THE TWENTY-ONE ELASTIC CONSTANTS OF TRICLINIC COPPER SULPHATE PENTAHYDRATE

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Abstract

The twenty-one elastic constants of triclinic copper sulphate pentahydrate have been determined at room temperature by the ultrasonic pulse echo method. An iteration technique is used for solving the full cubic Christoffel equation exactly, (J. Indian Inst. Sci., **50** *(1968) 170) to obtain the elastic constants of crystals from ultrasonic velocities along arbitrary directions. The stiffness coefficients are obtained from measurements along eleven directions. The elastic constants referred to the I.R.E. system of axes are :*

$c_{11}=5.65$; $c_{12}=2.65$; $c_{13}=3.21$; $c_{14}=-0.33$; $c_{15}=-0.08$; $c_{16}=-0.39$; $c_{22}=4.33$; $c_{23}=3.47$; $c_{24}=-0.07$; $c_{25}=-0.21$; $c_{26}=0.20$: $c_{33}=5.69$; $c_{34}=-0.44$; $c_{35}=-0.21$; $c_{36}=-0.16$; $c_{44}=1.73$; $c_{45}=0.09$; $c_{46}=0.03$; $c_{55}=1.22$; $c_{56}=-0.26$ and $c_{66}=1.00$ in units of $10^{10}\ N/m^2$.

The results are discussed in relation to other studies on $CuSO_4\ 5H_2O$.

1. Introduction

In spite of the developments in the experimental techniques for determining the elastic constants of crystalline solids, it is surprising to note that not many crystals belonging to the less symmetric systems have been investigated. Since 1946, after Mason's[1] study on monoclinic dipotassium tartrate, a handful of monoclinic crystals has been studied[2]. Copper sulphate pentahydrade $CuSO_4\ 5H_2O$ is the first triclinic crystal to be studied for its elastic constants.

In the case of a triclinic crystal the difficulties encountered in the determination of the elastic constants are two-fold. In order to determine the twenty-one constants, one has to carry out a minimum of twenty-one non-degenerate velocity measurements along different directions. Secondly, the Christoffel equation describing the elastic wave propagation cannot be resolved into pure modes for an arbitrary direction in an anisotropic material. Consequently, one has to solve a set of simultaneous cubic equations to obtain the elastic constants.

It was with a view to study triclinic crystals that an interation technique[3] to solve the Christoffel equation to connect the analytic expressions for the velocities in terms of the elastic constants was developed. The evalution of the elastic constants of $CuSO_4.5H_2O$ is now presented.

2. CHOICE OF CO-ORDINATE AXES

Large size crystals of $CuSo_4.5H_2O$ were grown by the slow evaporation of the aqueous solution. The crystal belongs to triclinic $\bar{1}$ group with $a{:}b{:}c$: : 0.5721 : 1 :0.5554 and $\alpha = 82°5'$, $\beta = 107°8'$ and $\gamma = 102°41'$ (Groth[4]). Among a large number of forms observed, most common is the one sketched in Figure 1 with vertical zones $a\,(100)$, $m\,(110)$, $\mu\,(1\bar{1}0)$, $\pi\,(1\bar{3}0)$ and $b\,(010)$ with $\omega'(1\bar{1}\bar{1})$ as end faces. The interfacial angles in a large crystal can be be measured by means of a contact goniometer.

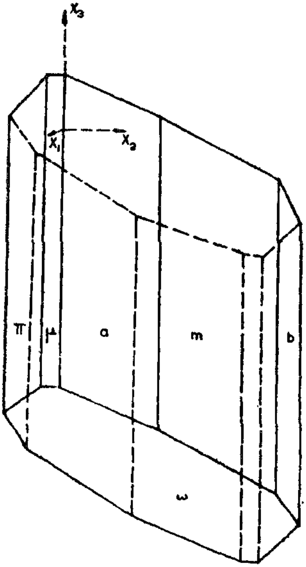

FIG. 1

Schematic view of $CuSO_4, 5H_2O$. Crystal. Choice of Axes X_1, X_2, X_3. X_1 Axis is outward Normal to a face. X_3 Axis is along a-μ Edge upwards

Once the '*a*' and '*m*' faces are located their intersection immediately gives the *c*-axis. In the original choice of the coordinate axes, identical to Sreedhar's[5] preference in his thermal expansion studies, the X_3-axis coincides with the *c*-axis of the crystal. The '*a*' face is taken as the X_2X_3 plane, the X_1-axis being the outward normal to the '*a*' face. The X_2-axis completes a right handed orthogonal system of coordinates. It lies on the '*a*' face and points horizontally towards right in the direction of the '*b*' face.

It was noticed later that this original choice does not conform with the I.R.E. convention[6]. Even though the choice of *X*, *Y*, *Z* axes in a triclinic crystal for describing the elastic properties is arbitrary to some extent, the I.R.E. committee seeks to establish a convenient pattern for all crystal systems. The crystallographic c-axis is chosen as the *Z*-axis. The *Y*-axis is taken as the outward normal to the crystallographic '*b*' face and is orthogonal to *Z*. The *X*-axis is then obtained by completing the right handed system of axes.

The present X_3-axis corresponds to the I.R.E. *Z*-axis; therefore a rotation of the present system by -10°48′ about X_3 will bring it into coincidence with the I.R.E. system. Reference to Figure 2 clearly shows the relative orientations of these sets in a plane perpendicular to the *c*-axis.

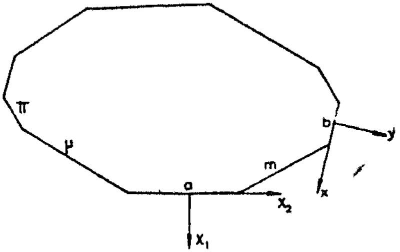

FIG. 2

Relative Disposition of the two sets of Axes. *c*-Axis (X_3Z) Perpendicular to and outwards from paper. X_1, X_2 present axes; *X*, *Y*, I.R.E. axes.

The original system of axes was chosen to facilitate comparison with the work of late Sundara Rao[7]. He was the first person to attempt studies on a triclinic specimen. However, there were some discrepancies in his results and they were not published. Sundara Rao's *X*-axis (denoted by X_1' to avoid confusion) is the inward normal to the '*a*' face and is thus $-X_1$, where X_1 is the axis used originally in this study. The edge common to the '*a*' and

TABLE 1

Orientations of Crystal Blocks

Sample	X_1'			X_2'			X_3'		
	α_{11}	α_{12}	α_{13}	α_{21}	α_{22}	α_{23}	α_{31}	α_{32}	α_{33}
Direction 1	1	0	0	0	1	0	0	0	1
2	1	0	0	0	0	-1	0	1	0
3	0	1	0	0	0	1	1	0	0
4	0.249_8	0.968_3	0	0	0	1	0.968_3	-0.249_8	0
5	0	-0.735_3	0.677_8	1	0	0	0	0.677_8	0.735_3
6	-0.797_2	0	-0.603_7	0	1	0	0.603^7	0	$-0,797_2$
7	-0.440_2	0.897_9	0	0	0	1	0.897_9	0.440_2	0
8	0.860_9	0.200_0	0.467_8	0	0.919_5	-0.393_1	-0.508_7	0.338_4	$0,791_6$
9	1	0	0	0	0.919_8	-0.392_3	0	0.392_3	0.919_8
10	-0.753_8	0.0	-0.657_2	0	1	0	0.657_2	0	-0.753_8
11	0.721_6	0.669_1	0.177_7	-0.508_7	0.338_4	0.791_6	0.469_5	-0.661_7	0.584_6

'ω' faces was taken by Sundara Rao as the X_2'-axis and its positive direction was outwards towards the 'b' face, from left to right. If the 'a' face is taken as the $X_2' X_3'$ plane, the X_3'-axis is taken normal to the X_2'-axis, its positive direction being down into the crystal. The X_1'-axis then completes a right handed orthogonal system. A rotation of his axes about X_1 brings his system into line with the present choice.

