ELASTIC CONSTANTS OF THE HEPTAHYDRATES OF MAGNESIUM AND ZINC SULPHATES

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1. INTRODUCTION

THE heptahydrates of the sulphates of magnesium and zinc belong to the orthorhombic system. The naturally occurring minerals form the Epsomite group consisting of $MgSO_4$, $7H_2O$, also called Epsom salt, $ZnSO_4$, $7H_2O$, or Goslarite and $NiSO_4$, $7H_2O$ or morenosite. They exhibit many similar properties as in their cleavage and other crystal habits. When these sulphates are grown from aqueous solutions at room temperature, they crystallize as the heptahydrates. Since good crystals of these salts can be easily grown, it is proposed to determine the elastic constants of two of these three salts, namely of $MgSO_4$, $7H_2O$ and $ZnSO_4$, $7H_2O$.

The crystal faces and axes are identified by using the crystallographic and the optical data given by Groth (1908).

In both the crystals, the following are the prominent faces: *m* (110), *b* (010), *o* (111), *w* $(1\bar{1}1)$, *r* (101) and occasionally also ***a*** (100). The relevant data used in identification are given below:

$MgSO_4$, $7H_2O$.—

$$m : m = (110) : (1\bar{1}0) = 89^\circ\, 26'$$

$$o : w = (111) : (111) = 52^\circ\, 40'$$

$$o : m = (111) : (110) = 50^\circ\, 49'$$

$$r : m = (101) = (110) = 69^\circ\, 13'$$

Cleavage is perfect in the plane (010).

$ZnSO_4$, $7H_2O$.—Forms from solutions under 30° C.

$$m:m = (110):(1\bar{1}0) = 89° 22'$$
$$m:q = (110):(011) = 69° 55'$$
$$m:r = (110):(101) = 69° 11'$$
$$0:m = (111):(110) = 50° 25'$$
$$0:a = (111):(100) = 63° 30'$$
$$0:b = (111):(010) = 63° 0'$$

Cleavage along *b* (010).

The cleavage is so good that by properly tapping with the sharp edge of a screw-driver, we get the X_2-sectional plane. With the help of the above data, the faces and axes are determined and the necessary sections cut.

2. Experimental Procedure

The orthorhombic system is characterised by the nine constants C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{23} and C_{31}. The procedure adopted to determine the constants and the technique employed are substantially the same as those described by the author in a previous publication (Sundara Rao, 1949). The *a*-, *b*-, *c*-crystallographic axes are respectively taken as the X_1-, X_2-, X_3-axes.

Six of the nine constants, *viz.*, those of the type C_{ii} come out directly from the axial cuts, using the secular Christoffel determinant. Thus a plate whose normal coincides with the X_1-axis gives C_{11}, C_{55} and C_{66}; the X_2-cut gives C_{22}, C_{66} and C_{44} and the X_3-cut yields C_{33}, C_{44} and C_{55}, which thus give the six constants C_{ii} with three checks. The remaining constants C_{12}, C_{23} and C_{31} are determined by using suitable oblique cuts. For these cuts, however, a method which obviates the necessity of using approximate solutions is adopted and given below.

For oblique cuts, the simplest method of using the Christoffel equation is to transform all the constants to a suitable co-ordinate system and then use the secular determinant. Here the normal to the plate is denoted by the transformed X_3'-axis and the constants are transformed to this new system of co-ordinates axes. After the transformation, we get the new form of the Christoffel determinant as given below:

$$\begin{vmatrix} C_{33}'-x & C_{34}' & C_{35}' \\ C_{34}' & C_{44}'-x & C_{45}' \\ C_{35}' & C_{45}' & C_{55}'-x \end{vmatrix} = 0 \qquad (1)$$

where $x = \rho v^2$ and ρ is the density of the medium and v the corresponding velocity of the elastic wave in it.

