THERMAL EXPANSION OF BORIC ACID

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INTRODUCTION

THE present investigation is in continuation of earlier measurements of thermal expansion of crystals having O_3 groups. The expansion coefficients of potassium chlorate (monoclinic) and potassium nitrate (orthorhombic) have been already determined (Lonappan, 1955 a, b). Orthoboric acid (H_3BO_3) is triclinic and crystallizes in the class $C_i - \bar{1}$ and belongs to the space group $P\bar{1}$. The unit cell containing four molecules has the dimensions $a = 7 \cdot 039$ Å, $b = 7 \cdot 053$ Å, $c = 6 \cdot 578$ Å, $\alpha = 92 \cdot 58°$, $\beta = 101 \cdot 17°$ and $\gamma = 119 \cdot 83°$ (Zachariasen, 1954). Since the crystal is triclinic none of the principal axes of the ellipsoid of expansion need coincide with any of the crystallographic axes. For the complete determination of the ellipsoid of expansion therefore, the principal expansions as well as the orientation of the principal directions with respect to a co-ordinate system in the crystal have to be obtained. This has been achieved by measuring the variation of the expansion coefficient with direction in three zones. The present study has been made for a range of temperature 30 to 80° C. Orthoboric acid on heating changes into metaboric acid at about 100° C. and on further heating changes into tetraboric acid at about 140° C. (Partington, 1946). Hence the expansion study could not be extended to higher ranges of temperature.

This appears to be the first time that an X-ray method has been adopted for measuring the thermal expansion of a triclinic crystal. Only one other triclinic crystal has been studied earlier, namely, copper sulphate by Sreedhar (1953) using Fizeau's optical method. In his study, however, only the minimum number of measurements necessary for the complete evaluation of the elements of the expansion ellipsoid were made. In the present study, a large number of extra measurements have been obtained and the estimated probable errors are quite small.

2. EXPERIMENTAL DETAILS

Orthoboric acid usually crystallizes in the form of plates; but occasionally some needle-shaped crystals with the c-axis as needle axis are also

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formed, the well-developed faces parallel to the needle axis being usually a (100), p (110) and q ($1\bar{1}0$) (Groth, 1910). These indices are with reference to the axes adopted by Groth, for which

$$a : b : c = 1 \cdot 7329 : 1 : 0 \cdot 9228$$

$$\alpha = 92° \, 30', \ \beta = 104° \, 25', \ \gamma = 89° \, 49'$$

However, the structure has a pseudo-hexagonal symmetry about the c-axis and this is represented in the unit cell adopted by Zachariasen (1934, 1954) for which

$$a : b : c = 0 \cdot 9980 : 1 : 0 \cdot 9327$$

$$\alpha = 92° \, 35', \ \beta = 101° \, 10', \ \gamma = 119° \, 50'$$

The b- and c-axes of Zachariasen are identical with those of Groth, while his a-axis has indices $\frac{1}{2}$ [$1\bar{1}0$] referred to Groth's axes. Denoting the faces by capital letters when referred to Zachariasen's cell, the well-developed faces in the needle-shaped crystals are A (100), B (010) and Q ($1\bar{1}0$). In all the discussions hereafter, all the indices will be with reference to Zachariasen's unit cell.

It is necessary to make measurements of expansions along directions lying in three different zones (the three zone-axes being non-coplanar) to obtain completely the elements of the expansion ellipsoid. In the X-ray method adopted by the author, it is possible to measure the expansion along the normals to various planes lying in a single zone by obtaining the rotation photographs about this zone axis at two different temperatures. The details are given in the earlier papers (Lonappan, 1955 *a*, *b*). Consequently, rotation photographs of the zero layer were taken about the *three* zone axes [100], [010] and [001] using a Unicam 19 cm. high temperature camera. The [001] zone was studied by setting the crystal with its needle axis along the rotation axis of the camera. Usually, no crystals are formed with a- or b-axis as needle axis. For obtaining the rotation photographs about the other two zones, these crystals (with c as needle axis) were suitably oriented on the camera. For example, to set the [010] axis along the axis of the camera, the crystal was oriented so that the line of intersection of the faces A (100) and C (001) is parallel to the axis of rotation.

