

Acta Cryst. (1953). 6, 428

The thermal expansion of awillite. By ROSEMARY SHAW, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

(Received 30 January 1953 and in revised form 18 February 1953)

The structure of awillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, has recently been worked out by Megaw (1952), who has shown that both long and short hydrogen bonds are present. An investigation of the anisotropy of the thermal expansion coefficient has been undertaken with the hope of relating it to the directions of the two types of hydrogen bonds.

Single crystals of natural awillite were examined over the temperature ranges -60° to 20°C. , and 30° to 120°C. A thermostat based on that described by Ubbelohde & Woodward (1946) was used to cool the crystals and a small furnace made of nickel foil, indirectly heated electrically, was used to raise their temperature. Reflexions from planes with high θ values for copper radiation were recorded on a flat back-reflexion plate placed at a distance of 10 cm. from the crystal. Exposures for the two temperatures were made on the same film, and the separation of the spots corresponding to a given reflexion was measured.

The values obtained for the expansion coefficients in the directions of the normals to the reflecting planes are given in Table 1 and the values of the principal coefficients in Table 2; Fig. 1 shows the variation of α in the (010) plane.

Table 1. *The thermal expansion coefficients in the direction of the normals to several reflecting planes*

| <i>hkl</i> | θ | $\alpha \times 10^6$ (per deg. C.) | |
|----------------|----------------|--|--|
| | | Average value 30° to 120°C. | Average value -60° to 20°C. |
| $\bar{4},0,14$ | $78^\circ 15'$ | 13.7 ± 1.4 | 9.0 ± 1.1 |
| $0,0,12$ | $79^\circ 57'$ | 17.1 ± 1.7 | 12.8 ± 1.2 |
| 608 | $78^\circ 40'$ | 21.4 ± 1.5 | 15.1 ± 1.1 |
| $18,0,\bar{4}$ | $86^\circ 44'$ | 28.2 ± 1.4 | — |
| $20,0,\bar{8}$ | $81^\circ 12'$ | 24.3 ± 1.7 | 13.7 ± 1.2 |
| $37\bar{3}$ | $77^\circ 10'$ | 9.0 ± 1.2 | — |

Table 2. *Principal expansion coefficients*

| | Average value 30° to 120°C. | Average value -60° to 20°C. |
|----------------|--|--|
| α_{11} | 7.1 ± 2.0 | 5.2 ± 1.5 |
| α_{22} | 9.8 ± 2.1 | * |
| α_{33} | 27.8 ± 3.0 | 18.0 ± 1.8 |
| ψ^\dagger | $90 \pm 3^\circ$ | $87 \pm 3^\circ$ |

* The low-temperature value of α_{22} was not determined as it was thought that little of interest would result from this measurement.

† ψ is the angle between α_{33} and $[001]$, and is positive if α lies in the obtuse angle β .

plane (average value for the range of temperature 30° to 120°C.). The crystal is monoclinic, so that the direction of α_{22} is fixed parallel to the y axis by symmetry. There is a large value of the expansion coefficient perpendicular to the z axis in the (010) plane. The values parallel to the y and x axes are much smaller and are approximately equal. The angles between the directions of the hydrogen bonds (Fig. 2) and the direction of maximum expansion are:

Short hydrogen bonds: $S_1 90^\circ$; $S_2 46^\circ$.
Long hydrogen bonds: $L_1 32^\circ$; $L_2 20^\circ$.

Since measurements have been made over only two temperature ranges it is not possible to draw detailed conclusions about the way the expansion coefficients vary with temperature. The percentage variation is approximately the same for all directions and there is no significant change in the orientation of the deformation ellipsoid.

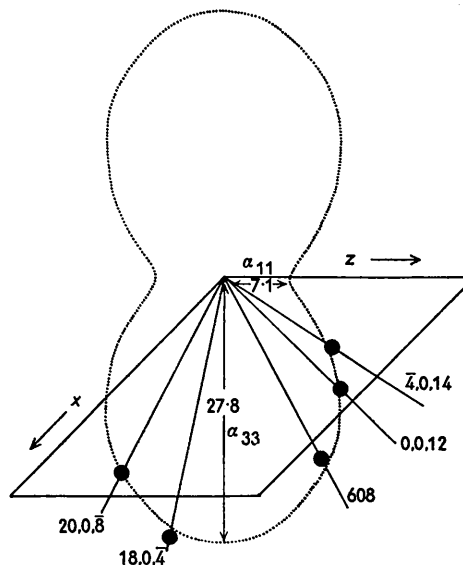


Fig. 1. The variation of α with direction for the temperature range 30° to 120°C. The values of α are expressed in units of 10^{-6} per deg. C.

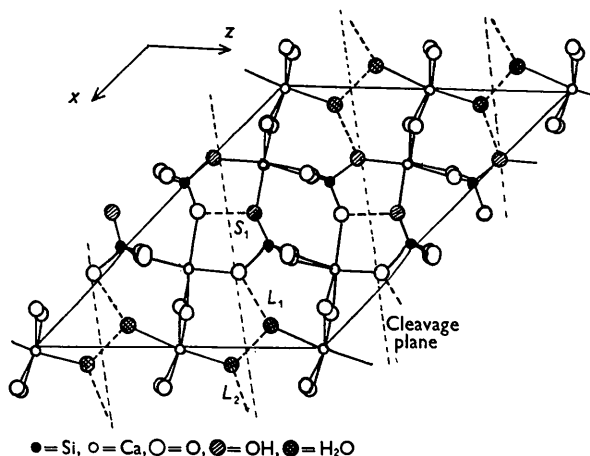


Fig. 2. Projection of the unit cell on (010). The atoms shown are approximately at height 0. A similar layer of atoms approximately at height $\frac{1}{2}$ has been omitted for the sake of simplicity.

