PROPAGATION OF HYPERSOUND AND ULTRASOUND IN THE ISOTROPIC PHASE OF A NEMATIC LIQUID CRYSTAL IN THE PHASE TRANSITION REGION

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The Mandel'shtam-Brillouin thermal scattering spectra in the isotropic phase of a nematic liquid crystal (MBBA + EBBA, 1 : 2) are investigated in the phase transition region. The velocity and absorption of hypersound with a frequency $\sim 5 \times 10^9$ Hz are determined from the spectra. The velocity of ultrasound with a frequency of 2.7 MHz is measured. Dispersion of the sound velocity is observed. Stimulated Mandel'shtam-Brillouin scattering is produced in the isotropic phase of a liquid crystal. The shift in the stimulated scattering components is greater than that of the thermal scattering components.

THE investigation of the spectra of scattered light and, in particular, the Mandel'shtam-Brillouin (MB) components have become one of the basic methods for the study of acoustical properties of various media at high frequencies.[1,2] Photoelectric recording of the MB spectra and correct allowance for the apparatus function of the experimental equipment make it possible to obtain high accuracy in the measurement of the velocity and absorption of the hypersound.[3] The study of the kinetics of MB spectra in phase transitions allow us, in particular, to observe the interesting features of the behavior of the hypersonic velocity near the critical point of stratification of liquid mixtures.[4,5]

The purpose of the present research was the study of the behavior of the velocity and absorption of hypersound and the dispersion of the sound velocity in the neighborhood of the isotropic liquid—nematic liquid crystal phase transition point from the spectra of thermal MB scattering and from the velocity of ultrasound.

1. EXPERIMENTAL PART

The crystal under study was a mixture of 1-mole methoxy- and 2-mole ethoxy-benzylidene-butylaniline (MBBA + EBBA, 1 : 2). The temperature T_t of the isotropic liquid—nematic liquid crystal phase transition was determined in the measurement of the index of refraction of the sample from the beginning of diffuseness of the light-dark boundary in the field of view of the ocular of the sight of an Abbe refractometer (IRF-22) amounted to 63.3 ± 0.1°C in a fresh sample. At 63.4°C, the refractive index n at the wavelength of the Ne-He laser, $\lambda_1 = 6328$ Å, was equal to 1.5872; at the wavelength of the ruby laser, $\lambda_2 = 6943$ Å, it was equal to 1.5733. Upon change in temperature, the index of refraction changed linearly, with the temperature coefficient $\Delta n/\Delta T \approx -4 \times 10^{-4}$ deg^{-1}.

Following repeated heating of the sample during the experiment to the isotropic state and then again cooling to the liquid-crystal state (thermal cycles), the temperature of the phase transition T_t was materially reduced (see Fig. 4 below). It is suggested that this decrease is associated with the effect on T_t of impurities formed upon decomposition of the sample.[6,7]

Experiments carried out with MBBA showed that the deviation from the regular course of such quantities as birefringence in the liquid-crystal phase, the Cotton-Mouton constant in the isotropic phase, and the relaxation time τ of the ordering fluctuations in the isotropic phase, all depend on the closeness to T_t and not on T_t itself.[6-8] It must be supposed that the deviation from the regular course of the acoustic parameters of the sample will also depend on $T - T_t$ and not on the absolute value of T_t. The refractive index of the sample changed very little with time. Thus, in an old sample, which had undergone many thermal cycles and which has a transition temperature of about 50°C, $n(\lambda_1) = 1.5823$ at T = 63.4°C, i.e., the refractive index changes by only about ~ 0.3% in comparison with the fresh sample. In the experiment, the transition temperature did not drop below 56.9°C.

In the study of MB scattering, the liquid crystal was poured into a cylindrical vessel of diameter 0.5 cm and length 5 cm. The vessel had a water jacket to change the temperature of the sample.

