THERMAL EXPANSION OF COPPER SULPHATE

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Summary

The expansion ellipsoid of a triclinic crystal, $CuSO_4$, $5H_2O$ has been determined. The necessary theory and the procedure to be followed in the case of triclinic crystals are given. The principal coefficients of expansion are:—

$41 \cdot 68 \times 10^{-6}$, $29 \cdot 27 \times 10^{-6}$ and $4 \cdot 45 \times 10^{-6}$.

Introduction

A survey of the literature on the thermal expansion of crystals reveals the striking lack of information about crystals belonging to the triclinic and monoclinic systems. It is found that not even a single triclinic crystal has so far been investigated thoroughly.

For crystals of the triclinic class, such as $CuSO_4$, $5H_2O$, the coefficient of linear expansion is not independent of the orientation of the specimen. As is well known, the thermal characteristics are completely known if the dilatation ellipsoid is fixed with respect to the crystallographic axes of the crystal. For this purpose, a knowledge of the three principal axes of expansion with respect to any three fixed axes in the crystal is essential.

It is shown below that a knowledge of the coefficient of expansion in any six general directions is sufficient for fixing the dilatation ellipsoid. The theory has been applied to the case of copper sulphate and its expansion characteristics have been completely determined.

The crystals of copper sulphate pentahydrate were artificially grown from solution and the best specimens were about an inch long. The faces were well formed and the crystals exhibited the *a* (100); *m* (110) and the w $(1\bar{1}\bar{1})$ faces predominantly. The intersection of the *a* and *m* faces gives at once the *c*-axis of the crystal. The *b*-axis of the crystal lies on the *a*-face and is inclined at 82°5′ with the *c*-axis. The *a*-axis is inclined at an angle of 102° 41′ and 107° 8′ with *b* and *c*-axes respectively. Thus the three crystallographic axes can be easily identified. The axial ratios as given by Groth are $a : b : c = 0 \cdot 5721 : 1 : 0 \cdot 554$.

The coefficient of variation of density of copper sulphate has been measured by Andreae (1911). This in itself is but of little value in understanding the extremely interesting case of the anisotropy of linear expansion.

2. EXPERIMENTAL TECHNIQUE

The well-known Fizeau interferometric method as modified by Merritt and Saunders is employed in the present investigation and the temperature range was about 40° C. from − 5° C. to + 35° C. Above 35° or 40° C. the crystal begins to lose its water of crystallisation and the readings will not be reliable. It is intended to carry out the investigations below room temperature down to liquid-air temperature in the near future.

3. PROCEDURE AND THEORY FOR TRICLINIC CRYSTALS

The number of independent experimental measurements necessary for a triclinic crystal is six. Thus, determinations of α along six general directions fixed with respect to the crystal axes are enough to fix the expansion ellipsoid with respect to the crystallographic axes.

The theory of arriving at the size and orientation of the expansion ellipsoid has been worked out and is presented below.

Let O′X′, O′Y′ and O′Z′ be the principal axes of the ellipsoid as yet unfixed, and α_p be the expansion measured in a direction O′P ($O'P = r_p'$) with direction cosines l_p', m_p' and n_p' with reference to OX′, OY′ and OZ′ respectively. Now if α_{11}, α_{22} and α_{33} are the principal coefficients of expansion, *i.e.*, along O′X′, O′Y′ and O′Z′ respectively, we have,

$$\alpha_p = \alpha_{11}\, l_p'^2 + \alpha_{22}\, m_p'^2 + \alpha_{33}\, n_p'^2. \tag{1}$$

The equation of the ellipsoid with reference to the X′ Y′ Z′ axes is

$$\frac{x'^2}{A^2} + \frac{y'^2}{B^2} + \frac{z'^2}{C^2} = 1, \tag{2}$$

where A, B and C are the semi-axes of the ellipsoid.

