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Determination of the Elastic and Photoelastic Constants of an $NaNO_3$ Single Crystal on the Basis of the Mandel'shtam-Brillouin Scattering Spectra

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The complete set of elastic constants of a sodium nitrate single crystal is calculated on the basis of the shifts of the Mandel'shtam-Brillouin components. The elastic constant values thus obtained considerably differ from the data of Bhimasenachare[2]. It is suggested that in determinations of the absolute values of the photoelastic constants of optically anisotropic crystals on basis of the relative intensities of the Mandel'shtam-Brillouin components, calibration can be carried out by using the values of the components of the antisymmetric part of the photoelasticity tensor $p_{ij[kl]}$, which are determined by the refractive indices of the given crystal. Within the experimental errors the absolute values of the photoelasticity constants $p_{ij(kl)}$ measured by calibration against a standard substance (crystalline quartz), or calibration involving $p_{ij[kl]}$, were identical.

THE singularities of Mandel'shtam-Brillouin (MB) scattering in optically-anisotropic crystals, such as splitting of the MB components as a result of birefringence, and an appreciable contribution of the antisymmetrical part of the photoelasticity tensor $P_{ij[kl]}$ to the intensity of the MB components, should become clearly pronounced in $NaNO_3$ single crystals, owing to their appreciable birefringence ($n_o - n_e \approx 0.25$), at $\lambda = 0.63\ \mu$. Sodium nitrate single crystals have a trigonal syngony of class $\bar{3}m$. $NaNO_3$ single crystals of high quality were grown from the melt. The values of the interplanar distances calculated from the Debyegram are in good agreement with the data of the ASTM (7–271) catalogue. The measured refractive indices of our crystals agree within 10^{-3} with the data of Smakula[1], and amount to $n_x = n_y = 1.58$ and $n_z = 1.335$ for $\lambda = 0.63\ \mu$. The 90° scattering spectra were registered photoelectrically. The exciting-light source was an He-Ne laser with $\lambda = 0.63\ \mu$. The Fabry-Perot interferometer was scanned by pressure. The wavelength scanning was with a pressure pickup that generated an electric signal proportional to the pressure. The scanning nonlinearity was ~1.5%. The scattering spectra were plotted with an automatic x-y recorder, and some of them are shown in Fig. 1. The samples were rectangular parallelepipeds cut in the following manner: sample 1 had the faces perpendicular to the principal crystallographic axes, the faces of sample 2 were perpendicular to the (101), (010) and ($\bar{1}01$) directions. The experimental values of the shifts of the MB components for sample 1 and the shifts calculated from the known elastic constants[2] are gathered in Table I.

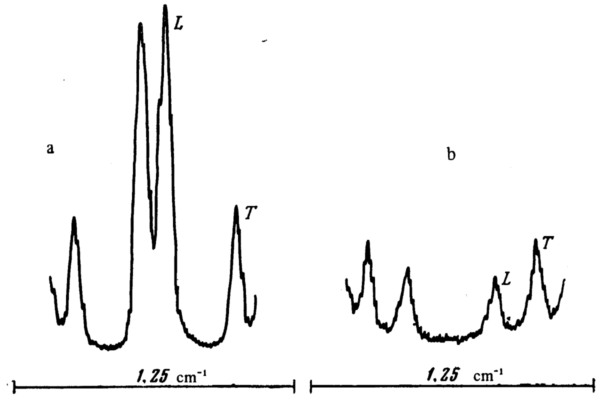

FIG. 1. Spectra of Mandel'shtam-Brillouin scattering in sodium nitrate: a) z(xx)y, b) –z(yx)y. The Stokes and anti-Stokes components of the neighboring orders are shown on each spectrum. L and T denote the MB components corresponding to quasilongitudinal and quasitransverse phonons. The intensity of the T component of (b) is determined mainly by the component $p_{ij[kl]}$. The interferometer dispersion region for all the spectra is 1.25 cm^{-1}.