In each zone, the spacings of the high-angle reflections for values of $\theta > 65°$ were measured accurately, as described earlier, at both temperatures and the corresponding coefficients were calculated. The indices of the reflections, determined by the reciprocal lattice diagrams, were confirmed by taking Weissenberg photographs of the crystal set so as to

give the required axis as the axis of rotation. The thermal expansions perpendicular to a number of crystallographic planes in the zone concerned were thus determined. The vapour pressure of the crystal is very high even at room temperature and it is still higher at higher temperatures. The crystals were therefore found to sublime away rapidly after mounting. The recording of the photographs with the crystals had therefore to be completed in the minimum period possible.

3. METHOD OF CALCULATION

In the case of the [001] zone, which was the first zone to be studied, four high-angle reflections were measured. The best values for the maximum and minimum of the expansion coefficient in this zone and the inclination of the direction of the maximum expansion with the a^*-axis were determined by calculation using the method of least squares, as described in the case of potassium chlorate for the [010] zone (Lonappan, 1955 a). In the [010] zone, four high-angle reflections were measured. Along with these, the value of thermal expansion along the a^* direction obtained from the study of the previous zone was also taken and the maximum and minimum values of the expansion coefficient and the inclination of the direction of the maximum with a chosen direction (a^*-axis) in the zone were determined. In the third zone, namely the [100] zone, six high-angle reflections could be measured. These, along with the values of the thermal expansion coefficients along the b^* and c^* directions (obtained from the study of the other two zones), were utilised to calculate the maximum and minimum values of the expansion coefficient in this zone and the inclination of the direction of the maximum with the c^*-axis. The measured and calculated values for the three zones are shown in Table I. The maximum and minimum values of the coefficient of expansion and the inclination of the maximum with a chosen direction are given in Table II for each of the three zones.

In order to determine completely the ellipsoid of expansion in the case of a triclinic crystal, the values of α along six general directions are required. Six representative data were therefore obtained from the above three zones. In order to utilise these, it is necessary to have an orthogonal system of co-ordinate axes in the crystal. The system Ox, Oy and Oz chosen is indicated in the stereographic projection in Fig. 1 and is related to the crystallographic axes as follows:—

Ox is taken normal to the c plane, $i.e.$, parallel to c^*-axis

Oy lies in the c^*-a^* plane and is perpendicular to Ox

Oz is perpendicular to Ox and Oy and the three together form a right-handed system.

TABLE I

Measured thermal expansion coefficients of the reflections in [001], [010] *and* [100] *zones*

Sl. No.	Indices of the reflections	With reference to OXYZ system			$\alpha \times 10^6$ (measured)	$\alpha \times 10^6$ (calculated)
		L	M	N		
1	4̄ 9 0	·1966	·8788	·4384	10·1	9·1
2	7 1 0	·2419	·5519	·7986	20·3	20·8
3	8 2̄ 0	·1794	·2504	·9511	18·1	17·8
4	2 6 0	·2924	·9763	·2588	19·4	19·1
5	0 0 8	·9897	·0218	·1392	250·4	250·9
6	7 0 5̄	·4120	·5000	·7547	48·9	48·7
7	7 0 1̄	·3420	·4226	·8387	36·8	36·9
8	7 0 4̄	·2979	·5150	·7986	26·0	28·6
9	0 7 5̄	·3584	·9336	·0436	30·7	29·7
10	0 6 4̄	·7071	·7030	·0610	126·8	126·2
11	0 0 8	·9897	·0218	·1392	251·4	250·9
12	0 7 2̄	·5075	·8639	·0436	65·4	63·2
13	0 7 4̄	·2546	·9681	·0349	13·8	13·2
14	0 7 1̄	·3987	·9182	·0262	40·1	37·6

