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Brillouin Scattering in a Liquid Crystal: Frequency and Temperature Dependences

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Abstract Brillouin scattering measurements have been carried out in the liquid crystal mixture Merck ZLI-2861 with a low viscosity and a broad nematic phase. Scattering from longitudinal acoustic phonons with different wave vectors was measured by changing the geometries from backscattreing to nearly forward scattering that cover the frequency range from 10 to 1 GHz. In the nematic phase the dispersion in both the hypersonic attenuation and sound velocity is describing by a single relaxation process with the characteristic frequency 3.2 GHz. Evident anomalies in attenuation and hypersonic velocity were found at lower temperatures in the vicinity of the phase transition from a nematic to, probably, a smectic state.

INTRODUCTION

Brillouin scattering has been widely used for studying different liquids and fluids. Except in very viscous liquids, most sound velocity and absorption dispersion regions occur at high frequencies suitable for examination by this technique. In the case of liquid crystals, additional interest is connected with the acoustic properties of nematic and ordered phases as well as with the acoustic anomalous near the phase transformations.[1,2] At low frequencies $f < 200$ MHz using ultrasonic techniques, an anomalies sound absorption increase and a corresponding dip in the sound velocity have been observed in the phase transition regions. However the response of liquid crystals at higher frequencies in the Brillouin scattering region has not been pronounced enough to reveal specific acoustic anomalies in the phase transformation range. The usual relaxor system of most fluids appears to be damped at such high frequencies and no coupling of the hypersonic phonons to liquid crystal order is observed.

It seems that the Brillouin scattering potentialities can be used in the case of liquid crystals with low viscosity. For this reason we chose for our Brillouin scattering measurements a liquid crystal mixture, E. Merck ZLI-2861. This complex mixture was created in accord with the modem tendency to reduce the liquid crystal viscosity within an extended nematic phase.

EXPERIMENTAL

According to the information from E. Merck Inc.,[3] the ZLI-2861 mixture contains ten compounds with different n-alkyl chains containing up to five carbon atoms. This liquid crystal mixture has a high clearing temperature at the nematic isotropic phase transition, T_{NI}, and a wide nematic phase $T_{SN} < 233$ K $< T < T_{NI} = 367$ K where T_{SN} is the temperature of the supposed nematic -smectic phase transition. The density of ZLI-2861 is about 0.97 g/cm^3 and we use an average index of refraction n =1.6.[3]

The liquid crystal mixture was placed between two parallel windows in a massive copper cell. The sample thickness is about 1.2 mm. We used samples without any preferred orientation, though there was a spread of some experimental points which we attribute to local orientation effects.

The scattering spectra were excited by an argon laser with λ=514.5 nm. The laser power did not exceed 50 mW and the laser beam was slightly defocused. The scattering light was analyzed with a Burleigh five-pass Fabry-Perot interferometer. The shift and half-width of the Brillouin components were measured. The true values of the amplitude attenuation coefficient (α) for hypersonic phonons were obtained after correction for aperture and instrumental broadening according to well-known formula.[4-6]

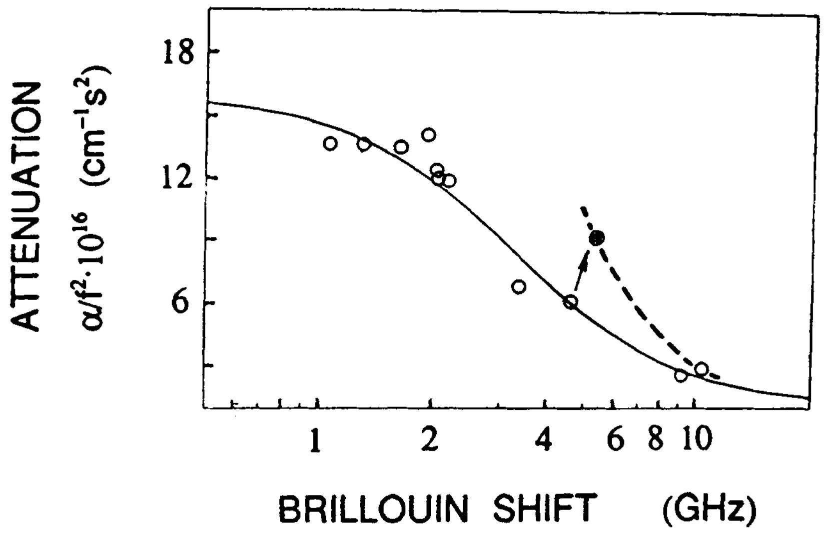

FIGURE 1 Attenuation of the longitudinal acoustic phonons vs. Brillouin shifts in the nematic phase of ZLI-2861 at room temperature (open circles). Solid line represents the fit to a single relaxation process. Dashed line shows a change for 52° scattering in the vicinity of the nematic-smectic phase transition at T~220 K.

