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DYNAMICAL YOUNG MODULUS OF NATURAL CRYSTAL OF GYPSUM, $CaSO_4 \cdot 2H_2O$*, **

By H. Swół and J. W. Rohleder

Institute of Organic and Physical Chemistry, Technical University, Wrocław***

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Measurements of the Young modulus have been carried out on (010) plane for a natural gypsum crystal by means of a dynamical method. The elastic constants calculated by the least squares procedure for 80 experimental points, given in Table II, are quite close to those obtained by Coromilas under static conditions. This illustrates the applicability of the resonance method for studying the elastic properties of crystals.

1. Introduction

Elastic properties of gypsum crystals were elucidated first by Coromilas [1] who measured the magnitude of strain of a thin lamellae supported at both ends and ballasted in the middle by a known weight. Full description of the elastic and thermoelastic tensors of that crystal has been given next by Haussühl [2], whose measurements were carried out by using the modified Schaefer-Bergmann method of diffraction of light on standing ultrasonic waves.

On the other hand, a simple and efficient method of measuring the dynamic Young modulus of a thin sheet of material has been described by Horio and collaborators [3, 4]. According to these authors the elastic constants can be deduced from the resonance characteristics of a thin lamellae attached to a loudspeaker which is supplied with a.c. current of variable acoustical frequency. It was of interest to compare the results of the application of this method to a material whose mechanical properties and structure are relatively well known. In this way we could get an idea about the applicability of the resonance method to study the problems of mutual correlation between physical properties of crystals and their structure.

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*** Address: Instytut Chemii Organicznej i Fizycznej, Politechnika Wrocławska, Łukasiewicza 2, 50-371 Wrocław, Poland.

2. *Experimental*

In the present study natural gypsum crystals were used, originating from a mineral deposit near Pinczow in the valley of the Nida river. From blocks free of macroscopic faults and intrusions, thin plates (0.1 mm) were cleaved. The Miller indices of the cleavage plane are (010). The plates were next divided by means of a razor blade into a number of lamellae of known orientation with respect to the crystallographic *a* axis. The best samples of an average size of $15 \times 4 \times 0.1$ mm were obtained while carrying out the cleavage and cutting procedure on a crystal immersed in water.

Viewing the samples in a polarizing microscope between crossed polars we have found that nearly all plates exhibited very subtle parallel tracks which were shown by means of the X-ray method to be parallel to the *a* axis. This greatly facilitated the identification of the orientation of samples by means of optical observations. The angle taken between the length of a sample and the crystallographic *a* axis will be denoted by ϑ.

The crystal structure of gypsum has been described by Atoji and Rundle [5] and its refinement has recently been reported by Cole and Lancucki [6]. In this paper the more recent results given in [6] were used. The gypsum crystal is monoclinic, space group $I2/a$, the unit cell contains four units $CaSO_4 \cdot 2H_2O$ and has the following dimensions (all length parameters known with an accuracy ± 0.002 Å)

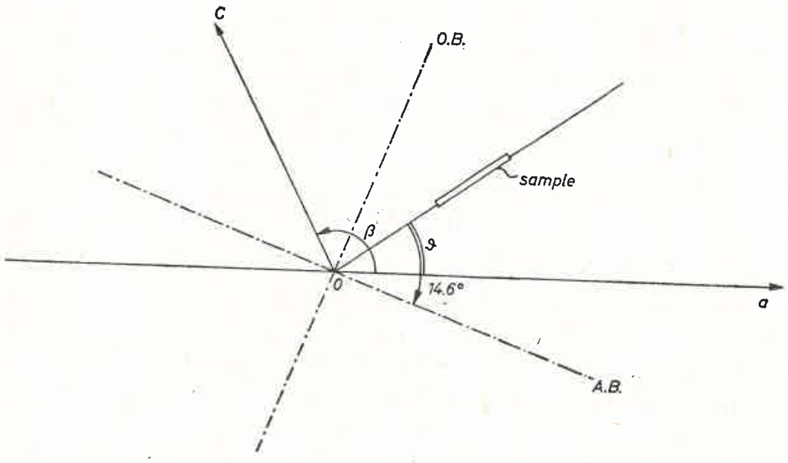

Fig. 1. The orientation of crystallographic and optical directions on (010) plane of gypsum crystal. O. B. — obtuse bisectrix, A. B. — acute bisectrix

$$a = 5.670, \quad b = 15.201, \quad c = 6.533 \text{ Å}, \quad \beta = 118°36' \pm 4'.$$

