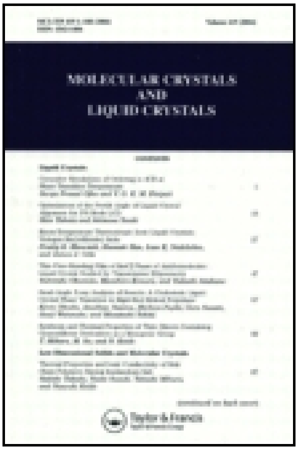

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Resonance Mode and Pretransitional Fluctuations Near the SmA - SmC* Phase Transition

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A low-frequency (0.1 – 100 kHz) resonance mode interpreted as a texture one has been investigated on ferroelectric liquid crystals (FLC). Compounds and mixtures showing different types of the phase transition into the SmC* phase (I – SmC*, N* – SmC*, SmA – SmC*) have been examined in order to find the resonance properties in the ferroelectric phase. It has been shown that the origin of the resonance response (resonance mode) is caused by strong pretransitional order parameter fluctuations in both SmA and SmC* phases near the second order SmA – SmC* phase transition. The principal factor causing the resonance mode origination is the presence of an external mechanical field in the well aligned uniform bookshelf FLC texture. An interaction between the texture resonance mode and bending modes of glass cell plates and the synchronization effect have been investigated.

Keywords: ferroelectric liquid crystals; low-frequency resonance mode; bookshelf texture; mechanical stress; synchronization effect

INTRODUCTION

A low-frequency (0.1 – 100 kHz) resonance mode interpreted as a texture one has been observed near the second order SmA – SmC* phase transition on a two-component FLC mixture containing a mesomorphic matrix and a chiral dopant [1]. This mode manifests itself as free damping collective director oscillations after the electric field reversal which are accompanied (and can be revealed) by oscillations of the in-

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duced polarization current [2], optical transmission oscillations of the sample placed between crossed polarizers [3] and mechanical vibrations of the sample cell plates [4,5]. It has been shown that the principal factor causing the resonance mode origination is the presence of an external mechanical field in the well aligned uniform bookshelf FLC texture [6]. A resonance which shows a continuous dependence of frequency on temperature and electric field strength has been discerned in the spectrum of the oscillations [1,7]. An interaction of this resonance with bending modes of the cell plates resulting in the change of its frequency and the synchronization on the nearest bending mode has been observed [1].

In the present work, we have studied a number of different ferroelectric mixtures based on lactic acid derivatives showing the spontaneous helix unwinding and the helix twist inversion in the chiral smectic C (SmC*) phase [8] and new FLC substances with four ester groups in the core [9]. The compounds and mixtures showing different types of the phase transition into the SmC* phase such as I – SmC*, N* – SmC*, SmA – SmC* have been examined in order to find the resonance properties in the ferroelectric phase. We have not found any signs of the resonance response (or oscillations) in such compounds that do not exhibit the SmA – SmC* phase transition. It has been shown that the origination of the resonance response (resonance mode) might be caused by strong pretransitional fluctuations of the order parameter in both SmA and SmC* phases near the second order SmA – SmC* phase transition.

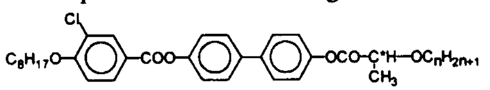
In is well known that the optical birefringence is in the SmA phase directly related to the mean-square fluctuations of the tilt angle [10]. Recently, M. Škarabot *et al.* reported results of high-resolution birefringence measurements on chiral tilted smectic materials that exhibit a direct phase transition from the SmA phase to tilted phases [11]. Close to the transition into the SmC* phase ($\Delta T < 5°C$), they observed a critical suppression of the birefringence, whish is due to pretransitional fluctuations of the order parameter. The amplitudes of these fluctuations were evaluated around several degrees.