3. EXPERIMENTAL SAMPLES

To determine all the 21 constants at least 21 non-degenerate velocities must be determined. Eleven specimens were used in all. Three of them were axial cuts *i.e.*, propagation along X_1, X_2 and X_3. Two each had propagation direction in the X_1X_2, X_2X_3 and X_3X_1 planes, while the two remaining propagation directions were completely arbitrary.

The orientations of these blocks may be specified as follows: X_3' is taken as the direction of propagation, giving a quasi-longitudinal mode q_3. X_2' and X_1' are the two perpendicular directions and q_2 and q_1 are the quasi-transverse modes having vibration directions respectively along X_2' and X_1'. The directions X_i' are related to the crystal axes X_j by the scheme $X_i' = \alpha_{ij} X_j$ A specification of α_{ij} now uniquely fixes the direction of propagation X_3' and the two transverse directions X_2' and X_1'. This is done for all the eleven blocks in Table 1.

The longitudinal and transverse velocities are measured by the ultrasonic pulse echo method[8]. The values of $q_i = \rho v_i^2$, where $\rho = 228_4\ kg/m^3$ is assumed are recorded in Table 2. All the velocities were determined for blocks 1, 3, 7, 9 and 10. For directions 2, 4, 5, 6 and 11, only the longitudinal mode was excited. For Directions 8, the L and T_2 velocities were obtained.

For propagation along X_3'-direction, the Christoffel equation is

$$| c_{3i3j}' - \delta_{ij}\, \rho v^2 | = 0 \qquad [1]$$

Here c_{ij}' are the constants in a rotated coordinate system and they can be expressed in terms of the elastic constants c_{ij} and the direction cosines of the rotated system [9,10,11]. For the sake of convenience this is given separately in Appendix I.

The iteration procedure starts with equation [1], $| c_{3i3j}' - \delta_{ii}\, \rho v^2 | = 0$, where if the off diagonal terms c_{3i3j}' are neglected, the c_{3i3i}' are obtained as the ρv_i^2 in the zero order approximation. Now, c_{3i3i}' involves the linear combinations of the elastic constants c_{kl}; so by solving a sufficient number of simultaneous equations for c_{3i3i}' along different directions the zero order values of the elastic constants $c_{kl}^{(0)}$ are obtained. These $c_{kl}^{(0)}$ are used to calculate c_{3i3j}' Then the corrections $\epsilon_i = \rho v_i^2 - c_{3i3i}'$ are obtained by numerically solving the cubic equations fully. This gives the first order values of c_{3i3i}' and $c_{kl}^{(1)}$ are evaluated from them. The operations are continued until the convergent limit is approached to the desired accuracy.

TABLE 2

Effective Velocities for the Eleven Samples

Direction	Description	$q_i = \rho v_i^2$ $(10^{10}\,N/m^2)$*		
		$c'_{55} = q_1$	$c'_{44} = q_2$	$c'_{53} = q_3$
1	X_3-cut	1.182	1.683	5 749
2	X_2-cut	......	......	4.224
3	X_1-cut	0.961	1.495	5.380
4	X_1 (-14°28′) X_2	......	......	5.765
5	X_2 (47°20′) X_3	......	......	5.490
6	X_1 (-52°52′) X_3	......	......	6.190
7	X_1 (26°7′) X_2	1.293	1.451	4.746
8	α, β, γ ($X_3' \perp$ to ω face)	......	1.134	5.674
9	X_2 (23°6′) X_3	0.964	1.468	5.468
10	X_1 (-48°55′) X_3	1.092	1.405	6.172
11	α, β, γ	......	......	6 081

* The third decimal is retained in the preliminary calculations to avoid serious propagation of errors.

4. ZEROTH APPROXIMATION TO THE VALUES OF c_{ij}

The zero order values of c_{ij} can be determined by neglecting the expressions for c'_{34}, c'_{35} and c'_{45} in equation [1]. Directions 1, 2 and 3 furnish the zeo order values

$$c_{11}^{(0)} = 5.380 \quad c_{22}^{(0)} = 4.224 \qquad c_{33}^{(0)} = 5.749$$
$$c_{44}^{(0)} = 1.683 \quad c_{55}^{(0)} = (1.182 + 1.495)/2 = 1.339 \qquad c_{66}^{(0)} = 0.961$$

in units of $10^{10}\,N/m^2$. (From hereon the units $10^{10}\,N/m^2$ are dropped for convenience). Directions 4 and 7 together yield,

$$c_{12}^{(0)} = 3.186\,; \quad c_{16}^{(0)} = -0.491\,; \quad c_{26}^{(0)} = 0.393\,; \quad c_{45}^{(0)} = 0.058$$

Similarly,

$$c_{23}^{(0)} = 3.301\,; \quad c_{24}^{(0)} = 0.043\,; \quad c_{34}^{(0)} = -0.403\,; \quad c_{56}^{(0)} = -0.439$$

are obtained from directions 5 and 9 and

$$c_{13}^{(0)} = 3.355\,; \quad c_{15}^{(0)} = -0.107\,; \quad c_{35}^{(0)} = -0.233\,; \quad c_{46}^{(0)} = -0.034$$

from directions 6 and 10.