TABLE II

Maximum and minimum values of the coefficient of thermal expansion and inclination of the direction of maximum for the three zones

Zone	Thermal expansion $\times 10^6$		Inclination of direction of maximum expansion
	Maximum value	Minimum value	
[001]	21·8	7·3	19° 17′ to a^*
[010]	250·8	7·2	76° 39′ to a^*
[100]	254·0	−2·9	6° 22′ to c^*

The direction cosines of the crystallographic axes a, b, c as well as the axes of the reciprocal lattice (a^*, b^*, c^*) with respect to this co-ordinate system are given in Table III.

TABLE III

Direction cosines of crystallographic axes and reciprocal lattice axes with respect to the co-ordinate system Oxyz

Direction	l	m	n
a	0	0·8704	—0·4924
b	0	0	1·000
c	0·9659	—0·2588	—0·0436
a^*	0·2493	0·9685	0
b^*	0·1662	0·4924	0·8557
c^*	1·000	0	0

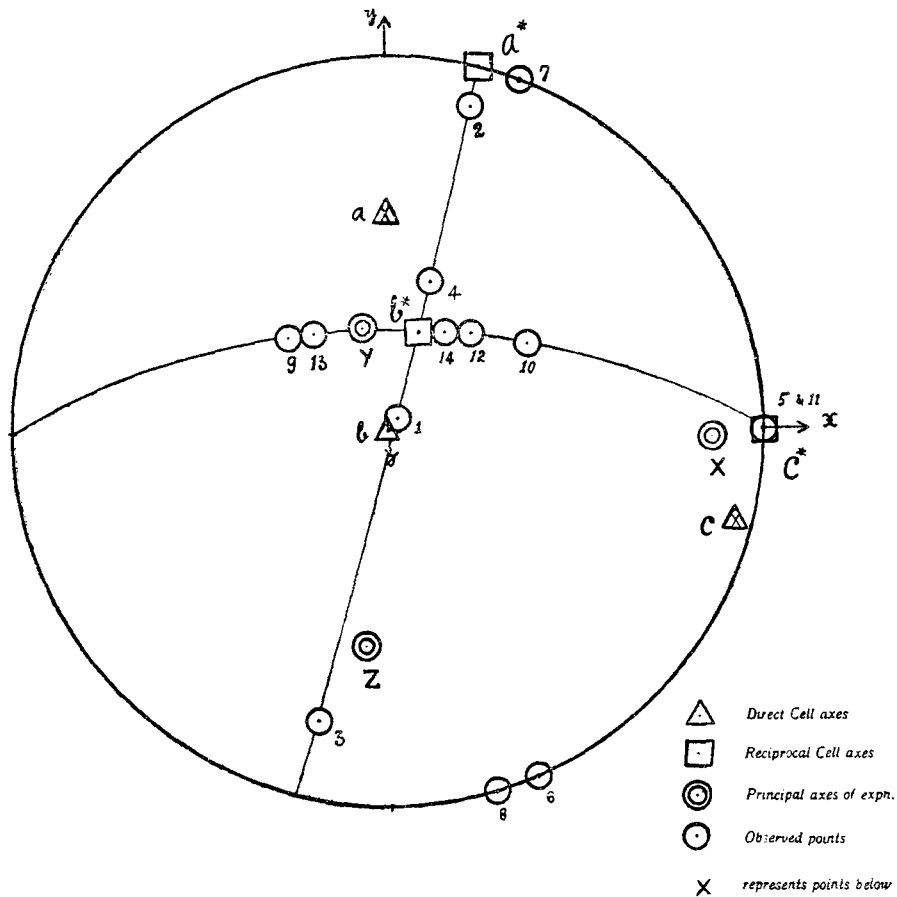Fig. 1. Stereographic projection of the various directions involved in the present study. Represented here are: (1) the system of co-ordinate axes Oxyz; (2) the direct cell axes, a, b, c; (3) the reciprocal cell axes a*, b*, c*; (4) the principal axes of expansion OX, OY, OZ, and (5) the directions (1–14) along which the thermal expansion coefficients were measured.

