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Measurement of the Elastic Constants of Lithium Acetate by Means of the Brillouin Effect

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The numerical values of the elastic constants at room temperature are given. The significance of the results and the various causes of uncertainty are discussed. Indices of refraction and density are also measured.

I. INTRODUCTION

As part of the research on the structure and physical properties of lithium acetate, carried out by our Department of Optics, the nine elastic constants have been measured on single crystals. Samples of dihydrated lithium acetate have been provided by the Laboratory of Crystalline and Molecular Physics.[1] In order to ascertain the elastic constants, it was necessary to proceed with accurate measurements of the density and the refractive indices in the visible spectrum.

II. THEORETICAL RESULTS USED FOR CALCULATIONS

Let $\vec{k}, \vec{k}', \vec{\chi}$, respectively, denote the wave vectors of the incident and scattered light and of the acoustic wave. The relation of momentum conservation is

$$\vec{k}' = \vec{k} \pm \vec{\chi} \ , \tag{1}$$

which gives

$$\vec{Q} = \frac{n'_{\mu'}\vec{q}\,' - n_\mu \vec{q}}{|n'_{\mu'}\vec{q}\,' - n_\mu \vec{q}|} \ , \tag{2}$$

where

$$\vec{Q} = \frac{\vec{\chi}}{|\vec{\chi}|} \ , \quad \vec{q} = \frac{\vec{k}}{|\vec{k}|} \ , \quad \vec{q}\,' = \frac{\vec{k}'}{|\vec{k}'|} \ ,$$

and n_μ, $n'_{\mu'}$ are the refractive indices of the crystal for the incident and scattered light, respectively (the subscripts μ and μ' refer to the direction of the electric displacement vector).

For a given $\vec{Q}$, the three values of

$$\gamma = \rho V^2 \tag{3}$$

and the three directions of vibration $\vec{u}^s$ are, respectively, the eigenvalues and eigenvectors of the second-rank tensor

$$\Gamma_{il} = C_{ijkl} Q_j Q_k \ , \tag{4}$$

where C_{ijkl} is the elastic-constant tensor, ρ the density, and V the velocity of the elastic waves. The Brillouin shifts are given by

$$\delta\nu = (\nu_0 V/c)(n_\mu^2 + n'^2_{\mu'} - 2n_\mu n'_{\mu'} \cos\theta)^{1/2} \ . \tag{5}$$

III. EXPERIMENTAL

A. Apparatus

The device is a classical one.[2] The incident light is provided by an argon-ion laser with an output power of 30 mW for $\lambda = 4880$ Å. The scattering angle is equal to 90°. The plane Fabry-Pérot interferometer has a 75-GHz free spectral range and a bandwidth equal to 1.5 GHz. The detector is a EMI 9502 SA photomultiplier. The linearity of the pressure scanning is controlled by a Michelson interferometer.[3] A typical trace of the spectrum is reproduced in Fig. 1; the observed linewidth is purely instrumental. In fact, a further study made with a single-frequency laser and a spherical Fabry-Pérot interferometer (30-MHz bandwidth) has proved that the Brillouin linewidth is less than 100 MHz. This linewidth is negligible in comparison with the 2.2-GHz linewidth of the Döppler line of the laser.

B. Choice of Samples

Dihydrated lithium acetate belongs to the orthorhombic point group *mmm*.[4,5] The orientation of the axes *Ox*, *Oy*, *Oz*, parallel to the binary axes in relation to the primitive solid, is shown on Fig. 2. We have cut four samples (see Fig. 2) so as to obtain elastic waves propagating along the axes and their bisectors. The angle of the faces is 90.0° ± 0.1°. The inaccuracy regarding the orientation of the faces in relation to the crystallographic

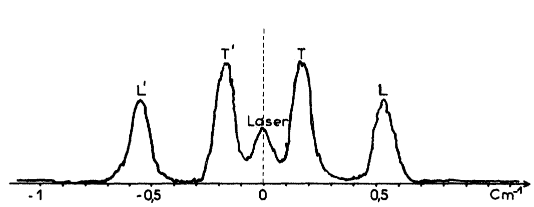

FIG. 1. Interferogram obtained with a plane Fabry-Pérot interferometer (spacing 2 mm). L, L' longitudinal modes; T, T' transversal modes.