In equation (2) we can put $x' = l' r'$, $y' = m' r'$ and $z' = n' r'$, where r' is the radius vector of any point on the ellipsoid. Thus

$$\frac{l'^2}{A^2} + \frac{m'^2}{B^2} + \frac{n'^2}{C^2} = \frac{1}{r'^2} \tag{3}$$

Comparing (3) with (1), we see that (1) corresponds to (3) if we take $\alpha_p = 1/r'^2$ and $\alpha_{11} = 1/A^2$; $\alpha_{22} = 1/B^2$ and $\alpha_{33} = 1/C^2$. (4)

If now we refer the ellipsoid to an aribitrary orthogonal system OX, OY and OZ, fixed with respect to the crystallographic axes, the equation of the ellipsoid will be

$$a'x^2 + b'y^2 + c'z^2 + 2f'yz + 2g'zx + 2h'xy + 2u'x + 2v'y + 2w'z - 1 = 0 \tag{5}$$

If we take the origin O to be the same as the centre O′ of the ellipsoid, the equation (5) reduces to,

$$ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy - 1 = 0 \qquad (6)$$

Equation (6) has six unknowns, a, b, c, f, g and h and hence six general points on the ellipsoid fix them. The distances of these six points $P_1 \ldots . P_6$ from the origin are proportional to the square root of the reciprocal of the expansion measured along the line joining them to the origin. This follows from equation (4). Further, equation (6) can be transformed as follows:

Put

$$x = l_p r_p; \quad y = m_p r_p; \quad z = n_p r_p,$$

where l_p, m_p and n_p are the direction cosines with reference to OX, OY and OZ of any radius vector r_p joining O with a point P on the ellipsoid. Then (6) becomes

$$al_p^2 + bm_p^2 + cn_p^2 + 2fm_pn_p + 2gn_pl_p + 2hl_pm_p - 1/r_p^2 = 0. \quad (7)$$

With the help of equation (4) this can be written as

$$al_p^2 + bm_p^2 + cn_p^2 + 2fm_pn_p + 2gn_pl_p + 2hl_pm_p - a_p = 0, \quad (8)$$

where a_p is the expansion in the direction $OP = r_p$.

This equation as before has six unknowns in a, b, c, f, g and h. The other quantities are a_p, the expansion in a direction OP making known direction cosines l_p, m_p and n_p, with respect to the chosen axes OX, OY and OZ respectively. Thus these quantities are known experimentally. Thus if we measure the expansion in six general directions with known direction cosines l, m and n, we get six simultaneous equations in a, b, c, f, g and h. These can be solved for the a, b, c, f, g and h, and hence also equation (6). The equation of the ellipsoid is thus known.

In order to get the principal axes of the ellipsoid we have to reduce (6) to its normal form. The reduction follows the usual method of solving the discriminating cubic (Bell).

If

$$ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy - 1 = 0$$

is the ellipsoid, the discriminating cubic is

$$\lambda^3 - a\lambda^2 + \beta\lambda - \gamma = 0, \qquad (9)$$

where

$$a = a + b + c, \ \beta = ab + bc + ca - f^2 - g^2 - h^2 \text{ and } \gamma = \text{Det.} \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix}$$

The cubic can be solved by the usual Cardan's method. Let the solution be λ_1, λ_2 and λ_3. The principal axes form of (6) is then

$$\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2 = 1 \qquad (10)$$

and the semi axes A B and C are

$$1/\sqrt{\lambda_1},\ 1/\sqrt{\lambda_2} \text{ and } 1/\sqrt{\lambda_3}.$$

Since by (4)

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

it follows at once that

$$a_{11} = \lambda_1;\ a_{22} = \lambda_2 \text{ and } a_{33} = \lambda_3.$$

Thus the roots of the discriminating cubic are themselves the principal expansion coefficients. One thus obtains the principal coefficients of expansion.

The next problem is to fix the relative orientation of the principal axes OX′, OY′ and OZ′ with respect to the chosen axes OX, OY and OZ. Let l_1, m_1 and n_1 be the direction cosines of that principal axis which corresponds to λ_1, with respect to the chosen axes OX′, OY′ and OZ′. Similarly let l_2, m_2 and n_2 and l_3, m_3 and n_3 be the direction cosines of the two other principal axes corresponding to λ_2 and λ_3. Then these nine direction cosines are solutions of the following three sets of equations (Bell).