There now remain c_{14}, c_{25} and c_{36} to be determined. It is worth mentioning here that even if the three velocities for Direction 8 had been determined, it would not have been possible to evaluate $c_{14}^{(0)}$, $c_{25}^{(0)}$ and $c_{36}^{(0)}$. The set of simultaneous equations (for Direction 8) becomes

$$q_3: \quad 0.2772\ c_{14} - 0.1844\ c_{25} - 0.4316\ c_{36} = \text{const.}$$

$$q_2: \quad 0.1244\ c_{25} + 0.2912\ c_{36} = \text{const.}$$

$$q_1: \quad -0.2772\ c_{14} + 0.0600\ c_{25} + 0.1404\ c_{36} = \text{const.}$$

and are hence not linearly independent. Therefore, the choice of another direction *viz* , Direction 11 became unavoidable. Using the q_3 and q_2 values of Direction 8 and the q_3 value of direction 11, the constants are evaluated as :

$$c_{14}^{(0)} = -0.842\,; \quad c_{25}^{(0)} = -0.646\,; \quad c_{36}^{(0)} = -0.329\,;$$

The complete set of zero order values are :

5.380	3 186	3.355	−0.842	−0.107	−0.491
	4.224	3.301	0.043	—0.646	0.393
		5.749	−0.403	−0.233	−0.329
			1.683	0.058	−0.034
				1.339	−0.439
					0.961

5. ITERATION PROCEDURE

The zero order values are evidently the results of neglecting the off diagonal elements in c'_{3i3j} and they serve as the starting point for the iterations. Using $c_{ij}^{(0)}$, the numerical values of c'_{34}, c'_{35}, c'_{45}, c'_{55}, c'_{44} and c'_{33} for all the crystal blocks are written down. The numerical corrections are calculated from the expressions,

$$\epsilon_1^3 + \epsilon_1^2 (2c'_{55} - c'_{33} - c'_{44}) + \epsilon_1 [(c'_{33} - c'_{55})(c'_{44} - c'_{55}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{45} (c'_{33} - c'_{55}) + c'^2_{35} (c'_{44} - c'_{55}) - 2c'_{34}\, c'_{35}\, c'_{45}] = 0 \qquad [2a]$$

$$\epsilon_2^3 + \epsilon_2^2 (2c'_{44} - c'_{55} - c'_{33}) + \epsilon_2 [(c'_{55} - c'_{44})(c'_{33} - c'_{44}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{34} (c'_{55} - c'_{44}) + c'^2_{45} (c'_{33} - c'_{44}) - 2c'_{34}\, c'_{35}\, c'_{45}] = 0 \qquad [2b]$$

$$\epsilon_3^3 + \epsilon_3^2 (2c'_{33} - c'_{44} - c'_{55}) + \epsilon_3 [(c'_{44} - c'_{33})(c'_{55} - c'_{33}) - c'^2_{34} - c'^2_{35} - c'^2_{45}] + [c'^2_{35} (c'_{44} - c'_{33}) + c'^2_{34} (c'_{55} - c'_{33}) - 2c'_{34}\, c'_{35}\, c'_{45}] = 0 \qquad [2c]$$

The first order values of c'_{ii} are, $c'_{55}=q_1-\epsilon_1$, $c'_{44}=q_2-\epsilon_2$ and $c'_{33}=q_3-\epsilon_3$. They are again solved to obtain the first order values $c_{ij}^{(1)}$. The choice of ϵ_i is such that $\epsilon_1+\epsilon_2+\epsilon_3=0$ for any particular direction, since the trace of the c'_{ij} matrix is a constant. The first order values of the diagonal constants are:

$c_{11}^{(1)}=5.325$ $c_{22}^{(1)}=4.177$ $c_{33}^{(1)}=5.697$

$c_{44}^{(1)}=1.720$ $c_{55}^{(1)}=(1.197+1.257)/2=1.227$ $c_{66}^{(1)}=1.255$

For directions 1, 2 and 3 the calculations are easy whereas for the other directions the computations are quite lengthy.

As mentioned earlier the values c_{14}, c_{25} and c_{35} obtained from arbitrary orientations depend on a knowledge of the other 18 terms The zero order values because of the neglect of off diagonal terms in two various directions are necessarily approximate. In particular, c_{14}, c_{25} and c_{35}, in directions 8 and 11, are expressed as the difference between two large quantities. In view of the errors in the eighteen $c_{ij}^{(0)}$ values, the zero order values $c_{14}^{(0)}$, $c_{25}^{(0)}$ and $c_{36}^{(0)}$ are quite unreliable and contain disproportionately large errors. The result of this is to give abnormal first iteration values to c'_{34}, c'_{35} and c'_{45} in directions 4 onwards leading to very large oscillations in the iterated value of c_{ij}.

The difficulty is obviously caused by the serious propagation of errors which occurs especially in equations containing c_{14}, c_{25} and c_{36}. In principle, there is no doubt that after a sufficient number of iterations the oscillations in the values of c_{ij} will damp out. In practice, it was felt, after spending a considerable amount of time and effort, that this may take a great many iterations and that it would be desirable to speed up the convergence of the iterations.

In the equations [2*a*, *b*, *c*] for ϵ_i the constant term depends on the product of c'_{34}, c'_{35} and c'_{45} with $(c'_{33}-c'_{55})$, $(c'_{33}-c'_{44})$ and $(c'_{44}-c'_{55})$. Of them, $(c'_{33}-c'_{44})$ and $(c'_{33}-c'_{55})$ are usually large, of the order of 3 - 5. When c'_{45} is also large, the corrections ϵ_1 and ϵ_2 for the shear modes will be large. The corrected values of c'_{44} and c'_{55} upset the entire procedure leading to either divergence or violent oscillations in the iterated values of c_{ij} Therefore, it appears that the best way to accelerate the convergence of the iteration is to choose initially the values of $c_{14}^{(0)}$, $c_{25}^{(0)}$ and $c_{36}^{(0)}$ such that c'_{45} is small in directions 4-11. The choice $c_{14}^{(0)}=-0.2$, $c_{25}^{(0)}=0.2$ and $c_{36}^{(0)}=-0.4$ is found to effect this. With this choice, the first order values of c_{ij} are :

$c_{12}^{(1)}=2.793$; $c_{16}^{(1)}=-0.483$; $c_{26}^{(1)}=0.096$; $c_{45}^{(1)}=0.148$;

$c_{23}^{(1)}=3.598$; $c_{24}^{(1)}=-0.096$; $c_{34}^{(1)}=-0.435$; $c_{56}^{(1)}=-0.180$;

$c_{13}^{(1)}=3.293$; $c_{15}^{(1)}=-0.197$; $c_{35}^{(1)}=-0.297$; $c_{46}^{(1)}=0.103$;

It was found that in the second iteration also it was desirable to select c_{14}, c_{25} and c_{36} to speed up convergence. Because of the serious propagation of errors in the case of these three constants it was necessary to continue the operation until the 18 terms approximately settled down to steady values. It was only in the 12th iteration that directions 8 and 11 were used to calculate c_{14}, c_{25} and c_{36} for the subsequent iteration.

The iterations were carried on until two successive values of c_{ij} agreed within the experimental errors. The velocity measurements indicate an error of ±0.2%. So ρv^2 is correct to ±0.5%. The diagonal terms have an error of this magnitude. In sets like c_{12}, c_{16}, c_{26} and c_{45} the errors can be estimated by knowing the uncertainties in ρv^2 and the values of the diagonal constants. They amount to be only ±0.02 to ±0.04. The error in the set c_{23}, c_{24}, c_{34} and c_{56} is also of the same order. However, in the set c_{13}, c_{15}, c_{35} and c_{46} the errors are somewhat large ±0.02 to ±0.10, mainly because directions 6 and 10 are only 4° apart. The propagation of errors in the case of c_{14}, c_{25} and c_{36} is dramatically seen when the errors are calculated to be ±0.2 for c_{14}, ±0.1 for c_{25} and ±0.1 for c_{36}. The iteration results are summarized in Table 3.