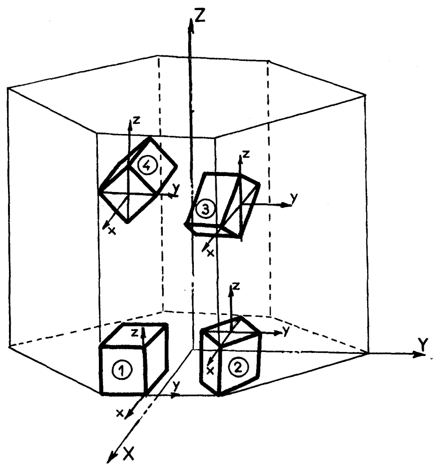

FIG. 2. Orientation of the four samples with respect to the primitive solid.

axes is less than 1°.

C. Additional Measurements

Relations (2), (3), and (5) show that it is necessary to know the principal indices and the density of the crystal with an accuracy of 10^{-3} at least. We have determined these characteristics, which—to our knowledge—have not been published before. The density has been measured by the classical method of immersion in three different liquids. At 20 °C it is equal to

$$\rho = 1.385 \pm 0.001 \text{ g cm}^{-3} .$$

The three principal indices have been measured on three prisms with edges parallel to Ox, Oy, Oz, respectively. The resulting values are gathered in Table I.

D. Determination of Elastic Constants

Table II gives the following information: (a) the acoustic mode responsible for the scattering (propagation direction and polarization), (b) the formula relating γ to the elastic constants, (c) the measured Brillouin splitting, and (d) the deduced value of γ.

The constants C_{11}, C_{22}, and C_{33} have been ascertained by means of the following six measurements: cases 1a, 1b, 4a, 4b, 7a, and 7b (cf. Ref. 6 and Table II). We could make use of eight measurements in order to determine C_{44}, C_{55}, and C_{66} (cases 3, 5, 6, 8, 9, 12, 15, 18). Starting from the measurements made in cases 10, 11, 13, 14, and 16, we find

$$\begin{aligned} S_1 &= C_{12} + C_{66} = \pm 1.07 \times 10^{10} \text{ N m}^{-2} , \\ S_2 &= C_{13} + C_{55} = \pm 0.75 \times 10^{10} \text{ N m}^{-2} , \qquad (6) \\ S_3 &= C_{23} + C_{44} = \pm 2.54 \times 10^{10} \text{ N m}^{-2} . \end{aligned}$$

With the help of the above results we have drawn up the polar diagrams of the velocities for the three acoustic branches in the planes (001), (010), and (100) (Fig. 3). For example, in the plane (001), the values of γ for a direction $\vec{Q} = (Q_1, Q_2, 0)$ are the roots of the equation

$$\begin{aligned} (C_{55}Q_1^2 + C_{44}Q_2^2 - \gamma)[\gamma^2 - (C_{11}Q_1^2 + C_{22}Q_2^2 + C_{66})\gamma \\ + (C_{11}Q_1^2 + C_{66}Q_2^2)(C_{66}Q_1^2 + C_{22}Q_2^2) \\ - (C_{12} + C_{66})^2 Q_1^2 Q_2^2] = 0 , \qquad (7) \end{aligned}$$

whose coefficients have been measured.

The strong acoustic anisotropy of lithium acetate is evident in Figs. 3(a)–3(c). These figures can be used as abacuses to obtain, without calculation, the three values of the velocity in any $\vec{Q}$ direction lying in a coordinate plane.

In order to determine the signs of C_{12}, C_{13}, and C_{23} we utilize the pure-mode directions. In fact, in each coordinate plane, there is a $\vec{Q}$ direction which is distinct from the crystallographic axes, and for which the polarization directions are purely longitudinal or purely transverse.[7] For instance, in the (001) plane this direction is given by

$$\frac{Q_1}{Q_2} = \pm \left(\frac{C_{11} - 2C_{66} - C_{12}}{C_{22} - 2C_{66} - C_{12}} \right)^{1/2} , \quad Q_3 = 0 . \qquad (8)$$

An extremum value of the longitudinal velocity corresponds to this direction.[8] For each possible value of C_{12} given by (6), the ratio Q_1/Q_2 is then calculated and the polar diagram of the velocity can be used to lift the ambiguity. However, in the case of lithium acetate, this method cannot be applied to C_{23} as the two possible $\vec{Q}$ orientations are too close, which hinders the use of the abacus.

A method approximating the one described above may be used instead. For each value of the constant to be determined (C_{12} for instance) the presumed pure-mode direction is calculated by (8); the corresponding values of γ for the longitudinal wave are then calculated from (7) and from the following expression:

$$\gamma = \frac{(C_{22} - 2C_{66} - C_{12})C_{11} + (C_{11} - 2C_{66} - C_{12})(2C_{66} + C_{12})}{C_{11} + C_{22} - 4C_{66} - 2C_{12}} \qquad (9)$$

which was obtained from the pure-mode condition.[7] The comparison between these values lifts the ambiguity (see Table III).

