crease in α near the transition is probably due to anharmonicity as the fluctuation amplitude becomes large.

Equations (6) and (7) predict maxima in $G(K, 0)$ and K_2/K_1^2 consistent with the peaks in τ_c. Such maxima are observed, but in both cases the amplitudes are less than predicted.

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Observation of Coupled Acoustic-Phonon–Reorientation Modes in a Plastic Crystal: Succinonitrile

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Rayleigh-Brillouin measurements of depolarized light scattering in the plastic phase of succinonitrile are reported as a function of crystal orientation. The Rayleigh wing is characterized by two distinct molecular-reorientation modes and strongly angular-dependent shear-wave peaks are seen with typical resonance line shapes. These spectra are understood as arising from coupling between acoustic phonons and reorientation modes. Excellent agreement with a hydrodynamic description of the coupled modes is obtained.

The reorientation of optically anisotropic molecules in plastic crystals produces a depolarized Rayleigh wing[1] similar to that observed in many liquids.[2] Several measurements have already been reported and in some cases shear modes have been seen.[3] The shear-phonon scattering strength in succinonitrile is already known to have a peculiar temperature dependence for which no satisfactory explanation has been given.[4] In view of the present interest in melting, and since the dynamical interaction of reorientation and translation is known to lead to interesting effects in liquids,[5] it seemed of importance to obtain the depolarized-light-scattering spectra in full detail. These are reported here at 45°C, that is, 13°C below melting. The results establish the existence of two reorientational relaxation times. Furthermore, the shear-wave component is not a simple Lorentzian but exhibits a well-developed resonance line shape.[6] To our knowledge, it is the first observation of this type of Brillouin spectra. They are explained by assuming static correlation between the reorientation and displacement of the molecules,[7] and constitute direct evidence for this new coupling. The parameters derived from the spectra are in full agreement with the known low-frequency elastic constants,[8] and with the high-frequency Kerr-effect anisotropy.[9]

The spectra were obtained with a single-mode argon-ion laser source (at 4880 Å and 100 mW power) and a piezoelectrically scanned Fabry-Perot interferometer of adjustable free-spectral range and finesse of ~40.

Succinonitrile single crystals were grown by the Bridgman-Stockbarger technique from highly purified zone-refined material.[10] Cylindrical samples were cut parallel to the $[\bar{1}10]$ direction and *Vh* scattering [*V* (*h*) denotes perpendicular (parallel) polarization relative to the scattering plane] was observed at 90° with the momentum exchange $\vec{q}$ in the $(\bar{1}10)$ plane. The cylinder orientation about its axis is indicated by the angle φ between $\vec{q}$ and the [001] direction in the scattering plane. In this geometry, a single acoustic mode (pure shear) is active in *Vh* scattering.[11] The samples were fitted in cylindrical Pyrex cells with a few drops of paraffin oil for index matching. The ampoule could be rotated around its axis in a temperature-regulated, square glass cell. Only scattered light from the center of the crystal was collected with an external collection angle always smaller than 2°.

The spectra obtained at 45°C are shown in Fig. 1 for eight different crystal orientations. The free spectral range of 15.06 GHz was selected to achieve a clear display of the shear-phonon component. With this value, the Rayleigh wings from different orders strongly overlap, as seen from the indicated baselines. In addition to the Rayleigh-wing components, the spectra of Fig. 1 also contain an unresolved background whose relative area was measured independently with a free spectral range of 75 GHz. For this value, the Rayleigh wings are well developed, the background still appears almost flat, and the phonon component becomes difficult to see, not only because of the limited resolution but also because it then rides on a Rayleigh wing which is much steeper as a result of the absence of strong overlapping.

