Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Dolganov, V. K. , Csillag, L. , Kroó, N. and Rosta, L.(1989) 'Inelastic light scattering from the liquid crystal and solid phases of MBBA', Liquid Crystals, 4: 6, 693 — 696
To link to this Article: DOI: 10.1080/02678298908033205
URL: http://dx.doi.org/10.1080/02678298908033205

LIQUID CRYSTALS, 1989, VOL. 4, NO. 6, 693–696

Inelastic light scattering from the liquid crystal and solid phases of MBBA

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(*Received 17 May 1988; accepted 22 January 1989*)

Brillouin spectra from 4-methoxybenzylidene-4′-*n*-butylaniline were measured for the nematic phase, a quenched liquid crystal (phase C_0), and a partially ordered structure (phase C_1). The difference in the velocities of the longitudinal hypersound waves in the nematic and the quenched liquid crystal structures is associated with temperature and relaxation effects.

1. Introduction

Brillouin scattering is one of the basic methods of studying the dynamics of solid and liquid states. In the present paper, Brillouin scattering has been used to study solid state structures with liquid-crystalline ordering. 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) was examined in its nematic phase, a quenched liquid-crystalline structure (phase C_0) and in a partially ordered phase C_1 [1]. Phase C_0 has an orientational order resembling that of the nematic. C_1 has an increased orientational order (compared with C_0), and also elements of translational ordering [2].

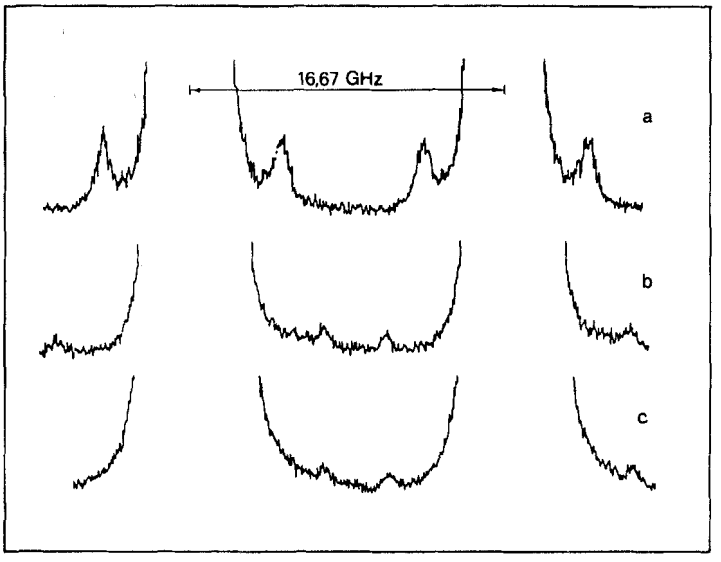
2. Experiment and results

The spectrum of scattered light was studied by a stabilized triple-pass Fabry–Perot interferometer with piezoelectric scanning. In different measurement sets the interferometer plate separation corresponded either to the free spectral region of 16·67 GHz or 25 GHz. A single mode Ar^+ laser (wavelength $\lambda = 5145$ Å, power $P = 10$–80 mW) was used as an excitation source. While measuring in the liquid-crystalline phase, the laser power was chosen below the threshold at which the liquid-crystalline structure may be reoriented by the electric field of the light. The Raman scattering and luminescence lines of uncontrolled impurities were eliminated by an interference light filter located in front of the interferometer. We used 100 μm thick MBBA samples oriented by the quartz cell surfaces. Measurements in the liquid-crystalline phase were carried out with the nematic director oriented perpendicular or parallel to the scattering plane. In most experiments the angle between the incoming laser beam and the scattered beam was 90°. The sample cell was positioned at 45° relative to the exciting beam, which was directed to the opposite surface of the cell with respect to the recording side. In this measurement geometry there is no need for refractive indices to be known in order to calculate the hypersound velocities [3].

The quenched liquid-crystalline structure (phase C_0) was obtained by fast cooling of the oriented sample from the room temperature nematic state to below 200 K. The samples should be of high quality for the Brillouin scattering to be recorded. When phase C_0 of MBBA was produced by fast cooling, the orientation in a quartz cell

0267-8292/89 $3.00

was partially destroyed and the sample cracked; this effect led to depolarization of the beam and to intense scattering from defects. Sections of the sample with undisturbed homogeneous orientation were selected for the measurements. The quality of samples was checked in transmitted light using crossed polarizers.



Brillouin scattering spectra of MBBA: (*a*) nematic phase, $T = 300\,\mathrm{K}$; (*b*) quenched liquid crystal (phase C_0), $T = 170\,\mathrm{K}$; (*c*) partially ordered phase C_1, $T = 170\,\mathrm{K}$.