TABLE I. Refractive indices (accuracy 3×10^{-4}).

λ(Å)	4678.2	4779.9	4880[a]	5085.8	6438.5
n_x	1.4198	1.4173	1.4163	1.4148	1.4105
n_y	1.4891	1.4882	1.4874	1.4859	1.4795
n_z	1.5411	1.5396	1.5387	1.5367	1.5272

[a]Obtained by interpolation.

TABLE II. Experimental results.

Case[a]	$\vec{Q}$	$\vec{u}$	γ calculated by (4)	$\delta\nu_B$ (10^9 Hz)	γ (expt. value) (10^{10} N m^{-2})
1a	(1, 0, 0)	(1, 0, 0)	C_{11}	19.11	2.541
1b	(1, 0, 0)	(1, 0, 0)	C_{11}	18.43	2.533
2	(1, 0, 0)	(0, 1, 0)	C_{66}	n. m.[b]	n. m.[b]
3	(1, 0, 0)	(0, 0, 1)	C_{55}	6.91	0.352
4a	(0, 1, 0)	(0, 1, 0)	C_{22}	29.44	6.040
4b	(0, 1, 0)	(0, 1, 0)	C_{22}	26.99	5.992
5	(0, 1, 0)	(0, 0, 1)	C_{44}	10.00	0.740
6	(0, 1, 0)	(1, 0, 0)	C_{66}	7.805	0.460
7a	(0, 0, 1)	(0, 0, 1)	C_{33}	27.50	5.632
7b	(0, 0, 1)	(0, 0, 1)	C_{33}	26.22	5.653
8	(0, 0, 1)	(1, 0, 0)	C_{55}	6.73	0.349
9	(0, 0, 1)	(0, 1, 0)	C_{44}	10.03	0.744
10	$2^{-1/2}(1,1,0)$	$(u_1^{10}, u_2^{10}, 0)$	γ^{10}	22.09	3.399
11	$2^{-1/2}(1,1,0)$	$(u_2^{10}, -u_1^{10}, 0)$	γ^{11}	13.93	1.352
12	$2^{-1/2}(1,1,0)$	(0, 0, 1)	$\frac{1}{2}(C_{44}+C_{55})$	8.69	0.545
13	$2^{-1/2}(0,1,1)$	$(0, u_2^{13}, u_3^{13})$	γ^{13}	23.57	4.570
14	$2^{-1/2}(0,1,1)$	$(0, u_3^{13}, -u_2^{13})$	γ^{14}	n. m.[b]	n. m.[b]
15	$2^{-1/2}(0,1,1)$	(1, 0, 0)	$\frac{1}{2}(C_{55}+C_{66})$	6.72	0.404
16	$2^{-1/2}(1,0,1)$	$(u_1^{16}, 0, u_3^{16})$	γ^{16}	20.54	3.145
17	$2^{-1/2}(1,0,1)$	$(-u_3^{16}, 0, u_1^{16})$	γ^{17}	13.48	1.356
18	$2^{-1/2}(1,0,1)$	(0, 1, 0)	$\frac{1}{2}(C_{44}+C_{66})$	9.23	0.614

Values of γ

γ^{10}	$\frac{1}{4}\{C_{11}+C_{22}+2C_{66}+[(C_{11}-C_{22})^2+4(C_{12}+C_{66})^2]^{1/2}\}$
γ^{11}	$\frac{1}{4}\{C_{11}+C_{22}+2C_{66}-[(C_{11}-C_{22})^2+4(C_{12}+C_{66})^2]^{1/2}\}$
γ^{13}	$\frac{1}{4}\{C_{22}+C_{33}+2C_{44}+[(C_{22}-C_{33})^2+4(C_{23}+C_{44})^2]^{1/2}\}$
γ^{14}	$\frac{1}{4}\{C_{22}+C_{33}+2C_{44}-[(C_{22}-C_{33})^2+4(C_{23}+C_{44})^2]^{1/2}\}$
γ^{16}	$\frac{1}{4}\{C_{33}+C_{11}+2C_{55}+[(C_{33}-C_{11})^2+4(C_{13}+C_{55})^2]^{1/2}\}$
γ^{17}	$\frac{1}{4}\{C_{33}+C_{11}+2C_{55}-[(C_{33}-C_{11})^2+4(C_{13}+C_{55})^2]^{1/2}\}$

Values of $\vec{u}$

Case	u_1	u_2	u_3
10	$(C_{12}+C_{66})/\lvert\vec{u}^{10}\rvert$	$(2\gamma^{10}-C_{11}-C_{66})/\lvert\vec{u}^{10}\rvert$	0
13	0	$(C_{23}+C_{44})/\lvert\vec{u}^{13}\rvert$	$(2\gamma^{13}-C_{22}-C_{44})/\lvert\vec{u}^{13}\rvert$
16	$(2\gamma^{16}-C_{33}-C_{55})/\lvert\vec{u}^{16}\rvert$	0	$(C_{13}+C_{55})/\lvert\vec{u}^{16}\rvert$

[a]Two different scattering planes relative to a given acoustic mode are denoted by a and b.