FREQUENCY DISPERSION IN THE NEMATIC PHASE

Brillouin spectra at room temperature in the nematic phase were measured as a function of scattering angles from 180^{o} to 10^{o} which was enough to cover over a decade of frequency range (10-1 GHz). Fig. 1 shows the dispersion of the hypersonic attenuation in the nematic phase. The normalized attenuation or the ratio of attenuation to square of the acoustic wave frequency, α/f^2, is shown. The solid line in Fig. 1 represents the dispersion behavior according to the well-known relationship for a single relaxation time process.[7]

$$\alpha/f^2 = A[1+(f/f_r)^2] + B \qquad (1)$$

where A and B are constants and f_r is the relaxation frequency. From fitting we found f_r =3.2 GHz and obtained evidence for an internal relaxation process in the hypersonic region. The frequency behavior of the Brillouin shifts (or hypersonic sound velocities) confirms this dispersion anomaly.

Measurements in an Ostwald-type viscometer [8,9]gave the bulk viscosity of an unaligned ZLI-2861 as υ' ~20 cP. We suppose that for unaligned samples of ZLI-2861 one can use an average sum of combined bulk and shear viscosities $\eta_{ave}=(4\upsilon/3 + \upsilon')$ and connect it with α/f^2 as for isotropic liquids.[7]

$$\alpha/f^2 = 2\pi\eta_{ave}/(\rho V_o^3) \qquad (2)$$

where ρ is the sound velocity and V_o is in the low-frequency limit if there is a dispersion process. We obtain η_{ave}.~30 cP. This is in a reasonable agreement with the bulk viscosity υ; above plus combined shear-bulk viscosities which are expected to influence the sound attenuation also.[10] However, this apparent correspondence is not confirmed by temperature measurements.

TEMPERATURE DEPENDENCE OF THE SOUND ATTENUATION

The ZLI-2861 liquid crystal mixture exhibits a wide nematic phase region. The temperature measurements in an Ostwald-type viscometer in this nematic phase show a drastic increase of the bulk viscosity from 20 to 2730 cP (Fig. 2a). However, the growing static viscosity does not affect the attenuation of the hypersonic phonons. Fig. 2b shows the behavior of the Brillouin components linewidth in three geometries of scattering; 180^{o} or backscattering , 129^{o} and 52^{o} . As it was mentioned above we expect α_η_{ave} and in this case the high-frequency portion of the viscosity remains nearly constant in the nematic phase. In spite of different temperature behavior of the three curves in Fig. 2b, a common reduction of α/f^2 was found on cooling in the nematic phase for the high frequency tail of the dispersion wave in Fig. 1. These three scattering geometries cover a narrow frequency region in Fig. 1, so we can only qualitatively judge by appearance that the relaxation frequency f_r decreases upon lowering temperature in the nematic phase.

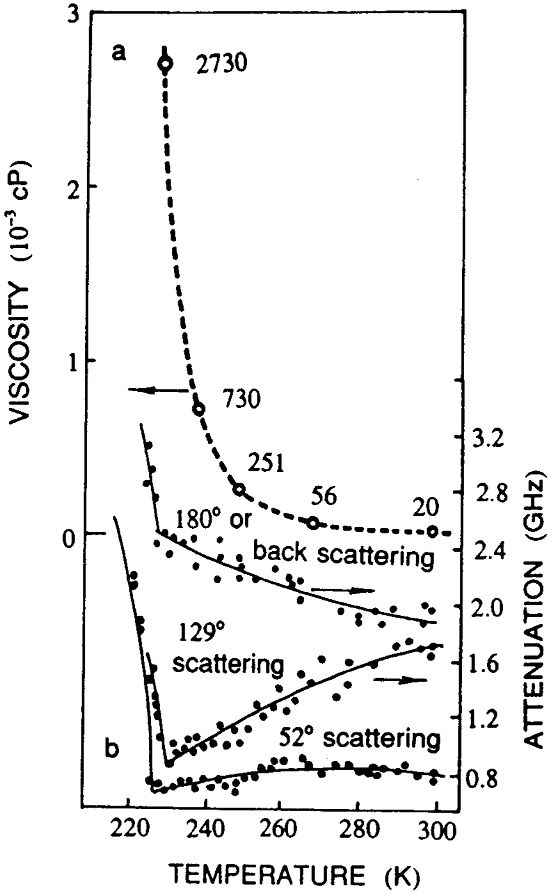

FIGURE 2 (a) Static bulk viscosity of ZLI-2861 vs. temperature (from Ref. 9), (b) Attenuation of the longitudinal acoustic phonons vs. temperature in three different geometries of scattering.