Considering a rotation about the X_1-axis, we shall take a section which has its normal in the X_2-X_3 plane, equally inclined to either of them, the $X_1\,45\,X_2$ ($X_1\,45\,X_2$ cut meaning that the normal is perpendicular to X_1-axis and is inclined at 45° to X_2 and so on) as in a previous notation. The relevant constants for the section are

$$\left.\begin{aligned} C_{33}' &= \tfrac{1}{4}(C_{22}+C_{33}+2C_{23}+4C_{44}) \\ C_{44}' &= \tfrac{1}{4}(C_{22}+C_{33}-2C_{23}) \\ C_{55}' &= \tfrac{1}{2}(C_{55}+C_{66}) \\ C_{34}' &= \tfrac{1}{4}(C_{33}-C_{22}) \\ C_{35}' &= C_{45}' = 0. \end{aligned}\right\} \qquad (2)$$

Substituting the above values in (1) we get one of the torsion modes, *viz.*, C_{55}' out of the determinant, the remaining part being the quadratic

$$(C_{33}'-x)(C_{44}'-x) - C'^2_{34} = 0 \qquad (3)$$

the two roots of which give the remaining torsion and the longitudinal mode. We get from (3)

$$x = \tfrac{1}{2}\left[C_{33}'+C_{44}' \pm \sqrt{(C_{33}'-C_{44}')^2 + 4C'^2_{34}}\right] \qquad (4)$$

the root with the + sign for the radical in (4) being obviously the longitudinal mode, which we shall denote as x_l. After a little transformation therefore, we get:

$$C_{23} = \pm\sqrt{[\{2x_l - (C_{33}'+C_{44}')\}^2 - 4C^2{}_{34}'} - C_{44}] \qquad (5)$$

Inspection shows that all the quantities on the right-hand side of (5) are known, x_l being experimentally determined, and the rest of the quantities previously determined, $C_{33}'+C_{44}'$ being equal to $\frac{1}{2}(C_{22}+C_{33}+2C_{44})$.

Here, however, there is an ambiguity in the sign of the radical in (5). But, it can be easily decided because one of the values of C_{23} often makes C_{33}' negative which is absurd; and moreover, in the limiting case when $C_{34}' \rightarrow 0$ the value of C_{23} shoud be that obtained by putting $x_l = C_{33}'$. This leaves us with only one correct value of C_{23}, the other being spurious, arising out of the arithmetical necessity of squaring the radical. Hence C_{23} is determined unambiguously. Thus for instance the values of C_{12} obtained by a similar procedure are $+1 \cdot 194$ and $-4 \cdot 818$, while the approximate value of C_{12} obtained by putting $x_l = C_{33}'$ is $1 \cdot 2$. The value $-4 \cdot 818$ of C_{12} makes C_{33}' negative, which being absurd by itself, leaves the other value $+1 \cdot 194$ as the correct one, very near to $1 \cdot 2$.

In a similar manner, the other constants C_{13} and C_{21} can be determined from $X_2 45 X_3$ and $X_3 45 X_1$ cuts. The relevant data for both are given below:

$$\left.\begin{aligned}
&\textit{X}_2 45 \textit{X}_3\textit{-cut.—}\\
&\quad C_{33}' = \tfrac{1}{4} C_{11} + C_{33} + 2C_{13} + 4C_{55})\\
&\quad C_{44}' = \tfrac{1}{4} (C_{11} + C_{33} - 2C_{13})\\
&\quad C_{55}' = \tfrac{1}{2} (C_{66} + C_{44})\\
&\quad C_{34}' = \tfrac{1}{4} (C_{33} - C_{11})\\
&\quad C_{35}' = C_{45}' = 0.\\
&\textit{X}_3 45 \textit{X}_1\textit{-cut.—}\\
&\quad C_{33}' = \tfrac{1}{4} (C_{11} + C_{22} + 2C_{12} + 4C_{66})\\
&\quad C_{44}' = \tfrac{1}{4} (C_{11} + C_{22} - 2C_{12})\\
&\quad C_{55}' = \tfrac{1}{2} (C_{44} + C_{55})\\
&\quad C_{34}' = \tfrac{1}{4} (C_{22} - C_{11})\\
&\quad C_{35}' = C_{45}' = 0.
\end{aligned}\right\} \qquad (6)$$

In the actual experiment, precautions are taken to see that the crystal plates are not heated up during the work, since both of them are extremely heat sensitive. Sometimes more than one section of the same description have been worked to eliminate possible errors due to heating, etc. Tourmaline plates have been avoided as the heating is considerable with them. Ultrasonic frequencies up to 10 Mc/sec. are used.