Suppose a is the coefficient of expansion along a direction (l, m, n). Then the general form of a is

$$a = al^2 + bm^2 + cn^2 + 2\,fmn + 2\,gnl + 2\,hlm \tag{1}$$

If $r = 1/\sqrt{a}$ is plotted as a polar diagram in three dimensions, the figure would in general be a conicoid whose equation is

$$ax^2 + by^2 + cz^2 + 2\,fyz + 2\,gzx + 2\,hxy - 1 = 0 \tag{2}$$

If OX, OY, OZ are the principal axes of this figure‡ and L, M, N are the direction cosines of a general direction referred to the axes OXYZ, then the expression for a takes the form

$$a = a_{11}L^2 + a_{22}M^2 + a_{33}N^2 \tag{3}$$

where a_{11}, a_{22}, a_{33} are the principal expansion coefficients. The corresponding equation to the conicoid becomes

$$\frac{X^2}{A^2} + \frac{Y^2}{B^2} + \frac{Z^2}{C^2} = 1,$$

where

$$A^2 = 1/a_{11}, \ B^2 = 1/a_{22}, \ C^2 = 1/a_{33} \tag{4}$$

The problem therefore reduces to finding the directions of the principal axes of the ellipsoid such that equation (2) is reduced to the form of equation (4). This can be done by forming the discriminating cubic (Bell, 1931) and solving it.

Writing equation (4) in the form

$$\lambda_1 X^2 + \lambda_2 Y^2 + \lambda_3 Z^2 = 1 \tag{5}$$

it can be shown that λ_1, λ_2, λ_3 are the roots of the equation.

$$\lambda^3 - a\lambda^2 + \beta\lambda - \gamma = 0$$

where

$$a = a + b + c,$$
$$\beta = ab + bc + ca - f^2 - g^2 - h^2$$

and

$$\gamma = \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix} \tag{6}$$

‡ Capital letters X, Y, Z are used to indicate the principal axes, as distinct from x, y, z which denote the co-ordinate system of reference.

The cubic can be solved by Cardan's method. The roots of the discriminating cubic themselves then give the principal expansion coefficients.

The orientation of each principal axis can be determined by substituting the appropriate root (λ_i) in the following set of equations (Bell, 1931) and solving for l_i, m_i, n_i.

$$(a - \lambda_i)\, l_i + \quad hm_i + gn_i \qquad = 0$$

$$hl_i \quad + (b - \lambda_i)\, m_i + fn_i = 0$$

$$gl_i \quad + fm_i + (c - \lambda_i)\, n_i = 0 \qquad (7)$$

4. RESULTS OF THE INVESTIGATION

The six representative values used for the calculation of the principal expansion coefficients were

(1) along the x-axis

(2) at 45° to the x-axis in the xy plane

(3) along the y-axis

(4) along the direction of the maximum in the a^*-b^* plane

(5) at 45° to the maximum in the same plane and

(6) at 45° to c^* direction in the c^*-b^* plane

In order to make full use of all the observed data, these representative values were calculated from the data given in Table II, as these give the best fit with observations in each zone. Table IV gives the orientation and magnitude

TABLE IV

Thermal expansion α *and direction cosines for the six values used for the final calculation*

$\alpha \times 10^{-6}$	l	m	n
250·7	1·00	0	0
124·4	0·7071	0·7071	0
7·3	0	1·00	0
21·8	0·2498	0·9104	0·3299
14·6	0·1476	0·4100	0·9001
153·8	0·7071	0·3518	0·6134

of the representative values used. These yield six linear equations of the type of equation (1) in a, b, c, f, g, h. Solving these, we have, omitting the factor 10^{-6},

$$a = 250 \cdot 7, \quad b = 7 \cdot 29, \quad c = 5 \cdot 074$$

$$f = -7 \cdot 017, \quad g = 35 \cdot 722 \text{ and } h = -4 \cdot 595.$$

The corresponding discriminating cubic is given by

$$\lambda^3 - 263 \cdot 064 \lambda^2 + 1790 \cdot 23 \lambda + 10176 \cdot 9 = 0$$

whose solutions are

$$\lambda_1 = 255 \cdot 913, \quad \lambda_2 = -3 \cdot 674, \quad \lambda_3 = 10 \cdot 826.$$