For the purpose identifying the Miller indices of the cleavage plane and crystallographic directions, X-ray oscillation photographs were taken with a Weissenberg camera. The orientation of *a*, *c* axes on (010) with principal optical directions determined in [7] is shown in Fig. 1.

The resonance curve of a sample while in a state of forced vibrations of variable frequency and, therefore, of variable amplitude, too, was measured at reduced pressure because of additional damping effects in conditions of normal atmospheric pressure. It has been found that at a pressure of 10 mm Hg or lower the width of the resonance curve becomes constant and independent of pressure.

At each frequency, ν, supplied by a RC generator and measured with a digital frequency meter, the amplitude of the forced vibrations of the free end of the sample, $A(\nu)$, has been observed by means of a microscope equipped with a Huygens ocular. The amount of pitch of the micrometric screw of the ocular has been determined using the transparent micrometric scale with divisions every 0.01 mm.

For further treatment the single and only slightly asymmetrical resonance curves were used, determined in the frequency range far enough from points corresponding to the "eigen-frequencies" of the loudspeaker. From a graphical plot of $A(\nu)$ the following constants were read: the resonance amplitude of the vibrations, A_r, the resonance frequency, ν_r, and the half-width of the curve between two points for which $A(\nu)$ dropped to $A_r/\sqrt{2}$. With an accuracy not worse than one per cent we have in a case of a rectangular lamellae [3, 4]

$$E_1 = \left[\frac{\nu_r}{0.162} \frac{l^2}{d}\right]^2 \times \varrho \tag{1}$$

and

$$E_2 = E_1 \times (\Delta\nu/\nu_r), \tag{2}$$

where l is the length of the lamellae, d its broadness and ϱ the bulk density of the material. E_1 denotes the dynamical Young modulus and E_2 is responsible for dynamical losses due to internal friction, η, at a given frequency

$$E_2 = 2\pi\nu_r\eta. \tag{3}$$

3. *Results and discussion*

The measurements were carried out on 58 samples in the range of $0 \leqslant \vartheta \leqslant 180$. A number of samples were re-examined for the second or third time under different physical conditions, such as variable air pressure or the amplitude of driving force, or the direction of approach to the point of resonance. As a whole 80 points have been obtained as listed in Table I and shown in Fig. 2.

For all experimental points the best curve can be calculated which describes the section of the elastic tensor with the (010) plane. This was done by means of the least squares procedure in the following manner. From E_1 values the corresponding components of the elasticity tensor, S_{mnpq}, were calculated

$$(E_1)^{-1} = S'_{1111} = a_{1m}a_{1n}a_{1p}a_{1q}S_{mnpq}, \tag{4}$$

where a_{1r} are cosines of angles between the direction x'_1 along which E_1 has been measured and a set of orthogonal x_r axes. The x_r axes are defined by a set of unit vectors, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$, given by the following relationships

$$e_1 = \frac{a}{|a|}, \quad e_2 = \frac{b}{|b|}, \quad e_3 = e_1 \times e_2. \tag{5}$$

TABLE I

Experimental values of the dynamical Young modulus, $CaSO_4 \cdot 2H_2O$, (010) plane