However, we have found that the hypersonic acoustic response of ZLI-2861 is not completely damped even for coupling to liquid crystal order. All three curves in Fig. 2b show an abrupt increase of the hypersonic attenuation in the region 230-220 K that is probably connected with a phase transition to the smectic state. In this new phase the sample ZLI-2861 becomes very turbid, the Brillouin doublet intensity reduces and nearly disappears so that accurate measurements become difficult. Nevertheless several points in the vicinity of the transition let us make some conclusions.

The attenuation growth is frequency dependent. At least, the point for α/f^2 in the 52° .scattering geometry shifts significantly while the corresponding point in the backscattering practically does not change (Fig. 1). It is presently impossible to understand whether the dashed line in Fig. 1 evidences a change to multiple relaxation near the smectic phase boundary similar to that at ultrasonic frequencies in MBBA near the clearing point or whether it only means a shift of the single relaxation frequency.

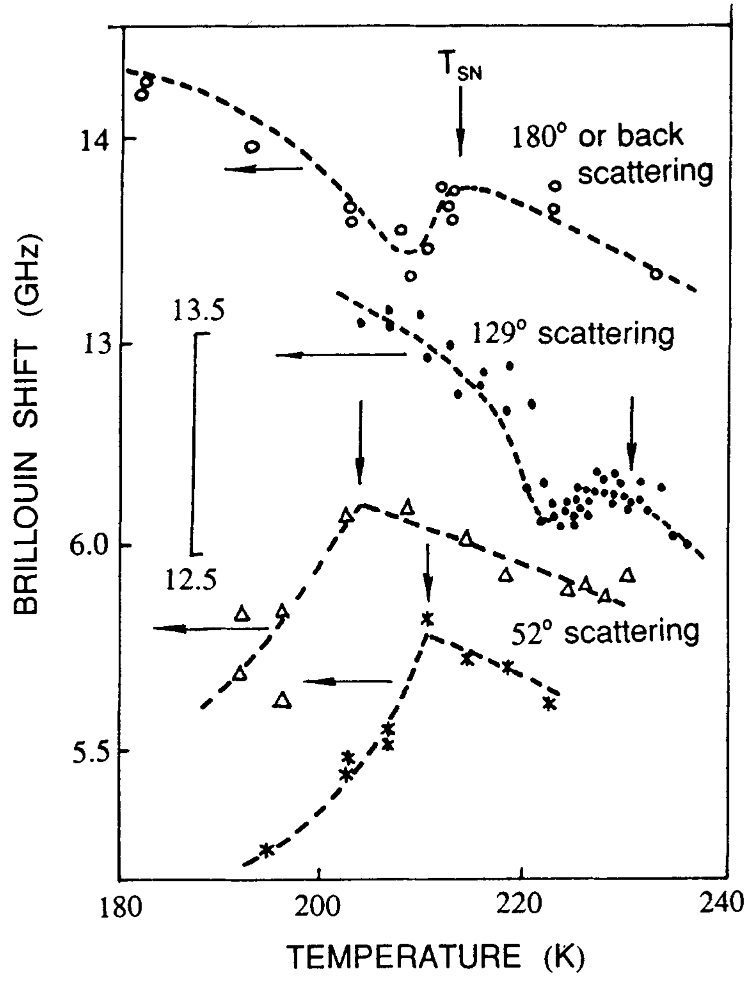

FIGURE 3 The behavior of Brillouin component shifts in the vicinity of the nematic-smectic phase transition in three scattering geometries.

The temperature behavior of the Brillouin shifts (or hypersonic velocity) confirms the existence of acoustic anomalies at the transition from a nematic to a supposed smectic phase and also the dispersion effect on their values (Fig. 3). All data were obtained upon gradual cooling. A large spread of the phase transition temperatures is clearly seen. We did not note some kind of regularity in this process, for example, due to aging. Probably, such a complex mixture as ZLI-2861 can be easy overcooled or the process of nucleation plays a determinant role. In spite of this spread in T_{SN} we found similar dips of about 3% in the hypersonic sound velocities for 180^{o} and 129^{o} scattering (the difference in the Brillouin shifts here is very small, about 7 %). For the 52^{o} scattering geometry the dip is expected to be not less than 8 % while the Brillouin shift differs from considered above more than twice.

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