The experimental arrangement for the study of thermal MB scattering is shown in Fig. 1. The method of recording and reduction of the spectra has been described elsewhere in detail.[3,9] The ultrasonic velocity v_u was measured in an acoustic interferometer[1] at a frequency f = 2.7 MHz. To excite stimulated MB scattering, we used a ruby laser with a pulse intensity of ~ 100 MW/cm^2 and duration ~ 20 nsec. The pulses were focused inside the vessel by a lens with a focal length F = 6 or 4 cm. The spectrum of stimulated MB scattering was photographed in back-scattered light. The spectrum of the scattered light was analyzed by means of a Fabry-Perot etalon with a dispersion range 0.625 and 0.833 cm^{-1}. After passage of the powerful laser pulse through the sample, dark regions appeared in it which indicated dissociation or even burning of the sample. Under the conditions of our experiment in the liquid-crystal phase, it was not possible to observe

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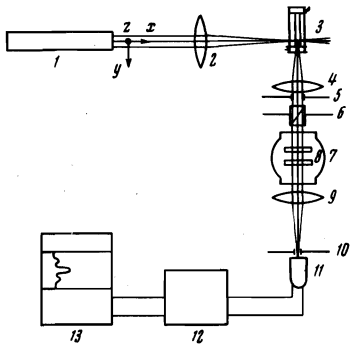

FIG. 1. Schematic diagram of the apparatus for the study of thermal Mandelśhtam-Brillouin thermal scattering: 1–multimode He-Ne laser LG-36A (power ~22 MW, wavelength 6328Å); 2–focusing objective (focal length F = 180 mm); 3–vessel with liquid crystal; 4–collimator objective (F = 180 mm); 5–aperture diaphragm (diameter d = 6 mm); 6–Nicol prism; 7–interferometer chamber; 8–Fabry-Perot interferometer, dispersion range 0.5 cm^{-1}; 9–camera objective (F = 270 mm); 10–photomultiplier diaphragm (d = 0.5 mm); 11–photomultiplier (FÉU-79); 12–linear intensity meter (PI-4-1); 13–recorder (EPP-09-MI). The angle of incidence of the light $\theta = 90° \pm 0.3°$. The width of the apparatus function was 0.03 cm^{-1}.

stimulated MB scattering, apparently because of a sharp increase in the threshold of the phenomenon due to the scattering and absorption of the laser light (see also the work of Rao and Agrawal[10], where stimulated MB scattering in MBBA was studied).

In the hypersonic and ultrasonic experiments, the temperature of the sample was maintained constant to within 0.1°C by means of an ultrathermostat.

2. RESULTS OF MEASUREMENT AND THEIR DISCUSSION

1. Velocity and Absorption of Hypersound. Velocity of Ultrasound.

Typical spectra of thermal MB scattering (I_{zz}, the first and second subscript denoting the polarization of the incident and scattered light) and are shown in Fig. 2 They are characterized by a huge intensity of scattering at the unshifted frequency, which exceeds by a factor of 100 the intensity of the MB components. The principal contribution to this intensity is made by scattering from fluctuations of the ordered phase, and not by the scattering from small particles present in the medium, inasmuch as the spectra of I_{zx} and I_{yx} have intensities comparable with I_{zz}. The onset of the phase transition was revealed in the spectra by an increase in the intensity at the unshifted frequency and in the form of intensity spikes over the entire spectrum (see Fig. 2, spectrum 3). These spikes are connected with the appearance in the sample of large scale "drops" of the liquid-crystal phase, which, entering into the scattering volume, shine as dust does. Although the scattering on such drops takes place without shift in the frequency, its intensity is smeared out over the spectrum by the apparatus function of the equipment.