These give the principal coefficients of expansion. The data regarding the orientation of the principal axes of the ellipsoid with respect to Ox, Oy Oz are given in Table V. The orientation of the principal axes are expected to be correct to $1°$, although the exact probable error is difficult

TABLE V

Data regarding principal axes of the ellipsoid of expansion

Value of principal expansion $\times 10^6$	$-3 \cdot 674$	$10 \cdot 826$	$255 \cdot 913$
l	$-0 \cdot 1113$	$-0 \cdot 0902$	$0 \cdot 9896$
m	$0 \cdot 5022$	$-0 \cdot 8644$	$-0 \cdot 0226$
n	$0 \cdot 8576$	$0 \cdot 4947$	$0 \cdot 1415$
Angle with Ox	$96° \ 23'$	$95° \ 11'$	$8° \ 16'$
Angle with Oy	$59° \ 51'$	$149° \ 48'$	$91° \ 18'$
Angle with Oz	$30° \ 58'$	$60° \ 21'$	$81° \ 52'$

to calculate. The measured data as well as the orientations of the various axes used in this study are also indicated in the stereographic net in Fig. 1. The agreement between the observed and calculated values for the three zones are brought out in Figs. 2 a, b and c, which represent the polar diagrams of thermal expansion for the three zones. The continuous curves represent the variations to be expected theoretically and the circles represent the observed values, which are found to be close to the continuous curves. The probable errors of the principal values of expansion were estimated
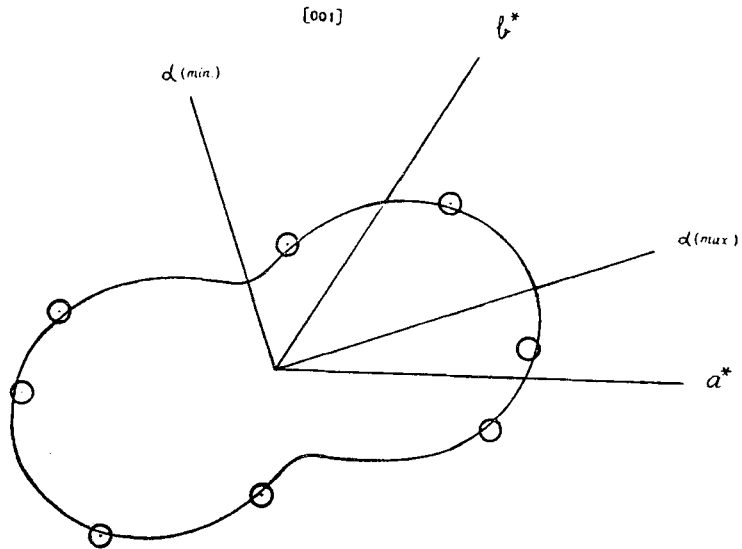
FIG. 2 a. Variation of expansion coefficient a with direction in the [001] zone. The continuous curve represents the theoretical variations to be expected and the circles represent the observed values.