The figure presents a typical scattering spectrum from a liquid-crystalline phase with the director oriented perpendicular to the scattering plane. Similar results were obtained with the director oriented in the scattering plane. The Brillouin components from the LC phase were observed in the VV-spectrum only (the electric field vector of the incident and scattered light is normal to the scattering plane). The frequency shift, ν, of the Brillouin components relative to the fixed frequency at the scattering vector $q = 1{\cdot}73 \times 10^5\,\mathrm{cm}^{-1}$ was $4{\cdot}6\,\mathrm{GHz}$ ($0{\cdot}154\,\mathrm{cm}^{-1}$). The velocity of the longitudinal sound waves $v_N \approx 1{\cdot}7 \times 10^5\,\mathrm{cm/s}$ was obtained from

$$v = \frac{2\pi\nu}{q}. \tag{1}$$

The results of Brillouin scattering from the quenched liquid-crystalline structure are shown in figure (*b*). In contrast to the nematic state the intensity of inelastic scattering in phase C_0 is considerably smaller, the components are shifted to higher frequencies. The frequency shift in the quenched structure increases to $6{\cdot}9\,\mathrm{GHz}$ ($0{\cdot}23\,\mathrm{cm}^{-1}$). From the Brillouin component shift the hypersound velocity v of $2{\cdot}5 \times 10^5\,\mathrm{cm/s}$ was calculated. Here, as in the nematic state we observed only one pair of Brillouin components in phase C_0. This can probably be explained by the small intensity of inelastic scattering of transverse acoustic phonons.

Phase transition from the quenched liquid-crystalline structure to the partially ordered phase C_1, ($T \approx 200\,\mathrm{K}$) is accompanied by some increase in intensity of scattering from defects due to deterioration of the sample quality (i.e. additional cracks). Nevertheless, even in this case rather perfect sections of the sample ($\sim 0{\cdot}5\,\mathrm{mm}$)

can be chosen and the Brillouin scattering recorded from their surface (see figure (*c*)). In the $C_0 \rightarrow C_1$ phase transition we observed no change in the velocity of hypersound waves. The $C_1 \rightarrow C_2$ phase transition on heating the sample to above 215 K leads to an essential increase of the background due to defect scattering, which made it impossible to record inelastic spectra from phase C_2.

3. Discussion

An increase in the velocity of longitudinal hypersound waves in phase C_0, as compared with the nematic state, can be associated with the following causes.

(1) The considerable difference in the temperature of measurements effects the phonon frequencies. Heating an MBBA crystal phase from 170 K to 270 K results in a decrease of the optical phonon frequencies by 20 per cent. If we assume a similar value of the frequency shift of acoustic phonons due to the temperature difference, the extrapolation of the Brillouin frequency for a solid state structure (see figure (*b*), (*c*)) to the liquid crystal temperature range, gives a value of the hypersound velocity v_T of about $1{\cdot}9 \times 10^5$ cm/s for the transverse component.

(2) This extrapolation does not take into account the variation of the Brillouin frequency due to the high molecular mobility in the nematic phase i.e. the structure was assumed to be frozen. At the same time molecular mobility leads to a considerable dispersion of sound velocities [4] (e.g. for the longitudinal component v_N of about $1{\cdot}54 \times 10^5$ cm/s was found at 3 MHz [5]). At 4·6 GHz, the condition

$$\nu > \frac{1}{2\pi\tau} \tag{2}$$

is fulfilled for the Brillouin frequency where τ labels the effective relaxation time for the nematic director fluctuations (τ_n) and for the rotation of the long molecular axes ($\tau_\perp$) [6]. It means that these types of molecular motions are essentially frozen for hypersound frequencies. In contrast, rotation of molecules around their long axes are characterized by the times $\tau_\parallel 10^{-11} 10^{-12}$ s. This type of motion is not frozen ($\nu < 1/2\pi\tau$) for the hypersound frequency of 4·6 GHz, and so should contribute to dispersion at higher frequencies. Indeed, the difference in the transverse and longitudinal components of the hypersound velocities ($v_T \approx 1{\cdot}9 \times 10^5$ cm/s, $v_N \approx 1{\cdot}7 \times 10^5$ cm/s) can be associated with the high frequency dispersion. We may also expect that the velocity of acoustic phonons should exceed the hypersound velocity.

To make a comparison of these Brillouin scattering results with neutron inelastic scattering measurements the following data are available for liquid-crystalline compounds; the dispersion relation of acoustic phonons was determined in the crystalline phase of 4,4′-diethoxyazoxybenzene [7]. The velocity of longitudinal acoustic phonons v_{PN} can be calculated as about 3×10^5 cm/s, which yields a value almost twice as high as we have obtained for the MBBA C_0 phase, in agreement with our previous assumption. On the other hand, the vibrational density of states was determined by incoherent inelastic scattering of neutrons for the ordered and disordered solid phases of MBBA [8]. It was found that the density of states $\varrho(\nu)$ in phases C_0 and C_1 is practically the same for the low frequency region, i.e. for the acoustic phonon

modes. This behaviour of $\varrho(v)$ can be interpreted from our light scattering data in terms of the constancy of the sound velocities in these structures.

It has been established [1, 2] that in the $C_0 \rightarrow C_1$ phase transition of MBBA the regions of correlated molecular arrangements i.e. the medium range ordering units are increased by about a factor of three. At the same time, as a conclusion of this Brillouin scattering experiment we can assume that this important increase of the medium range ordering is not accompanied by any considerable change in the arrangement of the nearest neighbour molecules and the elastic constants.

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