5 cm. Faces slightly rippled; white cloudy inclusion	74° 56.0'	0
2	1.5×3.5×1.5 cm. Faces good	105 5.2 105 5.2 74 55.0 74 55.0	2 2 2 2
3	3×5×3 cm. Large crystal, faces not perfectly cleaved	74 57.5	0
4	1×3×4 cm. Faces free from ripples	74 55.5 74 55.5	2 2
5	0.3×2.2×0.3 cm. Perfect faces.	74 54.9 74 54.9	3 3
6	1×3×3 cm. One cleavage face, one polished face	74 55.0 74 54.8 74 54.8 74 55.0	2 2 2 2

These give a most probable angle* of $74^\circ 55'.0 \pm .2'$. It will be seen that this value is in excellent agreement with that obtained by the usual

* The greater part of the variations in the readings seem to be due to accidental differences between the different crystals rather than to experimental errors. The probable error here used ($\pm .2'$) is therefore the probable difference of any one of the good crystals from the mean value.

goniometric methods. The angle α is the supplement and is $105^{\circ} 5'.0 \pm .2'$. From this angle β is calculated to be $101^{\circ} 55'.0 \pm .2'$, and $\varphi(\beta)$ is $1.09627 \pm .00007$ at 22° .

In view of the fact that the thermal expansion coefficient of calcite differs in different directions, the angle β will vary somewhat with the temperature. If k_p and k_s are respectively the expansion coefficients parallel and perpendicular to the crystal axis, it can be shown that the change of the angle β with the temperature is,

$$d\beta/dt = 2 \tan \frac{1}{2} \beta (1 - \frac{3}{4} \sin^2 \frac{1}{2} \beta) (k_s - k_p). \quad (4)$$

Using Benoit's values¹⁰, $k_p = .0000251 \text{ deg.}^{-1}$, and $k_s = -.0000056 \text{ deg.}^{-1}$, this gives an angular change of $d\beta/dt = -0.051'$ per centigrade degree. Similarly $\varphi(\beta)$ diminishes with increasing temperature by 0.000018 per degree. At 20°C we thus have,

$$\beta = 101^{\circ} 55'.1 \pm .2'$$

$$180^{\circ} - \alpha = 74^{\circ} 49'.9 \pm .2'$$

and

$$\varphi(\beta) = 1.09630 \pm .00007.$$

The present value of $\varphi(\beta)$ is to be compared with the value $1.09626 \pm .0007$ estimated by Uhler¹ in 1918 on the basis of data which he collected.

While more precise measurements of β would doubtless be possible by this method, the present determination has reduced the probable error in the grating space from this source to a value which is small compared with that from other sources, thus accomplishing the object of the experiments. The grating space of calcite calculated with the use of this measurement is given elsewhere in this journal.¹¹

In conclusion, the writer wishes to thank Professor A. H. Compton for his continued help and valuable suggestions throughout the course of the work.

RYERSON PHYSICAL LABORATORY,
THE UNIVERSITY OF CHICAGO.
January 31, 1925

¹⁰ Cf Kaye and Laby, "Physical and Chemical Constants" (1911), p. 53.

¹¹ A. H. Compton, H. N. Beets and O. K. DeFoe, following paper.