5. The only unusual values are the N(6)–O(7)–N(6″) angle which is only 68·3° and the N(2″)–O(7)–N(3′) angle which is 75·7°. For a comparison with hydrogen bonding in other molecules, the reader is referred to Fuller (1959) and Clark (1963).

We are grateful to Dr Jerome Karle for his continuing interest and we wish to express our appreciation to Mr Stephen Brenner and Dr Donald Mitchell who performed all the calculations. We wish to thank Professor John Bryden for helpful discussions.

References

BRYDEN, J. H. (1953). *Acta Cryst.* **6**, 669.
BRYDEN, J. H. (1955). *Acta Cryst.* **8**, 211.
BRYDEN, J. H. (1956). *Acta Cryst.* **9**, 874.
BRYDEN, J. H. (1958). *Acta Cryst.* **11**, 31.
CLARK, J. R. (1963). *Rev. Pure Appl. Chem.* **13**, 50.
FULLER, W. (1959). *J. Phys. Chem.* **63**, 1705.
KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496.
KARLE, I. L., HAUPTMAN, H., KARLE, J. & WING, A. B. (1958). *Acta Cryst.* **11**, 257.
KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.
KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 1356.
KARLE, I. L. & KARLE, J. (1965). *Acta Cryst.* **18**, 345.
KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 473.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
PALENIK, G. J. (1963). *Acta Cryst.* **16**, 596.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

Acta Cryst. (1967), **22**, 312

Optical Determination of Water Content in Spherulitic Vaterite

BY J. D. H. DONNAY
Crystallographic Laboratory, The Johns Hopkins University, Baltimore, Maryland, U.S.A.*

AND GABRIELLE DONNAY
Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., U.S.A.

(*Received* 6 *May* 1966)

From measured indices of refraction for vaterite crystals [n_ε 1·650, n_ω 1·550; Johnston, Merwin & Williamson, *Amer. J. Sci.* **41**, 473 (1916)] and for vaterite fibers [n_e 1·625, n_o 1·538; Meyer, *Z. Kristallogr.*. **121**, 220 (1965)], Wiener's formulae give two independent values for the interstitial water content of the fibers (5·9, 5·8 vol. %). The lowering of the density from 1·645 (crystal) to 1·54 (fiber) indicates 6·4 vol. % water. The decomposition product of $CaCO_3.6H_2O$ described by Johnston *et al.* can now be identified as fibrous aggregates of vaterite and water.

Introduction

It is well known that a spherulite is a radial aggregate of fibers, in which each fiber is itself an aggregate, composed of tiny crystals separated by some interstitial medium. Such a fiber exhibits form birefringence: positive or negative, according as the constituent crystals are acicular or platy, and the indices of refraction of the fiber can be predicted by means of Wiener's (1904, 1909–10, 1912) formulae. The latter were applied to coralline algae by Baas-Becking & Galliher (1931). Chalcedony was the first mineral† in which form birefringence was thus studied (Correns & Nagelschmidt, 1933; Donnay, 1936*b*). Chalcedony fibers are composed of quartz crystals and interstitial opal. Because opal has such a variable index of refraction, chalcedony was not a particularly felicitous example. In spherulitic calcite, on the other hand, the interstitial medium is water and the application of Wiener's formulae was straightforward (Donnay, 1936*a*)‡. The water content thus determined (10·5 vol.%) agrees with the result of a chemical analysis on the same material (10·0 vol.%). This test case established the validity of the analytical method based on optical measurements. In the same paper an attempt was made to explain the indices of fibrous vaterite, but it was unsuccessful for lack of good measured values. The only conclusions that could be reached at the time were that the form birefringence is negative and that the amount of interstitial water must be very small.

---

* National Science Foundation Grant No. GP-4947.

† Form birefringence was later observed in nemalite, which is fibrous brucite with interstitial magnetite (Donnay, 1945). It was also found to account for the refractive indices of layer crystal structures (where alternating structural slabs make up Wiener's *mixed body*) and in members of a solid solution in the series bastnaesite–vaterite (Donnay & Donnay, 1953, 1961).

‡ In 1936 spherulitic calcite was still called 'vaterite A', while the spherulitic form of μ-$CaCO_3$ was designated 'vaterite B'. The μ modification has now been found in nature (McConnell, 1960) and is called vaterite, whether it is spherulitic or not.