The only earlier work on thermal expansion which is of relevance for comparison with these results is that done by Ubbelohde and his collaborators. They found that in oxalic acid dihydrate (Robertson & Ubbelohde, 1939) and in Rochelle salt (Ubbelohde & Woodward, 1946) the maximum expansion lay nearly in the direction of the short hydrogen bond, and they therefore attributed the large value to a particularly large expansion of the bond itself. There is no evidence of any such large expansion in the results obtained for afwillite. It is not even possible to explain the experimental values by taking some account of the anisotropy of the electrostatic forces, and assuming that any expansion of the hydrogen bonds must be superimposed on a general large expansion perpendicular to the cleavage plane and a small one parallel to it. This also would lead to a large expansion approximately in the direction of the z axis, and not in a direction at right angles to it as has been observed. These results suggest that any simple interpretation of the total thermal expansion in terms of changes in individual bond lengths is not applicable to afwillite. The geometry of the structure as a whole must be considered, and some account taken of changes in bond angles as well as changes in the lengths of bonds.

If changes in bond angles are assumed to take place

a plausible mechanism of expansion can be postulated. The three contiguous hydrogen bonds form a zigzag line very nearly in the direction of maximum expansion. If, on heating, there are changes in the bond angles of the oxygens which result in a straightening out of this line, there will be an expansion along its length, and a contraction in a direction at right angles to it. It is suggested tentatively that this is the explanation of the large expansion in a direction within the cleavage plane, and the small one perpendicular to it.

I should like to thank Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their interest and encouragement, and Dr H. D. Megaw for many helpful discussions. I should also like to thank the Department of Scientific and Industrial Research for the award of a maintenance grant.

References

- MEGAW, H. D. (1952). *Acta Cryst.* **5**, 477.
 ROBERTSON, J. M. & UBBELOHDE, A. R. (1939). *Proc. Roy. Soc. A*, **170**, 241.
 UBBELOHDE, A. R. & WOODWARD, I. (1946). *Proc. Roy. Soc. A*, **185**, 448.

Acta Cryst. (1953). **6**, 429

The structure of oxamide. By C. ROMERS, *Laboratory of Organic Chemistry of the University, Leiden, Holland*

(Received 20 February 1953)

In connexion with investigations going on in this laboratory dealing with the structure and properties of the peptide bond we have redetermined the unit cell dimensions of oxamide. These dimensions,

$$a = 3.61, b = 5.17, c = 5.62 \text{ \AA}, \\ \alpha = 83^\circ 50', \beta = 113^\circ 54', \gamma = 115^\circ,$$

agree with the results of an earlier investigation (Misch & v. d. Wijk, 1938). The cell contains one molecule (density = 1.667 g.cm.⁻³). Assuming a centre of symmetry, the asymmetric unit of the molecule consists of one oxygen, one nitrogen and one carbon atom, neglecting the hydrogen atoms. All x parameters are zero; consequently the molecules are flat and form a layer structure very similar to the structure of cyanuric acid (Wiebenga & Moerman, 1938; Wiebenga, 1952). The y and z parameters are

| | y | z |
|---|--------|-------|
| C | 0.002 | 0.132 |
| N | -0.226 | 0.259 |
| O | 0.217 | 0.219 |

The crystals are frequently twinned with a twinning plane (100). This same plane shows a perfect cleavage. We find a C-C distance of 1.49 Å, in contradiction with Misch & v. d. Wijk's assumption that this distance

should have the abnormal length of 1.65 Å. The C-O and C-N distances are 1.25 and 1.31 Å respectively. The molecules are linked together in the plane (100) by hydrogen bonds of 2.91 and 2.96 Å. The distances between the planes (100) are van der Waals distances of the order of 3.5 Å. The C-N distance is short; however, rather short C-N distances are also found in cyanuric acid (1.345 Å) and in urea (1.345 Å) (Vaughan & Donohue, 1952). A three-dimensional refinement of the structure is in progress.

We wish to acknowledge the support given by the Organisation for Pure Research (the Hague).

Note added in proof, 14 March 1953.—We have found the positions of the hydrogen atoms in the section OYZ of the three-dimensional Fourier synthesis. Consequently, the whole molecule is flat.

References

- MISCH, L. & WIJK, A. J. A. VAN DER (1938). *C. R. Soc. Phys. Hist. nat. Genève*, **55**, 96.
 VAUGHAN, P. & DONOHUE, J. (1952). *Acta Cryst.* **5**, 530.
 WIEBENGA, E. H. & MOERMAN, N. F. (1938). *Z. Krystallogr.* **99**, 217.
 WIEBENGA, E. H. (1952). *J. Amer. Chem. Soc.* **74**, 6156.