In our experiment, due to the high orientation order in the uniform bookshelf texture and the synchronization effect by the electric field pulse and motion of a cell plate, the director fluctuations turn out to be coherent and result in the macroscopic phenomenon observed. A correlation between the strength of the electroclinic response (amplitude of the soft mode) and the initial amplitude of the collective director oscillations has been revealed. The oscillations reach the highest intensity at the phase transition point.

Since the molecules are tilted to the smectic layer normal in the ferroelectric phase, zigzag defects and chevron structure arise resulting in destruction of the uniform texture and the decrease in the oscillation amplitude. A mechanical stress in the FLC texture applied at a proper direction increases significantly (more than one order) the amplitude of the resonance response and causes expansion of the temperature range of the resonance mode existence by at least 15 – 20° C into the SmC* phase. It has also been noted that the zigzag defects disappear under the mechanical field. We assume that the mechanical stress application results in a decrease of the molecule tilt angle that causes the chevron texture to transform to the uniform bookshelf one [12]. This assumption is confirmed by the observed shift of the phase transition point under the mechanical stress.

EXPERIMENTAL

The formulas, phase sequences and transitions temperatures (°C) of the investigated compounds and mixtures are given below.

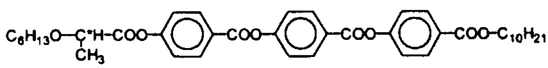


n = 5 1

n = 7 2

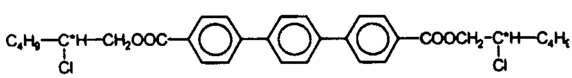
1 SmC* - 124.0 - N* - 124.3 - BP - 124.5 - Iso [8]

2 SmC* - 120.2 - Iso [8]



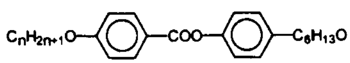
3

Cr - 70 - SmC* - 98 - SmA - 115 - Iso [9]



10 wt %

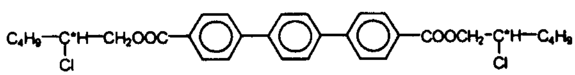
4



n=8: 45 wt%

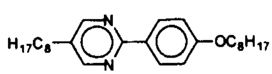
n=10: 45 wt%

Cr - 38 - SmC* - 65.0 - SmA - 88.5 - N* - 92.5 - Iso



26 wt %

5



74 wt %

Cr - 28 - SmC* - 65 - SmA - 72 - Iso [3,13]

Glass plates of 27×15×1 mm were used as substrates. They were separated by 15 μm thick teflon spacers. The working volume of the cell was 15×15×0.015 mm^3. The cell construction allowed small moving of the upper plate. The inner side of the cell plates was coated with transparent conductors which were under square electric voltage pulses of 100 Hz frequency. The electric field strength amounted a value up to 3.3 V/μm.

According to the work [14], the investigated uniform bookshelf texture (smectic layers are perpendicular to the cell plates) was built from the homeotropic one by applying mechanical vibrations to the upper plate under the electric field imposed at the temperature of 1 °C below the transition point into SmC* phase. To obtain a controllable mechanical stress in the investigated texture, a pressure directed perpendicularly to the smectic layers (*along the cell plates*) was applied to the upper plate. The value of the stress was varied up to 10^3 N/m^2. It was normalized to the working square of the cell.

With substances having a SmA – SmC* phase transition, both the spontaneous polarization P_S and the tilt angle θ increase continuously from zero when the temperature decreases from the phase transition point T_C. This behaviour is a manifestation of the second or weakly first order phase transition. The temperature dependence of the spontaneous polarization is fitted to the equation

$$P_S = P_0(T_C - T)^{\alpha'} \text{ for } T < T_C,$$

where α' is found to be 0.52 ± 0.05. Results of the optical tilt angle are fitted to the equation

$$\theta = \theta_0(T_C - T)^{\alpha''} \text{ for } T < T_C,$$

where $\alpha'' = 0.38 \pm 0.04$. Based on the results of the mean-field theory, α'' lower than 0.5 implies the existence of a biquadratic coupling and the piezoelectric coupling between the tilt angle and spontaneous polarization.