$$\left.\begin{array}{llll}
(a-\lambda_1)\,l_1 & + hm_1 & + gn_1 = 0 \\
hl_1 & + (b-\lambda_1)\,m_1 & + fn_1 = 0 \\
gl_1 & + fm_1 & + (c-\lambda_1)\,n_1 = 0 \\
(a-\lambda_2)\,l_2 & + hm_2 & + gn_2 = 0 \\
hl_2 & + (b-\lambda)\,m_2 & + fn_2 = 0 \\
gl_2 & + fm_2 & + (c-\lambda_2)\,n_2 = 0 \\
\text{and}\quad (a-\lambda_3)\,l_3 & + hm_3 & + gn_3 = 0 \\
hl_3 & + (b-\lambda_3)\,m_3 & + fn_3 = 0 \\
gl_3 & + fm_3 & + (c-\lambda_3)\,n_3 = 0
\end{array}\right\} \qquad (12)$$

These nine equations together with $l_1^2 + m_1^2 + n_1^2 = l_2^2 + m_2^2 + n_2^2 = l_3^2 + m_3^2 + n_3^2 = 1$ can be solved for l_1, m_1, n_1; l_2, m_2, n_2; and l_3, m_3, n_3.

Thus all the necessary information regarding the size and orientation of the expansion ellipsoid can be got.

4. Experimental Procedure and Results

In the present investigations the axes of reference (OX, OY and OZ) are chosen as follows:

The Z-axes is along the *c*-axis of the crystal. The Y-axis is on the (*bc*) plane or the (100) plane of the crystal and is perpendicular to *c*-axis and points in the sense of *b*. The X-axis is perpendicular to both OZ and OY and the whole axes form a right-handed system. The disposition of the various axes is shown in the figure (Fig. 1).