[b]n. m. stands for not measurable.

IV. DISCUSSION

We have thoroughly examined the effect of the various causes of uncertainty and tried to verify their influence by means of scattering experiments in so far as possible.

a. Accuracy and fidelity of device. The difference between the values of $\delta\nu_B$ measured on the same recording is less than 3×10^{-3} (relative value); It corresponds to the uncertainty entailed by the lack of linearity and mechanical and thermal stability of the Fabry-Pérot interferometer and to the errors in reading.

b. Adjustment. Errors can arise from an inaccuracy in determining the scattering angle, or from a defective adjustment of the orientation of the samples with respect to the beams. Several series of recordings have thus been carried out by repeatedly adjusting the scattering angle on one

TABLE III. Determination of the constants C_{12}, C_{13}, and C_{23}.

Possible values		$\vec{Q}$			Values of γ given by (9) or similar equations	Values of γ given by (7)
C_{12}	0.61	0.903	0.430	0	2.35	2.35
	−1.51	0.823	0.568	0	1.51	2.63
C_{13}	0.40	0.881	0	0.475	2.17	2.27
	−1.36	0.769	0	0.640	1.53	2.74
C_{23}	1.8	0	0.693	0.721	4.55	4.54
	−3.2	0	0.703	0.711	2.05	4.53

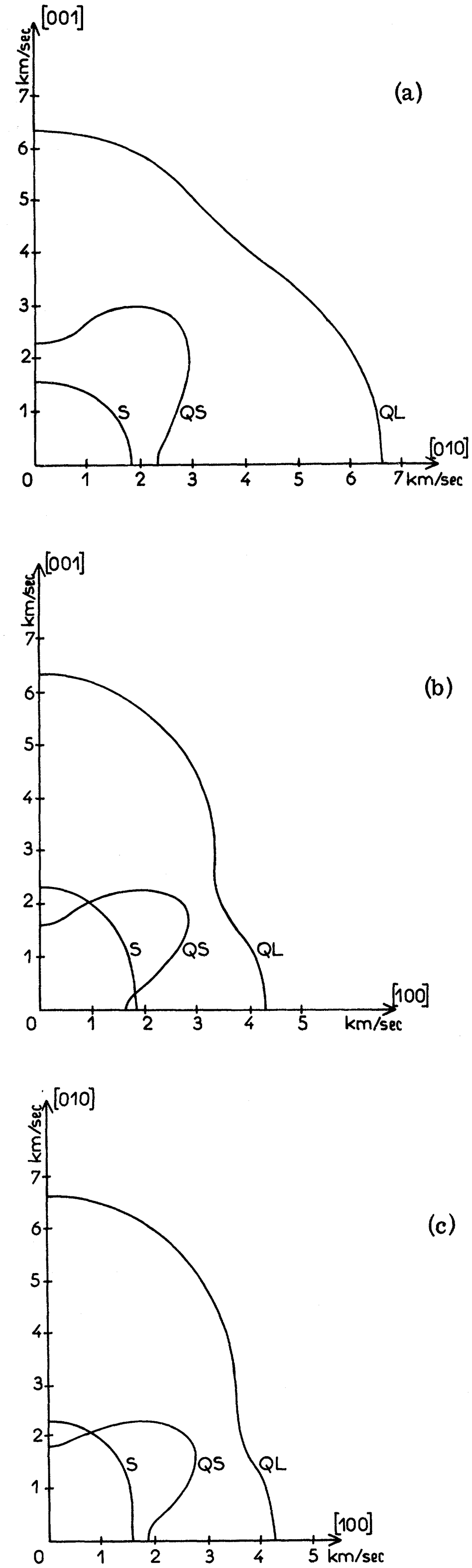

FIG. 3. Polar diagram of the velocities in the planes (1 0 0), (0 1 0), and (0 0 1) for Figs. 3(a)–3(c), respectively.

hand, and the orientation of the samples on the other hand, before each experiment. The results do not give any measurable difference.

c. Influence of temperature. The temperature in the laboratory measured during the experiments was (20 ± 1) °C. The dispersion on $\delta\nu_B$ is less than 3×10^{-3} (relative value).

d. Orientation of axes. The position of the crystallographic axes with respect to the edges of the crystals is determined with a tolerance of $\pm1°$. The relative uncertainty in the C_{ij} which might be caused by a defective orientation is easily calculated.