The deviations of the experimental shifts of the MB components from the calculated ones greatly exceed the experimental errors. From the shifts of the MB components we can calculate the complete set of elastic constants in our case, identifying the phonons that appear upon scattering by the selection rules for the MB components[3], namely: a quasilongitudinal phonon polarized in the scattering plane (ph_L) appears

Table I. Mandel'shtam-Brillouin component shifts (in cm^{-1}) in single-crystal $NaNO_3$, obtained experimentally and calculated from the elastic constants of Bhimasenachar (a) and from those obtained in the present work (b)

Scattering geometry	$ph_{T\parallel}$			$ph_{T\perp}$			ph_L		
	a	b	Experiment	a	b	Experiment	a	b	Experiment
$z(xx)y$	0.329	0,260	0.261	—	—	—	0.67	0.580	0,573
$z(yz)y$	0.310	0.251	0.250	—	—	—	0.604	0.520	0.515
$z(xz)y$	—	—	—	0.316	0,184	0,184	—	—	—
$-z(xx)y$	—	—	—	—	—	—	0,577	0,472	0,467
$-z(yz)y$	0.323	0.255	0.250	—	—	—	0,517	0.430	0.426
$-z(yx)y$	—	—	—	0.428	0.370	0,367	—	—	—
$-z(yy)x$	0.343	0.275	0.275	—	—	—	0,636	0,540	0.550
$-z(xz)x$	0.317	0.270	0.272	—	—	—	0.590	0.495	0.500
$-x(zz)y$	—	—	—	—	—	—	0.618	0.513	0.508
$-x(yz)y$	—	—	—	0.320	0.213	0.225	—	—	—
$-x(zx)y$	0.447	0.346	0.330	0.308	0.183	0.202	—	—	—

Table II. Elastic constants of sodium nitrate

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	C_{14}
Bhimasenachar	8.67	3.74	2.13	1,63	1.6	0.82
Present work	6,0	3,34	1.12	2,2	1,89	0,81

in the VV and HH spectra; a transverse phonon polarized perpendicular to the scattering plane ($ph_{T\perp}$) appears in the VH and HV spectra; and a quasitransverse phonon polarized in the scattering plane ($ph_{T\parallel}$) appears in the VV and HH spectra. Here V(H) is the vertical (horizontal) direction of the polarization of the exciting and scattered light relative to the scattering plane. To calculate the elastic constants of $NaNO_3$ we used the MB components shifts obtained for scattering in the xz plane of sample 2 (constants C_{11} and C_{33}) and for scattering in the yz plane of sample 1 (the remaining constants). The speed of sound was calculated from the formula[4]

$$v = \lambda c\Delta\nu / (n_i^2 + n_j^2)^{1/2}, \tag{1}$$

where n_i and n_j are the refractive indices of the exciting and scattered light, λ is the wavelength of the exciting light, and $\Delta\nu$ are the shifts of the MB components. The so-calculated elastic constants of sodium nitrate and the data of Bhimasenachar are gathered in Table II, where they are patently seen to disagree.

The constants C_{11} and C_{33} were measured for sample 1 by an ultrasonic method[1)]. The results agreed with our data within ~3%. The results, reported in[2], of Bridgman's measurements of the compressibilities of $NaNO_3$ turned out to be about 15% higher than those calculated from the elastic constants. On the other hand, the discrepancy between the experimental compressibilities of sodium nitrate and those calculated from our elastic constants is ~5%. A comparison of the experimental shifts of the MB components with those calculated from our elastic constants also shows satisfactory agreement for those shifts whose values were not used in the calculation of the elastic constants (for the scattering planes xz and xy, see Table I).

Owing to the large birefringence of sodium nitrate, the splitting of the MB components as a result of optical anisotropy exceeds significantly the experimental errors. This can be seen in Table I, by comparing the MB component shifts corresponding to ph_L in the VV and HH spectra, to $ph_{T\parallel}$ in the VV and HH spectra, and $ph_{T\perp}$ in the HV and VH spectra.

When the absolute values of the photoelastic constants $p_{ij(kl)}$ are determined by measuring the intensities of the MB components, the calibration is usually made against the intensities of the MB components in a substance with known photoelastic constants. For optically anisotropic crystals, however, it is possible to determine the absolute values of $p_{ij(kl)}$ by measuring only the relative intensities of the MB components without using a calibration substance. The scattering coefficient for the MB components is determined by the Motulevich formula[5]

$$R^{ij} = A\frac{n_j}{n_i}\frac{(\varphi_{ij})^2}{\rho v^2} \tag{2}$$

where $A = \pi^2 kT/\lambda^4$; n_i and n_j are the refractive indices of the exciting and scattered light; φ_{ij} is the component of the change of the dielectric tensor; v is the propagation velocity of the phonon corresponding to the given MB components. For crystals of class $\bar{3}m$, the components of the tensor φ_{ij} are