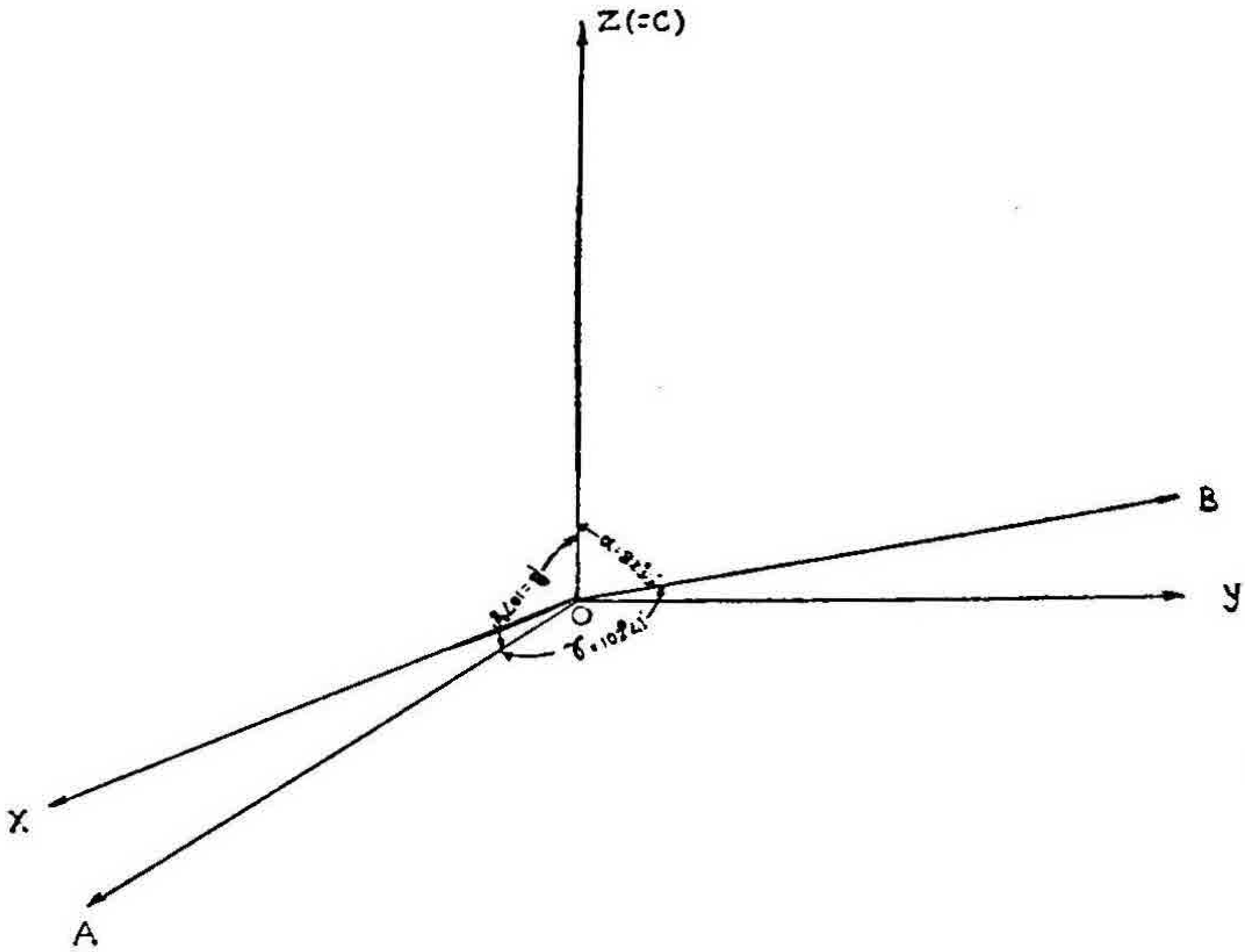

Fig. 1

The six directions (together with a seventh direction for verification purposes), along which the expansions are determined are tabulated below with their respective direction cosines and the observed values of expansion.

The seventh direction OG is taken for verification purposes.

The values of the constants *a*, *b*, *c*, *f*, *g* and *h* obtained after solving the six simultaneous equations are

$$a = +\,29 \cdot 35 \qquad f = -\,2 \cdot 571$$

$$b = +\,41 \cdot 26 \qquad g = +\,1 \cdot 393$$

$$c = +\,4 \cdot 68 \qquad h = -\,1 \cdot 245$$

TABLE

	Measured value of expansion $\alpha \times 10^6$	Direction cosines		
		l	m	n
1. Along the *a*-axis of the crystal (OA)	26·62	0·9385	−0·1806	−0·2946
2. Along the *b*-axis of the crystal (OB)	39·78	0	0·9905	0·1378
3. Along the *c*-axis of the crystal (OC)	4·68	0	0	1·0
4. Along the internal bisector of OA and OB (OD) ..	32·98	0·7519	0·6486	−0·1260
5. Along the internal bisector of OB and OC (OE) ..	7·91	0	0·6567	0·7542
6. Along the internal bisector of OC and OA (OF) ..	23·0	0·7901	−0·1521	0·5939
7. Along the bisector of the angle between the external bisector of OB and OC and OB (OG) ..	38·37	0	0·9585	−0·2851

and hence the equation of the ellipsoid as referred to the axes OX, OY and OZ is

$$29 \cdot 35x^2 + 41 \cdot 26y^2 + 4 \cdot 68z^2 - 5 \cdot 14yz + 2 \cdot 78zx - 2 \cdot 49xy - 1 = 0.$$

The discriminating cubic is then,

$$\lambda^3 - 75 \cdot 29\lambda^2 + 1531 \cdot 48\lambda - 5395 \cdot 54 = 0.$$

Here, putting $\lambda = x + 75 \cdot 29/3$, we obtain

$$x^3 - 358 \cdot 25x + 1422 \cdot 61 = 0.$$

This is of the form

$$x^3 + px + q = 0.$$

The solutions are thus given by $(u + v)$, where u and v are defined by

$$u \text{ or } v = [q/2 \pm \sqrt{p^3/27 + q^2/4}]^{\frac{1}{3}}$$

This gives 3-sets of values for u and v. Of these, combinations (u & v) are to be taken in such a way that $(u + v)$ is real. The solutions of the discriminating cubic obtained after following the above procedure are,

$$\lambda_1 = 29 \cdot 27; \quad \lambda_2 = 41 \cdot 58 \text{ and } \lambda_3 = 4 \cdot 45$$

and these are the principal coefficients of expansion.