TABLE 3

Elastic constants of Coppersulphate Pentahydrate at 25°C

Order of approx.	c_{11}	c_{12}	c_{13}	c_{14}	c_{15}	c_{16}
0	5.380	3.186	3.355	−0.2 (−0.842)	−0.107	−0.491
1	5.325	2.793	3.293	−0.2	−0.197	−0.483
5	5.313	2.964	3.089	−0.25	−0.241	−0.487
9	5.312	2.872	3.167	−0.3	−0.226	−0.483
12	5.315	2.879	3.163	−0.264	−0.226	−0.480
13	5.315	2.877	3.161	−0.270	−0.226	−0.480

Order of approx.	c_{22}	c_{23}	c_{24}	c_{25}	c_{26}
0	4.224	3.301	0.043	0.2 (−0.646)	0.393
1	4.177	3.598	−0.096	−0.2	0.096
5	4.213	3.577	−0.097	−0.15	0.131
9	4.218	3.515	−0.066	−0.14	0.062
12	4.221	3.518	−0.061	−0.133	0.069
13	4.221	3.520	−0.063	−0.149	0.061

Order of approx.	c_{33}	c_{34}	c_{35}	c_{36}	c_{44}
0	5.749	−0.403	−0.233	−0.4 (−0.329)	1.683
1	5.697	−0.435	−0.297	−0.4	1.720
5	5.686	−0.409	−0.303	−0.1	1.696
9	5.689	−0.399	−0.289	−0.1	1.687
12	5.691	−0.397	−0.290	−0.091	1.678
13	5.689	−0.397	−0.289	−0.101	1.679

Order of approx.	c_{45}	c_{46}	c_{55}	c_{56}	c_{66}
0	0.058	−0.034	1.339	−0.439	0.961
1	0.148	0.103	1.227	−0.180	1.255
5	0.152	0.156	1.283	−0.219	1.188
9	0.183	0.124	1.265	−0.238	1.232
12	0.171	0.124	1.269	−0.239	1.229
13	0.177	0.124	1.268	−0.237	1.231

The calculations were stopped with the 13th iteration. It was found that further iteration did not change the numbers appreciably. For example $c_{ij}^{(14)}$ were $c_{11}=5.315$, $c_{22}=4.221$, $c_{33}=5.689$, $c_{66}=1.230$, $c_{16}=-0.480$, $c_{34}=-0.396$, $c_{35}=-0.284$, $c_{45}=0.177$, and so on.

The final set of c_{ij} values in the original choice of the X_1, X_2, X_3 axes, is:

$$\begin{array}{cccccc}
5.315 & 2.877 & 3.161 & -0.270 & -0.226 & -0.480 \\
\pm 0.03 & \pm 0.03 & \pm 0.08 & \pm 0.2 & \pm 0.03 & \pm 0.02 \\
 & 4.221 & 3.520 & -0.063 & -0.149 & 0.061 \\
 & \pm 0.02 & \pm 0.04 & \pm 0.02 & \pm 0.1 & \pm 0.04 \\
 & & 5.689 & -0.397 & -0.289 & -0.101 \\
 & & \pm 0.03 & \pm 0.04 & \pm 0.04 & \pm 0.1 \\
 & & & 1.679 & 0.177 & 0.124 \\
 & & & \pm 0.01 & \pm 0.02 & \pm 0.02 \\
 & & & & 1.268 & -0.237 \\
 & & & & \pm 0.02 & \pm 0.03 \\
 & & & & & 1.231 \\
 & & & & & \pm 0.02
\end{array} \quad [3]$$

The manner in which the c_{ij} values have changed during the successive iterations is evident from Table 3 The final values are quite different from the zero orders values in the case of many constants. The least differences are among the diagonal terms c_{11}, c_{22}, c_{33} and c_{44} which have not changed by more than ~ 2%. c_{55} has changed by ~ 5% from the zero order to the final value. The two zero order values of c_{55}, 1.182 and 1 495 have finally come as close as 1.291 and 1.250. However, the final value of c_{66} is notably different from its zero order value. Among the principal off diagonal terms c_{12} and c_{13} are smaller in the final approximation than they are in the zero order calculation whereas final c_{23} is higher than zero order c_{23}. The changes are ~ 5-10%. The zero order sequence $c_{13} \gtrsim c_{23} \gtrsim c_{12}$ is changed to $c_{23} > c_{13} > c_{12}$. As regards the remaining minor off diagonal terms, the largest of them has a magnitude ~0.5. Nine of the elements have not changed in sign, though their magnitudes have changed by 0 01 to 0.35. Three constants have changed sign but the differences between the zero order and final values are again less than ~ 0.35. Such differences are not entirely unexpected.

The final c_{ij} values are substituted in the usual Christoffel equation

$$| \Gamma_{ij} - \delta_{ij} \rho v^2 | = 0 \qquad [4]$$

where $\Gamma_{ij} = c_{ijkl} \; \alpha_j \alpha_l$ to calculate the velocities and to see how far they agree with the measured values. This is nothing more than a mere check on numerical computations. For example, the calculated ρv_1^2 along the eleven directions are (with the measured values in brackets).

Direction 1 : 5.749 (5.749) ;
Direction 2 : 4.224 (4.224) ;
Direction 3 : 5.380 (5.380) ;
Direction 4 : 5.766 (5.765) ;
Direction 5 : 5.494 (5.490) ;
Direction 6 : 6.190 (6.190) ;
Direction 7 : 4.747 (4.746) ;
Direction 8 : 5.672 (5.674) ;
Direction 9 : 5.469 (5.468) ;
Direction 10 : 6.172 (6.172) ;
Direction 11 : 6.082 (6.081) .

6. DISCUSSION

As indicated earlier Sundara Rao, as early as 1950, had attempted a determination of the elastic constants of $CuSO_4.5H_2O$. The present work, though begun as early as 1967, took a considerable time in the absence of high speed computation. Meanwhile Siegert and Haussühl[12] have published an analysis of the elastic constants of $CuSO_4.5H_2O$ using Schaefer-Bergmann techniques of study.