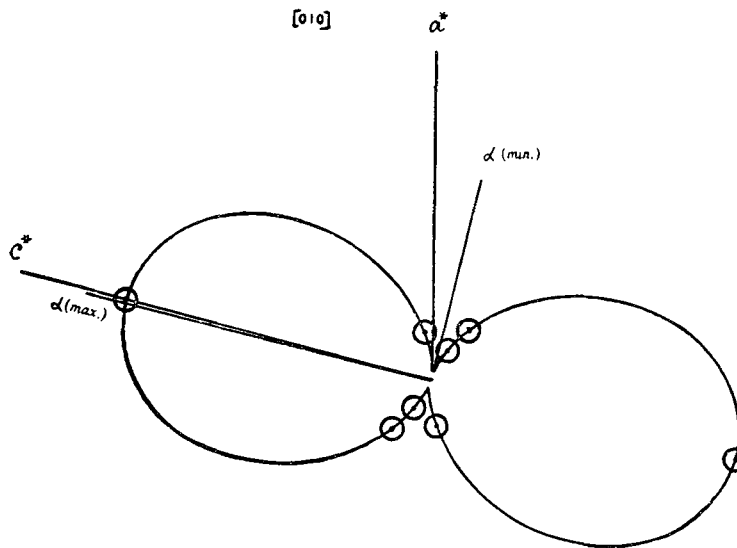

FIG. 2 b. Variation of expansion coefficient a with direction in the [010] zone. The continuous curve represents the variations to be expected theoretically and the circles represent the observed values.
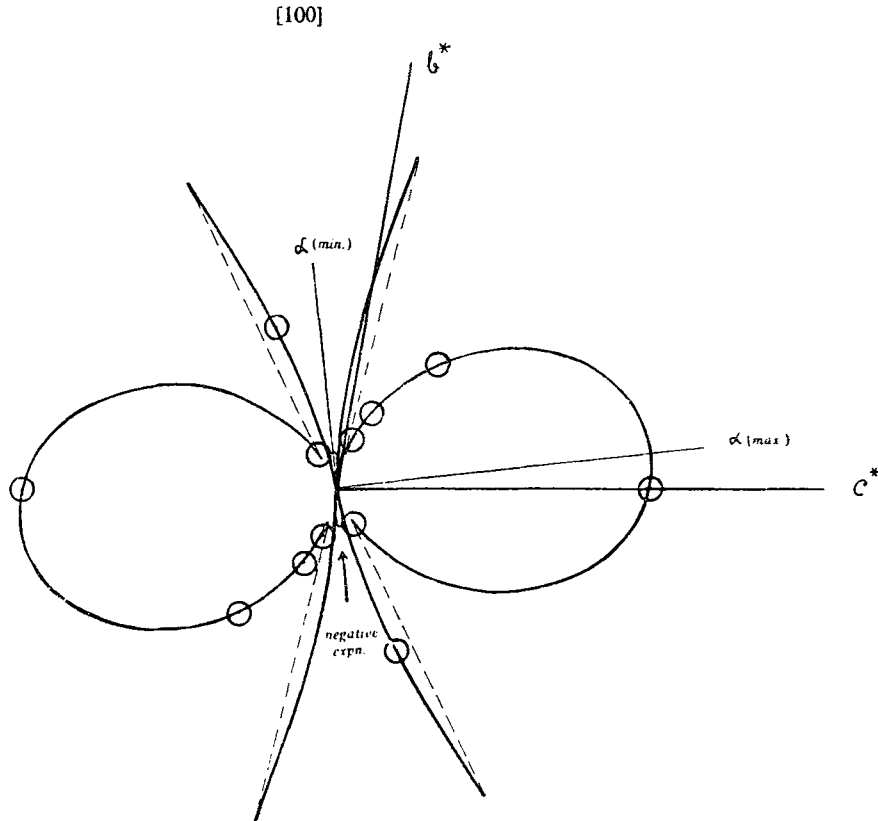
FIG. 2 c. Variation of expansion coefficient α with direction in the [100] zone. The continuous curves represent the variations to be expected theoretically and the circles represent the observed values. The two small loops represent the region where the value of α is negative. The portions of the curve corresponding to 20° on either side of the minimum are represented on a magnified scale, 10 times larger than the rest of the diagram.

from the differences between the calculated and observed values in Table I. The final values are

$$a_{11} = -3 \cdot 67 \pm 0 \cdot 6, \quad a_{22} = 10 \cdot 83 \pm 1 \cdot 0, \quad a_{33} = 255 \cdot 9 \pm 1 \cdot 0 \times 10^{-6}.$$