The normal form of the ellipsoid is then $\lambda_1 x'^2 + \lambda_2 y'^2 + \lambda_3 z'^2 - 1 = 0$. The equations for the principal directions are,

$$\left.\begin{array}{rrrr} 24 \cdot 904 l_3 & - \ 1 \cdot 245 m_3 & + \ 1 \cdot 393 n_3 & = 0 \\ - \ 1 \cdot 245 l_3 & + \ 36 \cdot 816 m_3 & - \ 2 \cdot 571 n_3 & = 0 \\ 1 \cdot 393 l_3 & - \ 2 \cdot 571 m_3 & + \ 0 \cdot 233 n_3 & = 0 \end{array}\right\}$$

$$\begin{array}{rrrr} - \ 12 \cdot 227 l_2 & - \ 1 \cdot 245 m_2 & + \ 1 \cdot 393 n_2 & = 0 \\ - \ 1 \cdot 245 l_2 & - \ 0 \cdot 315 m_2 & - \ 2 \cdot 571 n_2 & = 0 \\ 1 \cdot 393 l_2 & - \ 2 \cdot 571 m_2 & - \ 36 \cdot 898 n_2 & = 0 \end{array}$$

and,

$$\left.\begin{array}{rrrr} 0 \cdot 082 l_1 & - \ 1 \cdot 245 m_1 & + \ 1 \cdot 393 n_1 & = 0 \\ - \ 1 \cdot 245 l_1 & + \ 11 \cdot 994 m_1 & - \ 2 \cdot 571 n_1 & = 0 \\ 1 \cdot 393 l_1 & - \ 2 \cdot 571 m_1 & - \ 24 \cdot 589 n_1 & = 0 \end{array}\right\}$$

These give

$$\begin{array}{lll} l_1 = 0 \cdot 9926 & l_2 = - \ 0 \cdot 1088 & l_3 = - \ 0 \cdot 0523 \\ m_1 = 0 \cdot 1126 & m_2 = \ \ 0 \cdot 9917 & m_3 = \ \ 0 \cdot 0678 \\ n_1 = 0 \cdot 0445 & n_2 = - \ 0 \cdot 0688 & n_3 = \ \ 0 \cdot 9962. \end{array}$$

Thus if OP_3, OP_2, and OP_1 are the principal directions we have

$$\begin{array}{lll} P_1OX = \ 6^\circ \, 59' & P_2OX = 96^\circ \, 15' & P_3OX = 93^\circ \\ P_1OY = 83^\circ \, 32' & P_2OY = \ 7^\circ \, 24' & P_3OY = 86^\circ \, 7' \\ P_1OZ = 87^\circ \, 27' & P_2OZ = 93^\circ \, 57' & P_3OZ = \ 5^\circ \end{array}$$

The calculated value of the expansion along OG gives $a_{OG} = 39 \cdot 69$, which compares favourably with the experimental value of $38 \cdot 37$.

5. Discussion

A perusal of the results obtained shows the extreme anisotropy of the expansion. The lowest expansion being $4 \cdot 45$ and the highest being $41 \cdot 58$, nearly nine times as large. It was found experimentally that while in the c-direction only two fringes moved across the field of view, nearly twenty fringes moved in the a-direction.

The principal axes of the expansion ellipsoid point near about the same directions as the crystallographic axes of the crystal. The structure of copper $CuSO_4$, $5H_2O$ has been investigated by Beevers and Lipson and the results show that the copper atoms are arranged in a face centred lattice in the (001) plane. Of the five water molecules, four are arranged in the form of a square around the Cu-atoms and the fifth is unco-ordinated. The direction of lowest expansion is thus found to be perpendicular to the plane of the face-centred Cu-atoms. The investigations of Krishnan and Mookerji on the magnetic properties of $CuSO_4$, $5H_2O$ show that as far as magnetic properties are concerned the crystal has a symmetry axis. This axis coincides with the intersection of the two planes formed by the four water molecules around each Cu-atom. This line of intersection is inclined at an angle of 155°, 68° and 50° with the *a*, *b* and *c* axes of the crystal respectively. It is found that none of the principal expansion axes coincides with this direction. The magnetic symmetry of the crystal is thus not revealed by the expansion properties of the crystal.

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