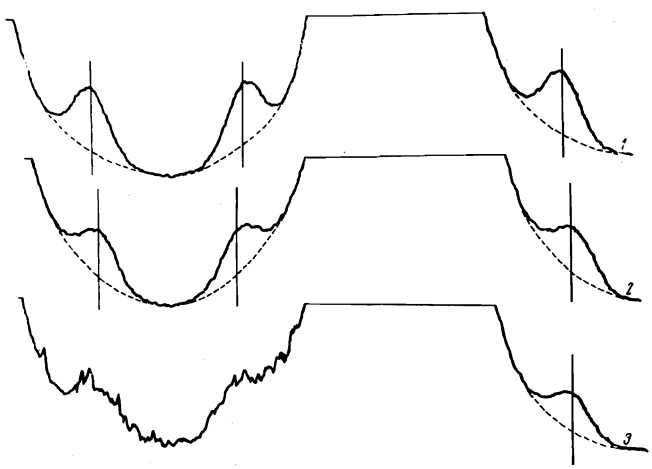

FIG. 2. Spectra of MB thermal scattering in the isotropic phase of a nematic liquid crystal for different temperatures: 1–$T - T_t = 18°$; 2–$T - T_t = 5°$; 3–$T - T_t \sim 1°C$. The dispersion range of the interferometer is 0.5 cm^{-1}.

The results of reduction of the data are shown in Fig. 3. The hypersonic velocity v_h at a frequency $f_h \sim 5 \times 10^9$ Hz, calculated from the shift $\Delta\nu$ in the MB components, is shown in Fig. 4. There also is shown the velocity of ultrasound v_u at a frequency of 2.7 MHz. Near T_t, the velocity v_u passes through a minimum. The character of the behavior of v_u is similar to the results obtained earlier for other liquid crystals.[11-13][2)]

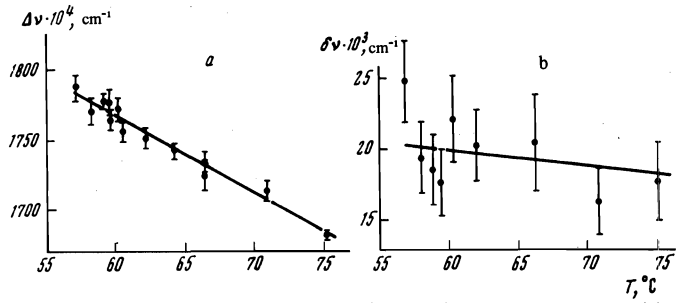

FIG. 3. Temperature dependence of the shift in the components (a) and the width of the components (b) of MB thermal scattering in the isotropic phase of a liquid crystal near the phase transition (T_t = 56.9°C).

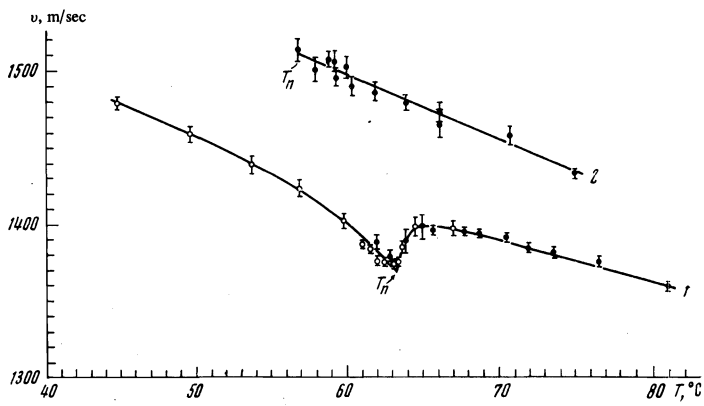

FIG. 4. Temperature dependence of the ultrasonic velocity (1) and the hypersonic velocity (2) in the region of the isotropic liquid–nematic liquid crystal phase transition. The temperature of the phase transition in case 1 is T_t = 63.3°C, and in case 2–T_t = 56.9°C.

[2)] Recently a paper appeared by Mullen et al. [14], in which the velocity of ultrasound was measured in MBBA. Their results agree with those of this paper.

An attempt has been made in the literature[15] to explain the temperature dependence of the ultrasonic velocity in liquid-crystal phase by means of a molecular-statistical theory of liquid crystals (see[16]). It must be assumed that the features of ultrasonic propagation of ultrasound in the isotropic phase are connected with the interaction of sound with fluctuations of the ordered phase. On approaching T_t, these fluctuations increase. The interaction of the acoustic wave with the fluctuations is appreciable if $f_u \lesssim 1/2\pi\tau$, where τ is the relaxation time of the bulk viscosity. It is evident that the hypersound "doesn't notice" the fluctuations, since the velocity and the absorption of the hypersound follow only their regular course.