5. DISCUSSION

It is interesting to note that the three principal values are quite different from one another, the highest being about 250 and the lowest -3×10^{-6}. The direction of maximum expansion is close to the normal to the O_3 planes, as has been found with other crystals with planar O_3 groups. The variation in the plane of the O_3 group of about 14×10^{-6} is of the same order as in the case of aragonite and potassium chlorate; but no negative value for expansion is given by any of these. Calcite however has a negative value of

$- 6 \times 10^{-6}$ in the plane of the O_3 group. The direction of maximum negative expansion in boric acid is almost perpendicular to the a-axis in the c plane. According to the structure of boric acid the shortest OH $\cdot \cdot \cdot$ O hydrogen bonds, i.e., the strongest bonds, are perpendicular to the a-axis. The average length of the two bonds in this direction is 2·712 Å. while the corresponding values in the other two directions at $\pm$ 120° to it are 2·725 and 2·725 Å. It is reasonable to expect that the smallest expansion would occur in the direction of the strongest bond, as is found to be the case.

The highest value of thermal expansion is nearly perpendicular to the plane of the O_3 group. However, it is tilted by about 8° towards the b-axis. Orthoboric acid has a layer structure almost parallel to the c plane occurring at hieghts of $\frac{1}{4}$ c and $\frac{3}{4}$ c, so that only Van der Waals' forces exist between them, which is exhibited by the perfect cleavage along the c plane. This accounts for the very large value of the expansion almost perpendicular to the c plane. However, the BO_3 planes are not exactly parallel to the c plane. The inclination of the different groups in the unit cell are different and it has not been found possible to correlate the exact direction of maximum expansion (namely its tilt from the normal to the c planes) with the orientation of the individual O_3 groups.

Another crystal for which negative expansion has been reported is hydrargillite (Megaw, 1933). Even though hydrargillite $Al(OH)_3$ has a layer structure and has the group $(OH)_3$ as in the case of boric acid $B(OH)_3$ the details of the structure are quite different. Hydrargillite contains pairs of closely packed planes of oxygen atoms with a layer of aluminium in between. Each aluminium atom is surrounded by six oxygen atoms in octahedral coordination. In view of this, the expansion of hydrargillite is not maximum normal to the layers of atoms parallel to the c plane. The maximum occurs at an angle of 45° to the c^* direction in the c^*-a^* plane. The situation is very different with boric acid. Consequently, the idea of the relative slipping of planes leading to a negative expansion coefficient, suggested by Megaw in the case of hydrargillite, cannot be applied to boric acid.

It may be added that even a cubic crystal such as α-AgI, is known to have a negative thermal expansion (Fizeau, 1867; Jones and Jelen, 1935; Cohen and Bredee, 1937), which has not been properly explained. Another case of negative thermal expansion is monoclinic platinum phthalocyanine (Ubbelohde and Woodward, 1942–43) for which also no adequate explanation was put forward. Boric acid is thus the fifth example of a crystal exhibiting thermal *contraction* along some direction in it.

The author wishes to record his deep indebtedness to Professor G. N. Ramachandran for the invaluable suggestions he gave and the keen interest he took in the course of this study.

SUMMARY

The principal coefficients of expansion and the orientation of the ellipsoid of expansion have been determined for orthoboric acid, a triclinic crystal, for the range of temperatures 30 to 80° C. by an X-ray method. The aniso-tropy of expansion is extremely large, the maximum expansion being 256 and the minimum $- 4$, $\times 10^{-6}$. The direction of the maximum expansion coefficient is close to the normal to the c plane, to which all the O_3 groups are closely parallel. The occurrence of a negative expansion is a special feature of this crystal, the direction of which is found to be parallel to the shortest hydrogen bonds. This is the first time that the thermal expansion of a triclinic crystal has been fully studied by an X-ray method.

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