$$\begin{aligned}
\varphi_{xx} &= n_x^4[p_{11}\varkappa_x\gamma_x + p_{12}\varkappa_y\gamma_y + p_{13}\varkappa_z\gamma_z + p_{14}(\varkappa_z\gamma_y + \varkappa_y\gamma_z)],\\
\varphi_{yy} &= n_y^4[p_{12}\varkappa_x\gamma_x + p_{11}\varkappa_y\gamma_y + p_{13}\varkappa_z\gamma_z - p_{14}(\varkappa_z\gamma_y + \varkappa_y\gamma_z)],\\
\varphi_{zz} &= n_z^4[p_{31}\varkappa_x\gamma_x + p_{31}\varkappa_y\gamma_y + p_{33}\varkappa_z\gamma_z],\\
\varphi_{yz} &= n_y^2 n_z^2[p_{41}(\varkappa_x\gamma_x - \varkappa_y\gamma_y) + p_{44}(\varkappa_z\gamma_y + \varkappa_y\gamma_z) + p_{23[23]}(\varkappa_z\gamma_y - \varkappa_y\gamma_z)],\\
\varphi_{xz} &= n_x^2 n_z^2[p_{41}(\varkappa_y\gamma_x + \varkappa_x\gamma_y) + p_{44}(\varkappa_z\gamma_x + \varkappa_x\gamma_z) + p_{13[13]}(\varkappa_z\gamma_x - \varkappa_x\gamma_z)],\\
\varphi_{xy} &= n_x^2 n_y^2[p_{14}(\varkappa_x\gamma_z + \varkappa_z\gamma_x) + 0{,}5(p_{11} - p_{12})(\varkappa_y\gamma_x + \varkappa_x\gamma_y)],
\end{aligned}$$

where κ_i and γ_j are the components of the unit vectors of the phonon propagation direction and polarization. Some components, namely φ_{xz} and φ_{yz}, contain components of the antisymmetrical part of the photoelasticity tensor $p_{ij[kl]}$, the values of which are known from independent measurements, namely from measurements of the refractive indices of the given crystal[6]: $p_{ij[kl]} = \frac{1}{2}|n_0^{-2} - n_e^{-2}|$. In our case $p_{23[32]} = p_{13[31]} = -p_{23[23]} = -p_{13[13]} = -0.081$. Elimination of the unknown factors transforms the system of equations with respect to $p_{ij(kl)}$, obtained on the basis of (2) with the right-hand sides determined by the experimental values of the relative intensities of the MB components, in the following manner: the left-hand sides of the equations are linear combinations of $p_{ij(kl)}$, and the right-hand ones are determined by the values of $p_{ij[kl]}$. Thus, in the case of optically anisotropic crystals, the values of $p_{ij[kl]}$ themselves can be used for calibration in the determination of the absolute values of $p_{ij(kl)}$ from the relative intensities of the MB components.

To confirm experimentally the applicability of the given method of measuring the absolute values of the photoelastic constants, we measured $p_{ij(kl)}$ for single-crystal $NaNO_3$ both by calibration against a standard substance (crystalline quartz) and by the method described above. When the relative intensities of the MB components are measured in a crystal with different refractive indices or in optically anisotropic crystals, it is necessary that the aperture of the scattered light in the crystal be the same for each recorded spectrum. This does not hold true in the widely used method for limiting the aperture of the scattered light. Figure 2 illustrates such a case. That is to say, in spite of the fact that the aperture of the scattered light outside the

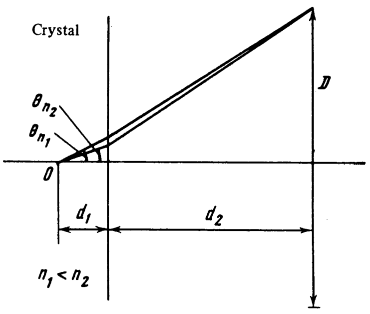

FIG. 2. Influence of the refractive index on the aperture of the scattered light in the crystal. O—point of scattering volume of crystal; θ_{n1} and θ_{n2}—apertures of scattered light in the crystal, corresponding to the refractive indices n_1 and n_2; D—diaphragm limiting the aperture of the scattered light outside the crystal. The relation $\theta_{n1}/\theta_{n2} \approx n_2/n_1$ holds true if D/d_2 is small and $d_1 \ll d_2$.