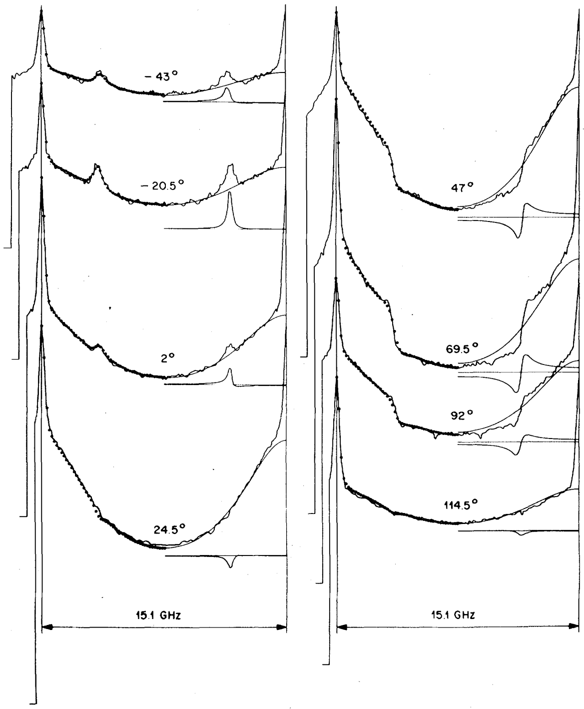

FIG. 1. Rayleigh-Brillouin spectra at 45°C for eight different sample orientations. The spectral region shown is one order of the interferometer, from laser frequency to laser frequency. The points on the left-hand side represent the fitted curve. The continuous lines on the right-hand side represent the calculated Rayleigh-wing contribution, and directly below it the phonon contribution, both before convolution with the experimental response function. These curves emphasize the various resonance line shapes of the phonon contributions.

These spectra are explained by a hydrodynamic theory taking into account the strain field $\vec{\epsilon}$, an anisotropy field $\vec{\alpha}$, and the coupling of these two fields.[7] The anisotropy field is formed from the traceless part of the optical polarizability tensor of single molecules. Equations of motion are derived from a Lagrangian by use of a potential

$$\mathcal{V} = \tfrac{1}{2}\vec{\epsilon}\cdot\overleftrightarrow{C}\cdot\vec{\epsilon} + \tfrac{1}{2}\vec{\alpha}\cdot\overleftrightarrow{B}\cdot\vec{\alpha} + \vec{\alpha}\cdot\overleftrightarrow{D}\cdot\vec{\epsilon}. \qquad (1)$$

Because $\vec{\alpha}$ has zero trace, and because of cubic symmetry in the present case, there are three elastic constants in $\overleftrightarrow{C}$, two orientational potential constants in $\overleftrightarrow{B}$, and two coupling constants in $\overleftrightarrow{D}$. The elastic constants in (1) are high-frequency values, the low-frequency response being dressed by the reorientational-translational interaction to give $\overleftrightarrow{C}_{\omega=0} = \overleftrightarrow{C} - \overleftrightarrow{D}\cdot\overleftrightarrow{B}^{-1}\cdot\overleftrightarrow{D}$. The orientational potential corresponds to the resistance to orientational ordering and is thus directly related to the high-frequency Kerr effect.[9] Finally, the coupling constants $\overleftrightarrow{D}$ correspond to the allowed static correlation between the anisotropic polarizability and the microscopic strains. Furthermore, the presence of frictional forces is accounted for by a dissipative function

$$f = \tfrac{1}{2}\dot{\vec{\epsilon}}\cdot\overleftrightarrow{\Gamma}^{\epsilon}\cdot\dot{\vec{\epsilon}} + \tfrac{1}{2}\dot{\vec{\alpha}}\cdot\overleftrightarrow{\Gamma}^{\alpha}\cdot\dot{\vec{\alpha}} + \dot{\vec{\alpha}}\cdot\overleftrightarrow{\Gamma}^{\alpha\epsilon}\cdot\dot{\vec{\epsilon}}. \qquad (2)$$

Using the Euler-Lagrange equations including dissipation, one obtains equations of motion describing eight coupled modes. In the absence of coupling ($\overleftrightarrow{D} = \overleftrightarrow{\Gamma}^{\alpha\epsilon} = 0$) they give the usual acoustic-phonon and overdamped-reorientation modes.