In discussing all these matters it appears best to follow the I.R.E.-recommended system of coordinate axes. The I.R.E. Z-axis and the original

X_3-axis chosen in the present studies are the same. The 'a' and 'b' faces of the crystal are inclined at 79°12′. Thus a rotation of the present original system by −10°48′ about the X_3-axis makes it coincide with the I.R.E. axes. This can be easily effected by a transformation matrix.

$$\begin{array}{c|ccc} & X_1 & X_2 & X_3 \\ \hline X & c & s & 0 \\ Y & -s & c & 0 \\ Z & 0 & 0 & 1 \end{array} \qquad c = \cos(-10^\circ 48') \qquad a = \sin(-10^\circ 48') \qquad [5]$$

With the aid of Table A-1 and the above direction cosine scheme it is easy to transform the c_{ij} to I.R.E. c_{ij}'s. They are :

$$\begin{array}{cccccc} 5.64 & 92.653 & 3.210 & -0.327 & -0.076 & -0.389 \\ \pm 0.03 & \pm 0.03 & \pm 0.08 & \pm 0.2 & \pm 0.03 & \pm 0.02 \\ & 4.329 & 3.470 & -0.068 & -0.206 & 0.201 \\ & \pm 0.02 & \pm 0.04 & \pm 0.02 & \pm 0.1 & \pm 0.04 \\ & & 5.689 & -0.444 & -0.210 & -0.159 \\ & & \pm 0.03 & \pm 0.04 & \pm 0.04 & \pm 0.1 \\ & & & 1.729 & 0.088 & 0.032 \\ & & & \pm 0.01 & \pm 0.02 & \pm 0.02 \\ & & & & 1.218 & -0.265 \\ & & & & \pm 0.02 & \pm 0.03 \\ & & & & & 1.004 \\ & & & & & \pm 0.02 \end{array} \qquad [6]$$

The c_{ij}'s are matrix-inverted to obtain s_{ij}'s in units of $10^{-12}\ m^2/N$.

$$\begin{array}{cccccc} 2.902 & -1.095 & -0.914 & 0.248 & 0.083 & 1.211 \\ & 5.174 & -2.641 & -0.649 & -0.006 & -1.857 \\ & & 3.976 & 0.711 & 0.319 & 0.866 \\ & & & 6.007 & -0.401 & 0.042 \\ & & & & 8.828 & 2.424 \\ & & & & & 11.570 \end{array} \qquad [7]$$

The relationship between Sundara Rao's choice of axes and the present coordinate system was already mentioned. The s_{ij} values given by Sundara Rao were first matrix-inverted to obtain the following c_{ij} (in his own system of axes)

$$\begin{array}{cccccc}
-1.86 & -0.67 & 0.49 & 0.94 & -0.39 & 0.47 \\
 & 1.07 & 0.65 & 0.33 & 0.01 & 0.67 \\
 & & 1.95 & -0.11 & -0.48 & 0.11 \\
 & & & -0.17 & 0.11 & -0.19 \\
 & & & & 0.44 & 0.26 \\
 & & & & & 0.41
\end{array} \tag{8}$$

Sundara Rao's results. though pioneering, are based on static measurements. Consequently, the accuracy is rather poor and there is also the risk of plastic deformation. Added to this, one is apt to expect large propagation of errors too in the calculations, especially when the specimen is a triclinic crystal like $CuSO_4.5H_2O$. Glancing at Sundara Rao's values (equation 8), it is striking to note negative c_{11} and c_{44} values, which are two of the principal elastic constants. It is well known from tbe conditions of the stability of a crystal that the principal diagonal terms must be positive and every major determinant should also be positive. Therefore, clearly there must be a serious error in Sundera Rao's determination of the elastic moduli. Furthermore, some of the off diagonal terms are even larger than the main diagonal terms. In view of these and other defects a transformation of Sundara Rao's c_{ij} to I R E. axes is not useful. Sundara Rao's work, though pioneering, contains serious errors which make his final results untrustworthy.

Coming to Siegert and Haussühls' results, the choice of axes is indentical to the I.R.E. recommendation. They employ 14 specimens in all and determine the longitudinal and one of the two shear wave velocities for all of them. Their values at 20°C are in $10^{10}\ N/m^2$,

$$\begin{array}{cccccc}
5.709 & 2.062 & 3.164 & -0.426 & -0.042 & -0.221 \\
0.1\% & 1\% & 1\% & 5\% & 20\% & 3\% \\
 & 3.577 & 2.340 & -0.281 & -0.012 & -0.058 \\
 & 0.2\% & 1\% & 5\% & 60\% & 20\% \\
 & & 5.841 & -0.084 & -0.284 & -0.075 \\
 & & 0.1\% & 10\% & 5\% & 20\% \\
 & & & 1.650 & -0.185 & +0.119 \\
 & & & 1\% & 3\% & 10\% \\
 & & & & 1.515 & -0.353 \\
 & & & & 1\% & 3\% \\
 & & & & & 1.205 \\
 & & & & & 1\%
\end{array} \tag{9}$$

s_{ij} can be obtained by matrix-inverting c_{ij}.

Comparing Siegert and Haussühls' values and our values, there is good agreement in the main terms c_{11}, c_{33} and c_{44}. Also the sequence $c_{33} > c_{11} > c_{22} > c_{44} > c_{55} > c_{66}$ is maintained. In the case of cross constants, save for c_{26} and c_{45}, there is general agreement in magnitude and sign. Even in these two cases the differences are ~ 0.2. This overall agreement considering the complexity of experiments and calculations must be considered good.

There are, however, small differences in details. For example, Siegert and Haussühls' value of c_{22} (3.58) is significantly smaller than the present value (4.33). c_{55} (1 52) and c_{66} (1.20) are larger than the present 1.22 and 1.00. As regards the off diagonal terms c_{13} (3.16) $> c_{23}$ (2 34) $> c_{12}$ (2.06) whereas in the present measurements c_{23} (3.47) $> c_{13}$ (3.21) $> c_{12}$ (2.65). It is also found that the largest of the set c_{13} (3.16) is only 10% smaller than c_{22} whereas in the pulse echo measurements the largest of the set c_{23} (3.47) is nearly 20% smaller than c_{22}. As for the remaining 12 terms, the largest magnitude for them is ~ 0.4 and ten of them agree in sign in both cases. Even those two that do not agree in sign are small.

The overall agreement must be considered satisfactory. Nevertheless, it seems desirable to discuss the relative merits of the two determinations.

Certain points arise from the studies of Siegert and Haussühl. Consider first of all, the overall accuracy of 0.1% quoted by them for c_{11} etc. This implies an accuracy of 0.05% in their velocity measurements. Siegert and Haussühl use a Schaefer-Bergmann pattern and in this case the accuracy of velocity determinations depends on the sharpness of the fringes. The precision of this procedure is generally 0.5%. Even pulse echo measurements which are generally considered more accurate show normal errors $\sim$ 0.1% in velocities. In the present measurements the estimated errors in velocities are not less than $\sim$0.2%. It is quite surprising that Siegert and Haussühl could claim an accuracy of 0.05% in velocities determined from Schaefer-Bergmann patterns.

Secondly, Siegert and Haussühl have used in their calculation, the iteration procedure developed by Neighbours and Schacher[13]. This is an elaboration of the earlier method of Neighbours and Smith[14]. In this method instead of solving the cubic equations exactly to obtain the correction ϵ_i to the effective velocities, the linearized equations are dealt with. Solving the linearized equations to obtain ϵ_i is, in principle, not an exact solution of the cubic Christoffel equation. Even if the errors in the individual values of ϵ_i are small, the final resultant error in the case of a triclinic crystal may be very serious because of the considerable propagation of errors. From that point of view Siegert and Haussühls' values of the elastic constants of $CuSO_4 5H_2O$ are not the 'true' values. In the present calculations the simultaneous cubic equations are solved fully for each crystal block in every step of iteration to obtain the exact corrections. Hence the convergent values of the elastic constants are the 'true' solutions of the full Christoffel equations.