A $\Delta\Gamma_{il}$ variation of the tensor Γ_{il} results from the variation $\Delta\vec{Q}$ of the vector perpendicular to the incident wave. The variation $\Delta\gamma$ of a given eigenvalue γ is in first order,

$$\Delta\gamma=\vec{U}\cdot\Delta\Gamma\cdot\vec{U}\ , \tag{10}$$

where $\vec{U}$ is the corresponding eigenvector of the nonperturbed tensor. In expressing $\vec{Q}$ by polar coordinates, we find for the longitudinal component, if for instance $\vec{Q}=(1, 0, 0)$,

$$\Delta\gamma=U_1\Delta\Gamma_{11}U_1=2.4\times10^{-4}$$

and $\Delta\gamma/\gamma=10^{-4}$ for a variation of 1°. This uncertainty of about 10^{-4} for C_{11}, C_{22}, and C_{33}, of 10^{-3} for C_{44}, C_{55}, and C_{66}, and of 10^{-2} for C_{12}, C_{13}, and C_{23} must be calculated for each case. Scattering experiments, however, permit the direct checking of the accuracy of the crystal cutting: If the orientation is suitable, the sample will have two faces perpendicular to a binary axis (samples 2–4) or three couples perpendicular to three binary axes, respectively (sample 1). A 180° rotation around the direction perpendicular to these faces should not modify the frequency shift. Furthermore, both scattering cases corresponding to the same acoustic mode are obtained from two different crystals. For instance, the acoustic wave (1, 0, 0) can be studied with samples 2 and 3. Our measurements have shown that the uncertainty in the orientation of the crystal is certainly less than 1°.

e. Shifting of Brillouin components due to overlapping. The shift has been evaluated in two different ways. First, it has been calculated by assuming Lorentzian or Gaussian shapes for the recorded lines. Second, it has been measured by a graphic method.[9] In the case of Fig. 1, the shift is less than 15 MHz.

f. Effect to solid angle of acceptance of spectrometer. Strictly speaking, the relations written in Sec. II are only exact for the central ray of the scattered beam. The uncertainties due to the finite aperture of the spectrometer are discussed below.

First, the effect of the nonflat nature of the velocity surfaces is examined. The aperture angle is equal to 2°, so the variation of the $\vec{Q}$ direction is equal to 1°. The related variation of γ, given in Sec. IV*d*, is negligible within the accuracy of our

TABLE IV. Elastic constants (in 10^{10} N m^{-2}).

$C_{11} = 2.537 \pm 0.012$	$C_{44} = 0.81 \pm 0.01$	$C_{12} = 0.64 \pm 0.03$
$C_{22} = 6.02 \pm 0.03$	$C_{55} = 0.350 \pm 0.005$	$C_{13} = 0.40 \pm 0.04$
$C_{33} = 5.64 \pm 0.03$	$C_{66} = 0.430 \pm 0.006$	$C_{23} = 1.75 \pm 0.10$

measurements. On the other hand, the effect of the $\sin\frac{1}{2}\theta$ dependence can be discussed. The Brillouin linewidth is not taken into account since it is negligible with regard to the Doppler linewidth of the laser. The recorded profile is the convolution product

$$Y = A * L * W ,$$

where A is the profile of the scattered light in the solid angle of acceptance of the spectrometer for monochromatic incident light, L the profile of the laser line, and W the apparatus function. The maximum broadening of the scattered line A for a 2° aperture angle is about 0.5 GHz and the asymmetry at half-height of this profile is equal to 0.02.[10] The asymmetry of the Y product is less than 5×10^{-3} and can obviously be neglected. The above-mentioned results as a whole permit us to calculate the uncertainty of the elastic constants.

V. CONCLUSION

All results are grouped under Table IV; they are in good agreement with the values obtained by Haussühl with the Schaeffer-Bergman method; to our knowledge, these values have not been published before.

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[10]Let ν_a and ν_b be the frequencies of the points at half-height on the profile of the scattered line A, and ν_M the frequency of the maximum. We define the asymmetry δ by $\delta = (\nu_a + \nu_b - 2\nu_M)/(\nu_b - \nu_a)$.