$E_1 \times 10^{-11}$			$E_1 \times 10^{-11}$		
No	deg	dynes per cm²	No	deg	dynes per cm²
1	0.0	4.023	41	97.9	5.509
2	0.0	4.023	42	98.9	4.645
3	0.0	4.051	43	98.9	4.645
4	0.7	4.051	44	106.9	4.587
5	1.0	3.808	45	106.9	4.587
6	1.0	3.808	46	106.9	4.587
7	1.0	3.854	47	106.3	4.703
8	1.4	4.328	48	106.3	4.703
9	4.8	4.437	49	110.8	6.853
10	12.4	3.584	50	110.8	6.853
11	18.5	4.155	51	110.8	6.853
12	21.8	3.154	52	114.0	5.926
13	21.8	3.154	53	114.0	5.898
14	35.4	2.571	54	114.0	5.898
15	35.4	2.571	55	115.2	6.931
16	44.6	3.052	56	115.2	6.931
17	44.6	3.052	57	115.2	6.931
18	44.6	3.052	58	115.3	6.074
19	45.6	2.622	59	115.3	5.921
20	49.6	2.476	60	115.3	6.074
21	52.4	2.580	61	117.2	6.987
22	54.4	2.501	62	117.2	6.987
23	59.2	2.529	63	130.8	5.646
24	60.0	2.437	64	132.1	5.299
25	60.0	2.437	65	142.5	4.458
26	62.6	2.592	66	152.2	5.001
27	62.6	2.592	67	152.2	5.001
28	65.0	2.724	68	152.2	4.832
29	65.0	2.724	69	152.2	4.832
30	65.0	2.811	70	156.0	5.225
31	68.3	2.962	71	156.7	4.395
32	70.8	2.626	72	156.7	4.395
33	70.8	2.488	73	161.2	4.811
34	74.7	3.216	74	161.6	4.998
35	77.8	3.916	75	170.1	3.688
36	83.6	3.401	76	170.1	3.688
37	83.6	3.382	77	172.7	4.316
38	83.6	3.565	78	178.7	4.342
39	97.0	4.206	79	178.7	4.300
40	97.6	5.179	80	179.3	4.377

Therefore, the S_{mnpq} components are given in the x_1, x_2, x_3 system of axes. Otherwise, we can express the direction of x'_1 by means of directional cosines l_1, l_2 and l_3 with respect to x_r axes. We have for a (010) section

$$l_1 = \cos\vartheta, \quad l_2 = 0, \quad l_3 = \sin\vartheta. \tag{6}$$

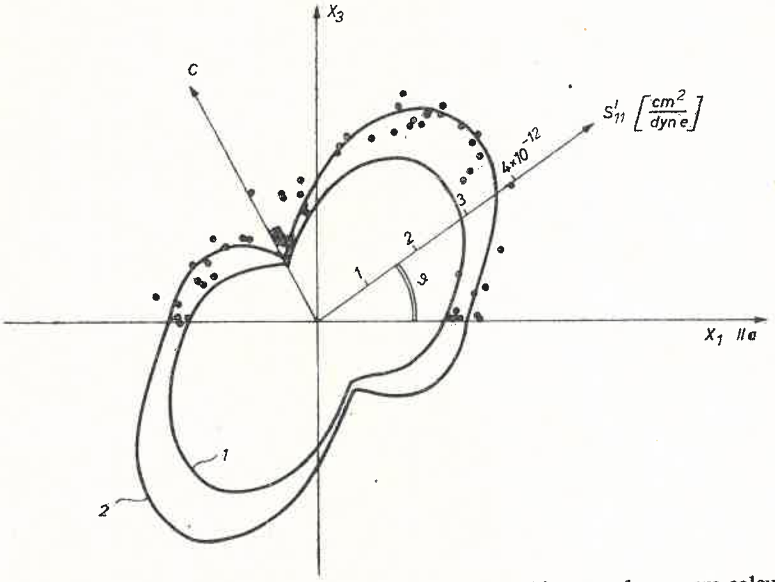

Fig. 2. The (010) section of elasticity tensor, S'. *a*, *c* crystallographic axes, *1* — curve calculated according to Haussühl results [2], *2* — least squares curve calculated from experimental points