The experimental data

In recent years our knowledge of the crystallography of vaterite has made good progress, culminating (Kamhi, 1963) in the determination of a crystal structure in space group $P6_3/mmc$, with a 7·16, c 16·98, Z 12, and D_x 2·645. Kamhi's cell, which is pseudo-H-centered, is twice as high as the hexagonal cell of McConnell (1960). Meyer (1959), while recognizing strong hexagonal pseudosymmetry, reported an orthorhombic cell a 4·13, b 7·153 ($=a\sqrt{3}$), c 8·48, with space group $Pbmn$. If his cell were C centered instead of primitive, it would give an orthohexagonal description of the pseudolattice used by Kamhi; as a P cell, however, it is incompatible with the results of the other authors. Fortunately it is immaterial for our purpose whether vaterite is truly hexagonal or only pseudohexagonal: optically crystals of vaterite behave like uniaxial entities.

As to the indices of refraction of pure vaterite, the values measured by Johnston, Merwin & Williamson (1916) are the highest on record:

$$n_\varepsilon 1{\cdot}650,\ n_\omega\ 1{\cdot}550\,.$$

They should be more accurate than the slightly lower values (n_ε 1·650–1·645, n_ω 1·548 – 1·545) published later by Gibson, Wyckoff & Merwin (1925), which may have been obtained on material containing a small amount of water. Be that as it may, the difference between the two sets of values is barely significant.

For the indices of fibrous vaterite, that is to say the aggregate* that goes into building spherulites, we now have new measured values (Meyer, 1965):

$$n_e\ 1{\cdot}625,\ n_o\ 1{\cdot}538\,.$$

The positive fiber birefringence (0·087) is smaller than the positive crystal birefringence (0·100) by 0·013, which represents the amount of negative form birefringence. It follows that the tiny crystals that constitute the fiber are platelets normal to the fiber axis. The known habit of vaterite crystals, in keeping with the large c/a ratio, is thin tabular (0001), which tells us that the optic axis of each individual crystal in a fiber is directed along the fiber axis. This inference is supported by direct observation: Meyer (1959) ascertained by X-ray diffraction that the c axis is rigorously parallel to the needle axis. The interstitial medium is water, as was proved by chemical analysis (Johnston *et al.*, 1916, *p.*485). The Wiener formulae to be applied in this case are:

$$n_e^2 = \frac{n_\varepsilon^2 n^2}{(1-\delta)n^2+\delta n_\varepsilon^2}\,,\quad n_o^2=(1-\delta)n_\omega^2+\delta n^2\,,$$

where n stands for the index of refraction of water ($n=1{\cdot}333$) and δ for the volume fraction of water in the fiber (100 δ% water by volume).

The theoretical curves

The curves (Fig. 1) calculated from Wiener's formulae show that the pair of values reported by Meyer (1965) for the indices n_e and n_o of fibrous vaterite do fall on the same vertical line, at ~6 vol.% water. Solving the n_e^2 and n_o^2 formulae for δ gives $\delta=0{\cdot}059$ and $\delta=0{\cdot}058$, respectively.

In the absence of a direct analytical determination of water on the Meyer specimen, the water content of fibrous vaterite can be determined from its measured density, knowing the density of the pure crystal (D_x 2·645) and that of water (taken as 1·000). Two measurements are on record: the original one made by Vater (1897) himself on fibrous aggregates and one performed by Johnston *et al.* (1916) 'on aggregates' of μ-CaCO$_3$, on 'material which was partly fibrous or platy'. Both give 2·54. The equation

$$1{\cdot}000\delta+2{\cdot}645(1-\delta)=2{\cdot}54$$

yields $\delta=0{\cdot}064$. For this value of the water fraction, the indices of the fiber (Fig. 1) would be n_e 1·623, n_o 1·537. This unexpectedly good check indicates that at least three specimens of vaterite fiber have a water content of the same low order of magnitude (~6 vol.% $=2{\cdot}4$ wt.%).

Vaterite aggregates from calcium carbonate hexahydrate

Johnston *et al.* (1916, p.492) describe how monoclinic crystals of calcium carbonate hexahydrate kept at room temperature under ether, 'benzol', or clove oil 'pass within a few hours into mixtures of calcite and

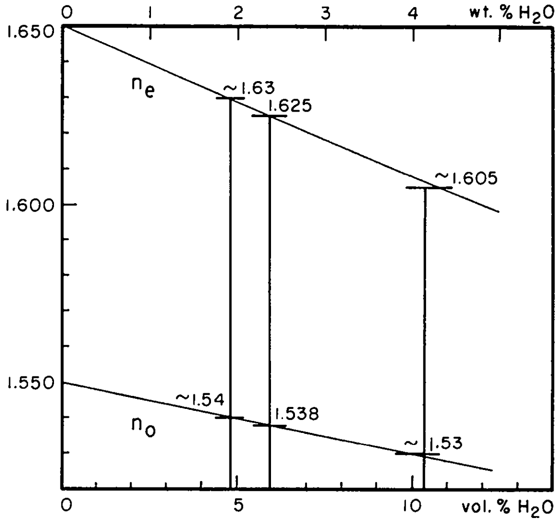

Fig. 1. Indices of refraction (n_e and n_o) of fibrous vaterite as functions of the water content. Indices of pure vaterite (n_ε 1·650, n_ω 1·550) after Johnston *et al.* (1916). Indices of fibrous vaterite (n_e 1·625, n_o 1·538) after Meyer (1965). Approximate indices (n_e ~1·63, n_o ~1·54) and (n_e ~1·605, n_o ~1·530) measured by Johnston *et al.* (1916) on decomposition product of calcium carbonate hexahydrate, a product unstable toward calcite, here identified as vaterite.