[1)] The authors are grateful to Yu. A. Pisarevskiĭ for performing the measurements.

crystal is fixed (by the diaphragm D), the aperture inside the crystal depends on the refractive index for the scattered light. At small apertures of the scattered light and if $d_1 \ll d_2$, as is frequently the case in experiments, the ratio of the apertures of the scattered light in the crystal for different refractive indices is given by $\theta_{n_1}/\theta_{n_2} \approx n_2/n_1$. For $\lambda = 0.63\ \mu$ the refractive index of quartz is n = 1.55 and $\theta_{1.55}/\theta_{1.33} \approx 1.33/1.55 = 0.86$, $\theta_{1.55}/\theta_{1.58} \approx 1.58/1.55 = 1.02$, and $\theta_{1.58}/\theta_{1.53} \approx 1.33/1.58 = 0.84$, i.e., the aperture corrections exceed in our case the errors in the measurement of the relative intensities of the MB components, and they must be taken into account.

The system of equations for the determination of $p_{ij(kl)}$ of sodium nitrate, obtained on the basis of formula (2) together with calibration against crystalline quartz, takes the following form:

$$\begin{gathered}
0.601p_{12} + 0.355p_{13} - 0.957p_{14} = \pm 0.219;\\
0.355p_{12} - 0.601p_{13} + 0.346p_{14} = \mp 0.063;\\
0.525p_{12} + 0.447p_{13} + 0.99p_{14} = \pm 0.17;\\
0.585p_{12} + 0.347p_{13} - 0.93p_{14} = \pm 0.21;\\
0.207p_{12} + 0.039p_{13} + 0.635p_{14} = \pm 0.04;\\
-0.45p_{41} + 0.995p_{44} + 0.006 = -0.078;\\
-0.461p_{41} + 0.093p_{44} + 0.081 = 0.049;\\
-0.382p_{41} + 0.595p_{44} + 0.048 = -0.103;\\
-0.149p_{41} + 0.558p_{44} - 0.045 = -0.083;\\
0.094p_{41} + 0.313p_{44} - 0.025 = -0.051;\\
|p_{13}| = 0,22;\ |p_{14} + p_{66}| = 0,044;\ |p_{12}| = 0.206;\ |p_{31}| = 0.25.
\end{gathered} \tag{3}$$

Actually, the relative intensities of the MB components determine the values of φ_{ij}^2 and therefore, when a system of equations is derived for φ_{ij}, a difficulty arises in connection with the choice of the signs in the right-hand sides of the equations in (3). This difficulty is overcome in part by the fact that the system (3) is overdefined and breaks up into several systems, each containing only a definite group of elements $p_{ij(kl)}$. The system (3) consists of equations that differ greatly in form, namely, the left-hand sides of some of the equations (relative to p_{41} and p_{44}) contain free terms determined by the components $p_{ij[kl]}$. For equations of this type, there exists a unique set of signs in the right-hand sides, such that the values of p_{41} and p_{44} satisfy simultaneously all the equations of the system. In practice, only three equations suffice (in the case of two unknowns) to find such a set of signs in the right-hand sides. For the system of equations whose right-hand sides do not contain free terms (the equations with respect to p_{12}, p_{13}, and p_{14}), the choice of the signs in the right-hand sides is no longer unique, i.e., there exist two opposite sets of signs, for which the values of p_{12}, p_{13}, and p_{14} satisfy simultaneously all the equations, and the solutions for these sets differ only in their signs. The components $p_{ij(kl)}$, determined from the system (3), have the following values:

$$\begin{gathered}
p_{12} = \pm 0.21;\ p_{13} = \pm 0.215;\ p_{14} = \mp 0.027;\ |p_{31}| = 0.25;\ p_{44} = -0.06;\\
p_{41} = 0.055;\ p_{66} = \pm 0.055 \pm 0.044.
\end{gathered} \tag{4}$$

The determination of the absolute values of $p_{ij(kl)}$ using a calibration against $p_{ij[kl]}$ reduces to the solution of a system analogous to (3). Such a system can be obtained from (3) by dividing each equation of the system by some equation containing $p_{ij[kl]}$, and this decreases the total number of equations only by one and eliminates the calibration against the quartz. A similar result is obtained if the right-hand sides of the equations are determined from the values of the relative MB-component intensities. In this case it is more convenient to start the solution by determining p_{41} and p_{44}. The components $p_{ij[kl]}$ determined in this manner, which differ from (4) by not more than ± 5%, a value governed in practice by the error in the measurement of the relative intensities of the MB components the elastic constants of the given crystal.

We note that the accuracy with which the absolute values of $p_{ij(kl)}$ with the aid of calibration against $p_{ij[kl]}$ is determined by the ratio of the accuracy with which the relative intensities of the MB components are determined to the contribution of $p_{ij[kl]}$ to the intensity of the MB components of the given crystal.

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