Calculation of the sound absorption coefficient from the formula $\alpha_h = \delta\nu\pi c/v_h$ (c is the velocity of light) in the isotropic phase (for example, for T = 70°) gives $\alpha_h \approx 11600$ cm^{-1} and $\alpha_h/f_h^2 \approx 46 \times 10^{-17}$ cm^{-1}sec^2. Assuming that the absorption at ultrasonic frequencies, far from T_t, is the same in the isotropic phase as in para-azoxyanizole, $\alpha_u \sim 0.15$ cm^{-1},[11] we obtain $\alpha_u/f_u^2 \approx 20 \times 10^{-15}$ cm^{-1}sec^2, which is much larger than a_h/f_h^2. For dispersion of the sound velocity, we have[1]

$$\frac{\Delta v}{v_u} \approx \frac{v_u}{4\pi^2\tau}\frac{a_u}{f_u^2}, \qquad (1)$$

where $\Delta v = v_h - v_u$. If the simple scheme from which Eq. (1) was derived holds, then the estimate gives $\tau \sim 2 \times 10^{-9}$ sec (T = 70° K).

The width of the MB components is equal to[1]

$$\delta\nu = \frac{\Gamma q^2}{\pi c}, \quad \Gamma = \frac{1}{\rho}\left\{\frac{4}{3}\eta + \eta' + \frac{\varkappa}{C_p}(\gamma - 1)\right\},$$

where ρ is the density, η and η' are the shear and bulk viscosities, respectively, κ is the thermal conductivity, $\gamma = C_p/C_V$, and C_V and C_p are the heat capacities at constant volume and pressure. As seen from Fig. 3b, $\delta\nu$ increases on approaching T_t by about 15% in the temperature range studied. Inasmuch as the bulk viscosity is absent, this increase should be attributed to the shear viscosity. In para-azoxyanisole, as T_t is approached from the side of the isotropic liquid, the viscosity increases linearly, and the value of the viscosity in the temperature range from $T - T_t \sim 15°$ to the transition point amounts to ~ 28%.[16]

2. Stimulated Mandel'shtam-Brillouin Scattering

The measured shifts $(\Delta\nu)_s$ in the Stokes components of stimulated MB scattering turned out to be larger than the shifts in the components of thermal scattering $(\Delta\nu)_t$, referred to the scattering angle $\theta = 180°$ and to the frequency of the ruby laser. Here the difference considerably exceeds the random error of measurement of the position of the MB components. This result has been observed both in fresh samples and in samples which have gone through many thermal cycles. At T = 70°C and with the focusing of a laser pulse with amplitude ~ 100 MW by a lens F = 6 cm, $(\Delta\nu)_s$ amounted to ~ 0.25 cm^{-1}, while $(\Delta\nu)_t \sim 0.22$ cm^{-1}. A decrease of $\Delta\nu$ is usually observed in the transition from thermal scattering to stimulated scattering.[17] Evidently, this is the first observation of such nature. It shows that the stimulated MB scattering in the isotropic phase of a liquid crystal is complicated appreciably by other phenomena which devlop upon propagation of a powerful laser pulse, and therefore cannot be used directly for the determination of the velocity of the hypersound.

One can attempt to explain the results thus obtained by assuming that the stimulated MB scattering is generated upon self-focusing of the laser light in a volume where the index of refraction and the sound velocity are larger. In our experiment, the phenomenon of self-focusing was not studied, but the self-focusing filaments in MBBA have already been observed experimentally.[10] The time of establishing the stimulated MB scattering, τ', is equal to $\tau' = 1/\delta\nu\pi c \sim 5 \times 10^{-10}$ sec, as follows from the data of thermal scattering. In order that the increase in the shift of the components of stimulated MB scattering $(\Delta\nu)_s = (\Delta\nu)_t$ amount to ~ 0.03 cm^{-1}, it is necessary that the nonlinear contribution to the index of refraction be ~ 0.2. It is still not clear how the nonlinear mechanism can assure such a contribution.

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