The depolarized *Vh* spectrum is calculated from these equations under the assumption that the intensity scattered by the shear mode arises entirely from the reorientational-translational coupling, or in other words, that it is the coupling that leads to the corresponding Pockels piezo-optic effect. For the present geometry, only one acoustic mode (out of three) and two reorientation modes (out of five) couple to the optical field. The spectrum is expanded in terms of the coupling constants under the assumption that they are small. In zeroth order, one obtains two Rayleigh wings.

$$I_R(\omega) \propto [1+\sin(2\varphi)]L(\omega,\gamma_1)/(B_{11}-B_{12})+[1-\sin(2\varphi)]L(\omega,\gamma_2)/2B_{44}, \tag{3}$$

where $L(\omega,\gamma_i)\equiv\gamma_i/\pi(\omega^2+\gamma_i^2)$, with $\gamma_1\equiv(B_{11}-B_{12})/(\Gamma_{11}{}^{\alpha}-\Gamma_{12}{}^{\alpha})$ and $\gamma_2\equiv B_{44}/\Gamma_{44}{}^{\alpha}$ (the abbreviated subscript notation of fourth-order tensors has been used). To first order in the coupling, these wings are slightly perturbed in width and strength, as explained elsewhere.[7] Also in first order, the shear phonon appears and has a resonant line shape.[6] With $P(\omega,\Gamma,\Omega)\equiv[\Gamma+i(\Omega-\omega)]/\pi[\Gamma^2+(\Omega-\omega)^2]$ the Stokes and anti-Stokes components are

$$I_P(\omega)\propto(16C)^{-1}\operatorname{Re}\left\{[P(\omega,\Gamma,\Omega)+P(-\omega,\Gamma,\Omega)]\left[\frac{\mathcal{D}_2}{\mathcal{B}_2}+\frac{\mathcal{D}_1}{\mathcal{B}_1}+\sqrt{2}\left(\frac{\mathcal{D}_2}{\mathcal{B}_2}-\frac{\mathcal{D}_1}{\mathcal{B}_1}\right)\cos(2\varphi+\tfrac{1}{4}\pi)\right]_{s=ivq}^{2}\right\}, \tag{4}$$

with the same proportionality constant as in (3). The following definitions have been used:

$$\mathcal{B}_1\equiv B_{11}-B_{12}+s(\Gamma_{11}{}^{\alpha}-\Gamma_{12}{}^{\alpha}),$$

$$\mathcal{B}_2\equiv B_{44}+s\Gamma_{44}{}^{\alpha},$$

$$\mathcal{D}_1\equiv D_{11}-D_{12}+s(\Gamma_{11}{}^{\alpha\epsilon}-\Gamma_{12}{}^{\alpha\epsilon}),$$

and

$$\mathcal{D}_2= D_{44}+s\Gamma_{44}{}^{\alpha\epsilon}.$$

The undressed shear-phonon velocity is $v=(C/\rho)^{1/2}$ with $C=C_{44}+\frac{1}{2}(C_{11}-C_{12}-2C_{44})\sin^2\varphi$. The frequency Ω and width Γ are dressed by the coupling with $\Omega=vq+\operatorname{Im}\delta$ and $\Gamma=\Gamma^{\epsilon}q^2/2\rho-\operatorname{Re}\delta$ where $\delta\equiv[(q^2/2\rho s)(\mathcal{D}_1{}^2\sin^2\varphi/2\mathcal{B}_1+\mathcal{D}_2{}^2\cos^2\varphi/\mathcal{B}_2)]_{s=ivq}$. Examination of (3) and (4) shows that two spectra (such as $\varphi=\pm45°$) are sufficient to determine all parameters of the theory except for the relative sign of $\mathcal{D}_1$ and $\mathcal{D}_2$. The additional spectra (Fig. 1) allow the determination of this relative sign and provide a check of the theory.

Before discussing the fits, two additional contributions to the spectra of Fig. 1 must be mentioned: (i) an elastic component attributed to crystal imperfections, which was accounted for in the fits by adding the *ad hoc* elastic peak to each spectrum; and (ii) the unresolved background independently measured with the 75-GHz free spectral range. An assumed area dependence in $1\pm\sin(2\varphi)$ as in Eq. (3) fitted that data fairly well with

$$R_{1,2}=\frac{\text{background area at } \varphi=\pm45°}{\text{Rayleigh-wing area at } \varphi=\pm45°}$$

given by $R_1=0.48$ and $R_2=0.97$ for 45°C. The fits shown by the points on the left-hand half of the spectra have been obtained by adding to these two contributions the first-order expansion expressions for $I_R(\omega)$ and $I_P(\omega)$. The overlap of spectral orders was accounted for by use of analytic expressions for the periodic sum of lines, and the result was convoluted with the experimental response function. The crystal orientation was determined by x-ray precession pictures. As it was necessary to transfer the crystal, a small angular error must be expected in handling this soft material. For this reason the angle φ was allowed to deviate slightly from the set values $(-45°+n\times22.5°)$ and the values that gave the best fit are shown in Fig. 1. Finally, because of random imperfections in the cylindrical surface of the crystal, illumination of the scattering region and collection of the scattered light was not strictly constant as a function of φ. For this reason, the intensity scale was left free for each separate angle during the fitting procedure. The final rms fluctuation in vertical scale was 5% and these fluctuations are statistically distributed in φ, which is considered satisfactory.