3. Experimental Data and Results

The experimental data obtained and the results calculated as indicated in the previous section are given below:—

TABLE I

$MgSO_4$, $7H_2O$. $\rho = 1{\cdot}687$ gm./cm.^{3}

Unit : 10^{11} dynes/cm.^{2}

Plate No.	Description	Thickness in mm.	Fundamental frequency in Mc/sec.	Mode of Vibration	Effective constant	Value of the constant
1	X_1-cut	1·585	2·028	(*l*)	C_{11}	6·976
1	do	do	1·144	(*t*)	C_{66}	2·219
1	do	do	1·179	(*t*)	C_{55}	2·358
2	X_2-cut	1·64	1·708	(*l*)	C_{22}	5·291
2	do	do	0·7688	(*t*)	C_{44}	1·073
2	do	do	1·104	(*t*)	C_{66}	2·211
3	X_3-cut	1·312	2·66	(*l*)	C_{33}	8·219
3	do	do	0·9605	(*t*)	C_{44}	1·072
3	do	do	1·405	(*t*)	C_{55}	2·292
4	$X_1 45 X_2$	1·80	1·656	(*l*)	x_l	5·998
5	$X_2 45 X_3$	1·72	1·945	(*l*)	x_l	7·555
6	$X_3 45 X_1$	1·74	1·885	(*l*)	x_l	7·261

(*l*) and (*t*) in the above table denote the longitudinal and the transverse modes.

TABLE II

$ZnSO_4$, $7H_2O$. $\rho = 1{\cdot}974\cdot$ gm./cm.^{3}

Unit : 10^{11} dynes/cm.^{2}

Plate No.	Description	Thickness in mm.	Fundamental frequency in Mc/sec.	Mode of Vibration	Effective constant	Value of the constant
1	X_1-cut	1·615	1·395	(*l*)	C_{11}	4·002
1	do	do	0·9025	(*t*)	C_{55}	1·685
1	do	do	0·9423	(*t*)	C_{66}	1·830
2	X_2-cut	1·15	1·756	(*l*)	C_{22}	3·221
2	do	do	1·311	(*t*)	C_{66}	1·795
2	do	do	0·726	(*t*)	C_{44}	0·550
3	X_3-cut	1·016	2·585	(*l*)	C_{33}	5·446
3	do	do	0·749	(*t*)	C_{44}	0·457
3	do	do	1·45	(*t*)	C_{55}	1·714
4	$X_1 45 X_2$	1·26	1·66	(*l*)	x_l	3·455
5	$X_2 45 X_3$	1·20	2·021	(*l*)	x_l	4·646
6	$X_3 45 X_1$	1·365	1·694	(*l*)	x_l	4·218

TABLE III

Unit : 10^{11} dynes/cm.^{2}

Salt	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
$MgSO_4$, $7H_2O$	6·98	5·29	8·22	1·07	2·33	2·22	3·90	2·82	2·83
$ZnSO_4$, $7H_2O$	4·00	3·22	5·45	0·50	1·70	1·81	1·32	1·08	1·19

The values of the elastic constants obtained from the above data are given in Table III, corrected to two decimal places.

The elastic moduli s_{ij} are also calculated and are given below in units of 10^{-13} cm²/dyne.

TABLE IV

Salt	s_{11}	s_{22}	s_{33}	s_{44}	s_{55}	s_{66}	s_{12}	s_{13}	s_{23}
$MgSO_4 \cdot 7H_2O$	24·5	34·1	15·0	93·5	42·9	45·0	−16·6	−2·68	−6·05
$ZnSO_4 \cdot 7H_2O$	29·5	37·7	20·4	200·0	58·8	55·3	−10·8	−3·49	−6·10

The linear compressibilities β_1, β_2, β_3 and the volume compressibility $\beta = \beta_1 + \beta_2 + \beta_3$ are also calculated and given in the units of 10^{-13} cm.²/dyne. The linear compressibility β_i is given by

$$\beta_i = s_{i1} + s_{i2} + s_{i3}$$

TABLE V

Salt	β_1	β_2	β_3	$\beta = \Sigma\beta_i$
$MgSO_4$, $7H_2O$ ..	5·19	11·5	6·26	22·9
$ZnSO_4$, $7H_2O$ ..	15·2	20·8	10·8	46·8

In the literature, no data concerning the two salts are available.

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4. SUMMARY

The elastic constants of the orthorhombic crystals, magnesium and zinc sulphate heptahydrates have been determined by the ultrasonic method. The elastic moduli and the compressibilities for the same are also calculated.

REFERENCES

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