Another feature of the Schaefer-Bergmann measurement of Siegert and Haussühl is that only one transverse velocity is identified for all the 14 specimens. Normally along a general direction in an infinite anisotropic crystal one quasi-longitudinal and two quasi-shear modes can propagate. For a given boundary condition, *viz* , a specified vibration direction of the transducer, these will involve some linear combination of the three amplitudes to satisfy the boundary condition. Within the crystal, necessarily all the three modes will be launched simultaneously with appropriate amplitudes. In the Schaefer-Bergmann pattern there is an additional complication because the intensity of the light spot depends on the piezooptic coefficients also. It is surprising to note that the second transverse velocity has not been observed even for one sample.

In a finite crystal block there is an additional complication arising from mode conversion at the boundaries. When a compressional wave is reflected from a boundary at an arbitrary angle, the reflected wave is, in general, compressional plus shear[15]. The admixture of modes is unavoidable in anisotropic crystals even for normal incidence, the relative amplitudes depending on the presence of symmetry elements, boundary orientation and elastic constants. Such a mode conversion has been observed by Joel[16] in LiF.

There is no doubt that an exciting transducer gives rise to the simultaneous propagation of the three waves. Even in pulse work, this has been clearly demonstrated by Briscoe and Norwood.[17] The three waves moving independently of one another with a characteristic velocity will have different transit times. But in a standing wave pattern such as the Schaefer-Bergmann histogram all the three waves must so exist with different amplitudes. But the two shear modes have not been identified in Siegert and Hauseühls' experiments. In other words, the spots obtained by Siegert and Haussühl cannot be due to pure transverse modes, but due to an admixture of T_1 and T_2 modes in some proportion.

To quote a few numerical examples, Siegert and Haussühls' block 3 is identical to our Direction 1 for which the propagation direction is the crystallographic *c*-axis. Siegert and Haussühls' measured value of ρv^2 of (1.364) is midway between the present values (1.182 and 1.683). Similarly, for propagation perpendicular to the '*a*' face, the Schaefer-Bergmann ρv^2 of 1.031 is again in between the pulse echo values of 0.961 and 1.495. This is in support of the point discussed earlier.

In this connection it is worth mentioning that Haussühl's[18] values of the elastic constants of sodium chlorate and sodium bromate obtained from Schaefer-Bergmann patterns show large deviations in the cross constant c_{12}. For $NaClO_3$, the averages of our pulse echo measurements[3] and those obtained by the resonance method by Mason[19] and by Bechmann[20] are $c_{11}=4.96$, $c_{44}=1.16$ and $c_{12}=1.41$ ($10^{10}\,N/m^2$), while Haussühl's values are $c_{11}=5.00$, $c_{44}=1.16$ and $c_{12}=1.55$. For $NaBrO_3$ the average values obtained from pulse echo[21] and resonance studies are $c_{11}=5.85$, $c_{44}=1.54$ and $c_{12}=2.05$ whereas Haussühl gets respectively 5.48, 1.57 and 1.63. It is clear that the agreement of c_{12} is less satisfactory than that for c_{11} and c_{44}.

In the pulse echo method these complications arising from the simultaneous presence of more than one mode are avoided, because the transducer filters out one mode at a time and furthermore, the L, T_1 and T_2 modes would be received separated in transit times. In the present measurements small uncertainties could have crept in from two of the blocks used. The block corresponding to Direction 6 had a thickness 2.64 mm just sufficient enough to give echoes separated by a small time interval 1.02 μ sec. Further, Direction 2, had a rather small sectional area for the transmission of the pulse. Therefore in the measurements made with these two blocks the errors may have been more. Because of the propagation of errors, these two blocks affect the overall accuracy of the other constants. Perhaps the combined accuracy of the present measurements can be improved by higher precision in velocity measurements.

Finally, the relationship between the elastic constants and other properties of $CuSO_4.5H_2O$ may be briefly indicated. X-ray studies[22] show that in $CuSO_4.5H_2O$ the Cu atoms are arranged in a face centred lattice surrounded by four water molecules which are at the corners of a square. The fifth water molecule is not coordinated and all the waters show two oxygen bonds each. Neutron diffraction study[23] of the water molecules provides full details of the shape and environment of these water molecules and of hydrogen bonds which link together the atoms in the structure. Studies[24] on the magnetic properties reveal a symmetry axis, coinciding with the intersection of the two planes formed by the water molecules around each Cu atom. Unfortunately this symmetry axis is not seen in other properties, which must therefore be an accidental symmetry.

Sreedhar[5] in his thermal expansion studies has chosen a system of axes, which coincides with our original choice. The thermal expansion coefficients $\lambda_1=29.27$, $\lambda_2=41.58$ and $\lambda_3=4.45$ (10^{-6}) show extreme anisotropy of expansion. It is interesting to note that $\lambda_2>\lambda_1>\lambda_3$ whereas $c_{33}>c_{11}>c_{22}$ for the longitudinal elastic constants. But the elastic constants do not show the extreme anisotropy exhibited by λ_i Neither do these properties reveal the magnetic symmetry axis.