Making use of the fact that $x_2 \| b$ where b is a two-fold symmetry axis of the crystal we can reduce (4) to the following equation of the section of elasticity tensor S_{ij}

$$(E_1^{(i)})^{-1} = A_1\cos^4\vartheta_i + A_2\cos^3\vartheta_i\sin\vartheta_i + A_3\cos^2\vartheta_i\sin^2\vartheta_i + A_4\cos\vartheta_i\sin^3\vartheta_i + A_5\sin^4\vartheta_i = \sum_j A_jF_j(\vartheta_i), \tag{7}$$

where $i = 1, 2, \ldots 80$, $j = 1, 2, \ldots 5$, and

$$A_1 = S_{11}, \quad A_2 = 2S_{15}, \quad A_3 = 2S_{13}+S_{55}, \quad A_4 = 2S_{35}, \quad A_5 = S_{33}. \tag{8}$$

A_j are the unknown constants of the section so that the normal equations are of the form

$$\frac{\partial}{\partial A_j}\{(E_1^{(i)})^{-1} - \sum_j A_jF_j(\vartheta_i)\}^2 = 0 \tag{9}$$

and lead to five equations linear with respect to A_j's.

TABLE II

S_{ij} constants of the (010) section of elasticity tensor in crystal of gypsum, in 10^{-12} cm²/dyne units

S_{11}	S_{15}	S_{35}	$2S_{13}+S_{55}$	S_{33}	Ref.
2.48	0.29	2.06	6.56	2.34	this work
2.072	0.577	1.362	4.590	2.016	Haussühl [2]

Fig. 3. Superposition of the section of tensor on the view of crystal structure on the (010) plane. Ca^{2+} ions are omitted

The calculated S_{ij} constants are given in Table II. We see that the agreement between our values and the S_{ij} constants obtained from data given by Haussühl [2] is, in general, quite good. Some discrepancies, not exceeding 30 per cent in numerical values of the elasticity constants, may be due to certain systematic difference in the properties of the crystal samples used as well as to specific difference between the static and dynamical methods. Also the cutting procedure, which is necessary to obtain samples of proper dimensions, may effect the results of measurements as it increases the significance of edges of the sample in comparison to its cross-sectional area. Nevertheless, the resonance method leads to reasonably good results and, owing to its simplicity, can be used to determine the section of the elasticity tensor for crystal plates.

If we make a superposition of the results from Fig. 2 (curve *2*) on a view of structure on the (010) plane we can find an interesting correlation between mechanical properties of a gypsum crystal and the distribution of SO_4^{2-} ions and water molecules, Fig. 3. Ca^{2+} ions are omitted because, owing to high symmetry, they take special positions on (010) and have no influence on the orientation of tensor section on that plane. The direction of minimum S', corresponding to the minimum of strain of the lattice at a given stress, nearly coincides with the direction of O_1O_1' of sulphate ions. This is understandable because the strongest overlapping of electron distributions round neighbouring oxygen atoms occurs while compressing the lattice in that direction. Maximum of strain can be reached in a direction parallel to the bisectrix of O_1O_{11} angle, and this approximately points to the maximum of S'. Intermediate values of S' are met approximately in a direction parallel to chains of hydrogen bonded water molecules. However, it can be anticipated that hydrogen bonding involves some increase of stiffness of the lattice.

This work has been carried out as part of a larger research program of "Material Science". Calculations have been made with a computer ODRA 1204 in the Computing Center of the Technical University of Wrocław.

REFERENCES

[1] L. A. Coromilas, *Z. Kristallogr.* **1**, 407 (1877).
[2] S. Haussühl, *Z. Kristallogr.* **122**, 311 (1965).
[3] M. Horio, S. Onogi, C. Nakayama, K. Yamamoto, *J. Appl. Phys.* **22**, 966 (1951).
[4] M. Horio, S. Onogi, *J. Appl. Phys.* **22**, 971 (1951).
[5] M. Atoji, R. E. Rundle, *J. Chem. Phys.* **29**, 1306 (1958).
[6] W. F. Cole, C. J. Lancucki, *Acta Cryst.* **B30**, 921 (1974).
[7] J. Rohleder, *Rocz. Chem.* **46**, 2089 (1972).