---

* To such aggregates, some German writers apply the term *Somatoid*, the usefulness of which is not obvious.

radiating or branching masses of rough crystals'. They measured the indices of refraction of the latter and give, as approximate values, '$\alpha = 1{\cdot}530$, $\gamma = 1{\cdot}605$, if formed under ether' and '$\alpha = 1{\cdot}54$, $\gamma = 1{\cdot}63$, if formed under benzol'. They report that after two days these crystals had changed almost entirely to well formed calcite.

Johnston *et al.* (1916) refer to these masses of branching crystals as the hexahydrate, but they give no explanation for the aberrant values of the indices, which (although approximate) are seen to be quite different from those they measured on good crystals of $CaCO_3.6H_2O$: 1·460, 1·535, 1·545. It is now clear that the radiating and branching aggregates were fibrous vaterite: each pair of measured indices corresponds to a definite water content (see curves, Fig. 1): ~10·5 vol.% for the smaller indices, ~5 vol.% for the larger ones. Note that, within their limited accuracy, the latter can be considered equal to those given by Meyer (1965). The source of interstitial water was, of course, the water of hydration of the hexahydrate.

Remark on the 'indices of a spherulite'

Spangenberg (1922) thought he could measure the refractive indices of the spherulite as a whole. His measurements, quoted by Meyer (1965), are n_E 1·62, n_O 1·56. Such values are meaningless, in that they do not refer either to the vaterite crystal or to the vaterite fibers. The value n_E, if measured at the two ends of the axis of revolution of a spherulite, does approach n_e very closely. The value n_O, however, measured transversely to n_E, at the re-entrant angles of the equatorial constriction, cannot be close to n_o because there the fibers do not rigorously radiate from the center on account of Popoff's *Zweiblatt* (Morse & Donnay, 1936). In fact one should expect n_O to be larger than n_o, which is what Spangenberg observed.

The true optical unit, on which indices should be measured, is the constituent fiber, not the whole spherulite.

Our thanks are due to Professor C. E. Tilley, who kindly read the manuscript.

References

Baas-Becking, L. G. M. & Galliher, E. W. (1931). *J. Phys. Chem.* **35**, 467.

Correns, C. W. & Nagelschmidt, G. (1933). *Z. Kristallogr.* **85**, 199.

Donnay, G. & Donnay, J. D. H. (1953). *Amer. Min.* **38**, 932.

Donnay, J. D. H. (1936*a*). *Ann. Soc. géol. Belgique*, **59**, B215.

Donnay, J. D. H. (1936*b*). *Ann. Soc. géol. Belgique*, **59**, B289.

Donnay, J. D. H. (1945). *Univ. Toronto Studies, Geol. Ser.*, **49**, 5.

Donnay, J. D. H. & Donnay, G. (1961). *Bull. Soc. franç. Minér. Crist.* **84**, 25.

Gibson, R. E., Wyckoff, R. W. G. & Merwin, H. E. (1925). *Amer. J. Sci.* **10**, 325.

Johnston, J., Merwin, H. E. & Williamson, E. D. (1916). *Amer. J. Sci.* **41**, 473.

Kamhi, S. R. (1963). *Acta Cryst.* **16**, 770.

Meyer, H. J. (1959). *Angew. Chem.* **71**, 678. (Also in *Fortschr. Miner.* **38**, 186, 1960.)

Meyer, H. J. (1965). *Z. Kristallogr.* **121**, 220.

Morse, H. W. & Donnay, J. D. H. (1936). *Amer. Min.* **21**, 391.

McConnell, J. D. C. (1960). *Miner. Mag.* **32**, 535.

Spangenberg, K. (1922). *Z. Kristallogr.* **56**, 432.

Vater, H. (1897). *Z. Kristallogr.* **27**, 486.

Wiener, O. (1904). *Phys. Z.* **5**, 332.

Wiener, O. (1909–1910). *Ber. kgl. sächs. Akad. Wiss., math.-phys. Kl.* **61**, 113; **62**, 256.

Wiener, O. (1912). *Abh. math.-phys. Kl. sächs. Ges. Wiss.* **32**, 507.