Table A-1

Transformation Equations of Elastic Constants

c_{ij}	c'_{45}	c'_{35}	c'_{34}	c'_{55}	c'_{44}	c'_{33}
c_{11}	$\alpha_1\beta_1\gamma_1^2$	$\alpha_1\gamma_1^3$	$\beta_1\gamma_1^3$	$\alpha_1^2\gamma_1^2$	$\beta_1^2\gamma_1^2$	γ_1^4
c_{12}	$\alpha_1\beta_2\gamma_1\gamma_2+\alpha_2\beta_1\gamma_1\gamma_2$	$\alpha_1\gamma_1\gamma_2^2+\alpha_2\gamma_1^2\gamma_2$	$\beta_1\gamma_1\gamma_2^2+\beta_2\gamma_1^2\gamma_2$	$2\alpha_1\alpha_2\gamma_1\gamma_2$	$2\beta_1\beta_2\gamma_1\gamma_2$	$2\gamma_1^2\gamma_2^2$
c_{13}	$\alpha_1\beta_3\gamma_1\gamma_3+\alpha_3\beta_1\gamma_1\gamma_3$	$\alpha_1\gamma_1\gamma_3^2+\alpha_3\gamma_1^2\gamma_3$	$\beta_1\gamma_1\gamma_3^2+\beta_3\gamma_1^2\gamma_3$	$2\alpha_1\alpha_3\gamma_1\gamma_3$	$2\beta_1\beta_3\gamma_1\gamma_3$	$2\gamma_1^2\gamma_3^2$
c_{14}	$\alpha_1\beta_3\gamma_1\gamma_2+\alpha_3\beta_1\gamma_1\gamma_2+$ $\alpha_1\beta_2\gamma_1\gamma_3+\alpha_2\beta_1\gamma_1\gamma_3$	$\alpha_3\gamma_1^2\gamma_2+\alpha_2\gamma_1^2\gamma_3$ $+2\alpha_1\gamma_1\gamma_2\gamma_3$	$\beta_3\gamma_1^2\gamma_2+\beta_2\gamma_1^2\gamma_3$ $+2\beta_1\gamma_1\gamma_2\gamma_3$	$2\alpha_1\alpha_3\gamma_1\gamma_2+2\alpha_1\alpha_2\gamma_1\gamma_3$	$2\beta_1\beta_3\gamma_1\gamma_2+2\beta_1\beta_2\gamma_1\gamma_3$	$4\gamma_1^2\gamma_2\gamma_3$
c_{15}	$\alpha_1\beta_3\gamma_1^2+\alpha_3\beta_1\gamma_1^2+2\alpha_1\beta_1\gamma_1\gamma_3$	$3\alpha_1\gamma_1^2\gamma_3+\alpha_3\gamma_1^3$	$3\beta_1\gamma_1^2\gamma_3+\beta_3\gamma_1^3$	$2\alpha_1^2\gamma_1\gamma_3+2\alpha_1\alpha_3\gamma_1^2$	$2\beta_1^2\gamma_1\gamma_3+2\beta_1\beta_3\gamma_1^2$	$4\gamma_1^3\gamma_3$
c_{16}	$\alpha_1\beta_2\gamma_1^2+\alpha_3\beta_1\gamma_1^2+2\alpha_1\beta_1\gamma_1\gamma_2$	$3\alpha_1\gamma_1^2\gamma_2+\alpha_2\gamma_1^3$	$3\beta_1\gamma_1^2\gamma_2+\beta_2\gamma_1^3$	$2\alpha_1^2\gamma_1\gamma_2+2\alpha_1\alpha_2\gamma_1^2$	$2\beta_1^2\gamma_1\gamma_2+2\beta_1\beta_2\gamma_1^2$	$4\gamma_1^3\gamma_2$
c_{22}	$\alpha_2\beta_2\gamma_2^2$	$\alpha_2\gamma_2^3$	$\beta_2\gamma_2^3$	$\alpha_2^2\gamma_2^2$	$\beta_2^2\gamma_2^2$	γ_2^4
c_{23}	$\alpha_2\beta_3\gamma_2\gamma_3+\alpha_3\beta_2\gamma_2\gamma_3$	$\alpha_3\gamma_2^2\gamma_3+\alpha_2\gamma_2\gamma_3^2$	$\beta_3\gamma_2^2\gamma_3+\beta_2\gamma_2\gamma_3^2$	$2\alpha_2\alpha_3\gamma_2\gamma_3$	$2\beta_2\beta_3\gamma_2\gamma_3$	$2\gamma_2^2\gamma_3^2$
c_{24}	$\alpha_2\beta_3\gamma_2^2+\alpha_3\beta_2\gamma_2^2+2\alpha_2\beta_2\gamma_2\gamma_3$	$3\alpha_2\gamma_2^2\gamma_3+\alpha_3\gamma_2^3$	$3\beta_2\gamma_2^2\gamma_3+\beta_3\gamma_2^3$	$2\alpha_2^2\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_2^2$	$2\beta_2^2\gamma_2\gamma_3+2\beta_2\beta_3\gamma_2^2$	$4\gamma_2^3\gamma_3$
c_{25}	$\alpha_2\beta_3\gamma_1\gamma_2+\alpha_3\beta_2\gamma_1\gamma_2+$ $\alpha_2\beta_1\gamma_2\gamma_3+\alpha_1\beta_2\gamma_2\gamma_3$	$\alpha_1\gamma_2^2\gamma_3+\alpha_3\gamma_1\gamma_2^2+$ $2\alpha_2\gamma_1\gamma_2\gamma_3$	$\beta_1\gamma_2^2\gamma_3+\beta_3\gamma_1\gamma_2^2+$ $2\beta_2\gamma_1\gamma_2\gamma_3$	$2\alpha_1\alpha_2\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_1\gamma_2$	$2\beta_1\beta_2\gamma_2\gamma_3+2\beta_2\beta_3\gamma_1\gamma_2$	$4\gamma_1\gamma_2^2\gamma_3$
c_{26}	$\alpha_2\beta_1\gamma_2^2+\alpha_1\beta_2\gamma_2^2+2\alpha_2\beta_2\gamma_1\gamma_2$	$3\alpha_2\gamma_1\gamma_2^2+\alpha_1\gamma_2^3$	$3\beta_2\gamma_1\gamma_2^2+\beta_1\gamma_2^3$	$2\alpha_1\alpha_2\gamma_2^2+2\alpha_2^2\gamma_1\gamma_2$	$2\beta_1\beta_2\gamma_2^2+2\beta_2^2\gamma_1\gamma_2$	$4\gamma_1\gamma_2^3$
c_{33}	$\alpha_3\beta_3\gamma_3^2$	$\alpha_3\gamma_3^3$	$\beta_3\gamma_3^3$	$\alpha_3^2\gamma_3^2$	$\beta_3^2\gamma_3^2$	γ_3^4
c_{34}	$\alpha_3\beta_2\gamma_3^2+\alpha_2\beta_3\gamma_3^2+2\alpha_3\beta_3\gamma_2\gamma_3$	$3\alpha_3\gamma_2\gamma_3^2+\alpha_2\gamma_3^3$	$3\beta_3\gamma_2\gamma_3^2+\beta_2\gamma_3^3$	$2\alpha_2\alpha_3\gamma_3^2+2\alpha_3^2\gamma_2\gamma_3$	$2\beta_2\beta_3\gamma_3^2+2\beta_3^2\gamma_2\gamma_3$	$4\gamma_2\gamma_3^3$
c_{35}	$\alpha_3\beta_1\gamma_3^2+\alpha_1\beta_3\gamma_3^2+2\alpha_3\beta_3\gamma_1\gamma_3$	$3\alpha_3\gamma_1\gamma_3^2+\alpha_1\gamma_3^3$	$3\beta_3\gamma_1\gamma_3^2+\beta_1\gamma_3^3$	$2\alpha_1\alpha_3\gamma_3^2+2\alpha_3^2\gamma_1\gamma_3$	$2\beta_1\beta_3\gamma_3^2-2\beta_3^2\gamma_1\gamma_3$	$4\gamma_1\gamma_3^3$