Two distinct reorientational relaxation frequencies are clearly recognized at $\varphi=45°$ and $-45°$. These values are $\gamma_1=23.9\times10^9$ and $\gamma_2=41.6\times10^9$ rad/sec, and this is in agreement with the spectra taken with the 75-GHz free-spectral range. The allowed molecular positions are known in succinonitrile.[12] The *trans* isomers, which are the most anisotropic, presumably give a large contribution to depolarized scattering in spite of their lower abundance. γ_2 describes the relaxation of the off-diagonal components α_{ij} $(i\neq j)$, which for the *trans* molecules can occur either by isomerization or by a quarter-turn rotation around the fourfold axis along which they are aligned.[12] γ_1 describes the relaxation of $\alpha_{11}-\alpha_{22}$, which for the *trans* molecules demands an isomerization. Hence one expects $\gamma_1<\gamma_2$ as observed.

The bare elastic constants we obtain are $\frac{1}{2}(C_{11}$

$-C_{44}) = 0.75 \times 10^{10}$ erg/cm^2 and $C_{44} = 0.67 \times 10^{10}$ erg/cm^3. From these one finds the dressed values $\frac{1}{2}(C_{11} - C_{12})_{\omega=0} = 0.69 \times 10^{10}$ erg/cm^3 and $(C_{44})_{\omega=0} = 0.66 \times 10^{10}$ erg/cm^3 in perfect agreement with ultrasonic results.[8] It is interesting to note that the bare values show more anisotropy than the dressed ones. It was felt that the spectra do not contain sufficiently detailed linewidth information to assess the anisotropy of the loss tensor $\overleftrightarrow{\Gamma}^{\epsilon}$. A single value was obtained, $\Gamma^{\epsilon} \simeq \Gamma_{44}{}^{\epsilon} \simeq \frac{1}{2}(\Gamma_{11}{}^{\epsilon} - \Gamma_{12}{}^{\epsilon}) \simeq 3 \times 10^{-2}$ erg sec/cm^3, where correction for the finite collection angle was made. It should be noted that for certain angles the contribution Reδ to the dressed linewidth Γ results in appreciable narrowing.

The spectra give $(B_{11} - B_{12})/B_{44} = 1.27$ which corresponds to a high-frequency Kerr-effect anisotropy $\zeta = 0.18$ in agreement with the value measured independently.[9] In principle, the absolute calibration of the scattered intensity leads to $B_{11} - B_{12}$, but this is known to be rather delicate. From the strength of the Kerr effect one calculates $B_{11} - B_{12} = 1.58 \times 10^{56}$ erg/cm^3.[9]

Finally, the relative values of the coupling constants are $(D_{11} - D_{12})/[2(B_{11} - B_{12})]^{1/2} = \mp 2.53 \times 10^4$ (erg/cm^3)$^{1/2}$ and $D_{44}/(B_{11} - B_{12})^{1/2} = \pm 1.03 \times 10^4$ erg/cm^3)$^{1/2}$, and $(\Gamma_{11}{}^{\alpha\epsilon} - \Gamma_{12}{}^{\alpha\epsilon})/[2(B_{11} - B_{12})]^{1/2} = \pm 1.81 \times 10^{-7}$ sec (erg/cm^3)$^{1/2}$ and $\Gamma_{44}{}^{\alpha\epsilon}/(B_{11} - B_{12})^{1/2} \pm 4.99 \times 10^{-7}$ sec(erg/cm^3)$^{1/2}$, where either all upper or all lower signs must be selected. These four values are believed to be accurate to 10% and their size justifies the expansion of the spectrum in the coupling strength.

In conclusion, the first observation of orientational-translational coupling in a plastic crystal succinonitrile has been reported. The results are accounted for by a hydrodynamic description of the coupling.

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