c_{36}	$\alpha_3\beta_2\gamma_1\gamma_3+\alpha_2\beta_3\gamma_1\gamma_3+$ $\alpha_3\beta_1\gamma_2\gamma_3+\alpha_1\beta_2\gamma_2\gamma_3$	$\alpha_2\gamma_1\gamma_3^2+\alpha_1\gamma_2\gamma_3^2+$ $2\alpha_3\gamma_1\gamma_2\gamma_3$	$\beta_2\gamma_1\gamma_3^2+\beta_1\gamma_2\gamma_3^2$ $2\beta_3\gamma_1\gamma_2\gamma_3$	$2\alpha_1\alpha_3\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_1\gamma_3$	$2\beta_1\beta_3\gamma_2\gamma_3+2\beta_2\beta_3\gamma_1\gamma_3$	$4\gamma_1\gamma_2\gamma_3^2$
c_{44}	$\alpha_3\beta_3\gamma_2^2+\alpha_2\beta_2\gamma_3^2+\alpha_3\beta_2\gamma_2\gamma_3$ $+\alpha_2\beta_3\gamma_2\gamma_3$	$2\alpha_3\gamma_2^2\gamma_3+2\alpha_2\gamma_2\gamma_3^2$	$2\beta_3\gamma_2^2\gamma_3+2\beta_2\gamma_2\gamma_3^2$	$\alpha_2^2\gamma_3^2+\alpha_3^2\gamma_2^2+$ $2\alpha_2\alpha_3\gamma_2\gamma_3$	$\beta_2^2\gamma_3^2+\beta_3^2\gamma_2^2+$ $2\beta_2\beta_3\gamma_2\gamma_3$	$4\gamma_2^2\gamma_3^2$
c_{45}	$\alpha_2\beta_1\gamma_3^2+\alpha_1\beta_2\gamma_3^2+\alpha_3\beta_1\gamma_2\gamma_3$ $+\alpha_1\beta_3\gamma_2\gamma_3+\alpha_2\beta_3\gamma_1\gamma_3+$ $\alpha_3\beta_2\gamma_1\gamma_3+2\alpha_3\beta_3\gamma_1\gamma_2$	$2\alpha_2\gamma_1\gamma_3^2+2\alpha_1\gamma_2\gamma_3^2$ $+4\alpha_3\gamma_1\gamma_2\gamma_3$	$2\beta_2\gamma_1\gamma_3^2+2\beta_1\gamma_2\gamma_3^2+$ $4\beta_3\gamma_1\gamma_2\gamma_3$	$2\alpha_1\alpha_2\gamma_3^2+2\alpha_3^2\gamma_1\gamma_2+$ $2\alpha_1\alpha_3\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_1\gamma_3$	$2\beta_1\beta_2\gamma_3^2+2\beta_3^2\gamma_1\gamma_2+$ $2\beta_1\beta_3\gamma_2\gamma_3+2\beta_2\beta_3\gamma_1\gamma_3$	$8\gamma_1\gamma_2\gamma_3^2$
c_{46}	$\alpha_3\beta_1\gamma_2^2+\alpha_1\beta_3\gamma_2^2+\alpha_3\beta_2\gamma_1\gamma_2$ $+\alpha_2\beta_3\gamma_1\gamma_2+\alpha_2\beta_1\gamma_2\gamma_3$ $+\alpha_1\beta_2\gamma_2\gamma_3+2\alpha_2\beta_2\gamma_1\gamma_3$	$2\alpha_1\gamma_2^2\gamma_3+2\alpha_3\gamma_1\gamma_2^2$ $+4\alpha_2\gamma_1\gamma_2\gamma_3$	$2\beta_1\gamma_2^2\gamma_3+2\beta_3\gamma_1\gamma_2^2+$ $4\beta_2\gamma_1\gamma_2\gamma_3$	$2\alpha_1\alpha_3\gamma_2^2+2\alpha_2^2\gamma_1\gamma_3$ $+2\alpha_1\alpha_2\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_1\gamma_2$	$2\beta_1\beta_3\gamma_2^2+2\beta_2^2\gamma_1\gamma_3+$ $+2\beta_1\beta_2\gamma_2\gamma_3+2\beta_2\beta_3\gamma_1\gamma_2$	$8\gamma_1\gamma_2^2\gamma_3$
c_{55}	$\alpha_3\beta_3\gamma_1^2+\alpha_1\beta_1\gamma_3^2+$ $\alpha_3\beta_1\gamma_1\gamma_3+\alpha_1\beta_3\gamma_1\gamma_3$	$2\alpha_1\gamma_1\gamma_3^2+2\alpha_3\gamma_1^2\gamma_3$	$2\beta_1\gamma_1\gamma_3^2+2\beta_3\gamma_1^2\gamma_3$	$\alpha_1^2\gamma_3^2+\alpha_3^2\gamma_1^2$ $+2\alpha_1\alpha_3\gamma_1\gamma_3$	$\beta_1^2\gamma_3^2+\beta_3^2\gamma_1^2$ $2\beta_1\beta_3\gamma_1\gamma_3$	$4\gamma_1^2\gamma_3^2$
c_{56}	$\alpha_3\beta_2\gamma_1^2+\alpha_2\beta_3\gamma_1^2+\alpha_1\beta_2\gamma_1\gamma_3$ $+\alpha_2\beta_1\gamma_1\gamma_3+\alpha_1\beta_3\gamma_1\gamma_2$ $+\alpha_3\beta_1\gamma_1\gamma_2+2\alpha_1\beta_1\gamma_2\gamma_3$	$2\alpha_2\gamma_1^2\gamma_3+2\alpha_3\gamma_1^2\gamma_2$ $+4\alpha_1\gamma_1\gamma_2\gamma_3$	$2\beta_2\gamma_1^2\gamma_3+2\beta_3\gamma_1^2\gamma_2$ $+4\beta_1\gamma_1\gamma_2\gamma_3$	$2\alpha_1^2\gamma_2\gamma_3+2\alpha_2\alpha_3\gamma_1^2$ $+2\alpha_1\alpha_2\gamma_1\gamma_3+2\alpha_1\alpha_3\gamma_1\gamma_2$	$2\beta_1^2\gamma_2\gamma_3+2\beta_2\beta_3\gamma_1^2+$ $2\beta_1\beta_2\gamma_1\gamma_3+2\beta_1\beta_3\gamma_1\gamma_2$	$8\gamma_1^2\gamma_2\gamma_3$
c_{66}	$\alpha_2\beta_2\gamma_1^2+\alpha_1\beta_1\gamma_2^2$ $\alpha_2\beta_1\gamma_1\gamma_2+\alpha_1\beta_2\gamma_1\gamma_2$	$2\alpha_1\gamma_1\gamma_2^2+2\alpha_2\gamma_1^2\gamma_2$	$2\beta_1\gamma_1\gamma_2^2+2\beta_2\gamma_1^2\gamma_2$	$\alpha_1^2\gamma_2^2+\alpha_2^2\gamma_1^2+$ $2\alpha_1\alpha_2\gamma_1\gamma_2$	$\beta_1^2\gamma_2^2+\beta_2^2\gamma_1^2+$ $2\beta_1\beta_2\gamma_1\gamma_2$	$4\gamma_1^2\gamma_2^2$

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APPENDIX

In the iteration calculation, values of c'_{33}, c'_{44}, c'_{55}, c'_{34}, c'_{35}, and c'_{45} are required along arbitrary directions X'_i. They may be expressed in terms of c_{ij} and the direction cosines defining X_i' with respect to X_j. The direction cosine scheme may be written as

$$\begin{array}{c|ccc} & X_1 & X_2 & X_3 \\ \hline X_1' & \alpha_1 & \alpha_2 & \alpha_3 \\ X_2' & \beta_1 & \beta_2 & \beta_2 \\ X_3' & \gamma_1 & \gamma_2 & \gamma_3 \end{array}$$

In terms of the direction cosines (written as α_i, β_i, γ_i to avoid confusion with the α_{ij} used in the text), the values of c'_{ij} are given in Table A-1.

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