RESULTS AND DISCUSSION

We have not found any signs of the resonance response (or oscillations) in such compounds that do not exhibit the SmA – SmC* phase transition (compounds **1** and **2**). We have also not observed dependence of oscillation parameters on either the helix pitch in the SmC* phase or the helix twist inversion.

It is remarkable that the resonance effects are not found near the N* – SmC* phase transition. Even though this transition is of the first order, it is also characterised by pretransitional tilt fluctuations [15]. We cannot give a satisfying explanation of this contradiction here, further experimental investigations are necessary, but a possible reason could be the difficulty in obtaining a well-aligned monodomain for compounds that do not have the SmA phase.

Dependence of the oscillation parameters such as initial amplitude and frequency on the mechanical stress for the mixture **4** at the temperature of 61.8°C (SmC* phase) are shown in Fig. 1. The amplitude of oscillations grows nonlinearly with the mechanical stress increasing. As a result of stress applying, the initial amplitude can be increased almost in a decade. When the value of the mechanical stress reaches 450 N/m^2 the upper cell plate undergoes an irreversible shift. It is caused by the bond breaking between the FLC molecule and the plate surface and results in destroying the uniform bookshelf texture. Due to this texture destruction, the oscillation amplitude drops abruptly. The oscillation frequency also grows nonlinearly with mechanical stress increasing.

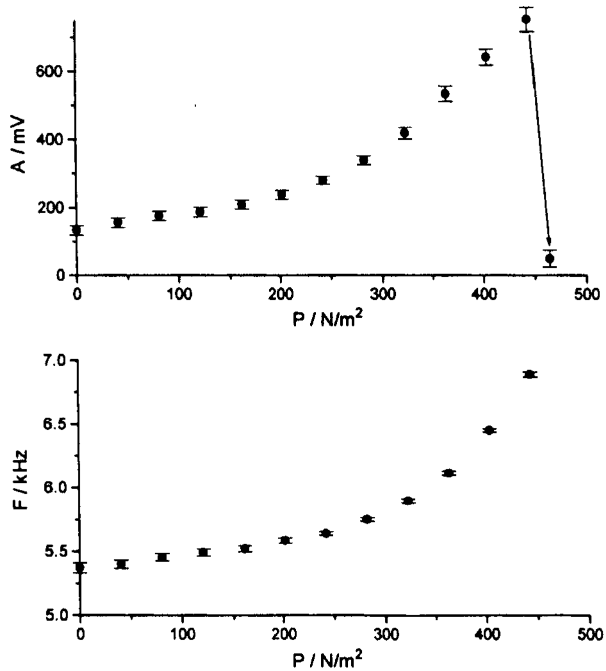


FIGURE 1 Dependence of the amplitude (A) and frequency (F) of the oscillations on the mechanical stress for the mixture 4 at the temperature of 61.8°C (SmC* phase).

The maximum frequency deviation due to the stress application amounts to about 30 % of the frequency value for the undisturbed FLC.

Similar dependence of the oscillation parameters are observed also at other temperatures of SmC* phase. The oscillation parameter changes resulted from the mechanical stress application remain reversible until the FLC texture is destroyed.

As can be seen in Fig. 1, the elastic mechanical stress arising in the FLC texture as a result of the applied mechanical strength increases the oscillation amplitude significantly. However, the oscillations with initial amplitude of 120 mV observed at the absence of the external mechanical strength also take place due to a mechanical stress but the internal one. This internal stress is evoked by existence of domains with different director orientations. One can select such magnitude and direction of the external strength that the internal mechanical stress will be compensated thoroughly and the oscillations vanish.

Temperature dependence of the oscillation amplitude at the constant external mechanical stress of 320 ± 4 N/m^2 and without it are shown in Fig. 2 (curve 1 and 2, respectively). Comparison of curves 1 and 2 evidences that the external mechanical stress is the main factor of the director oscillations appearance in SmC* phase at a temperature more than 1°C below the phase transition point. When only a weak in-

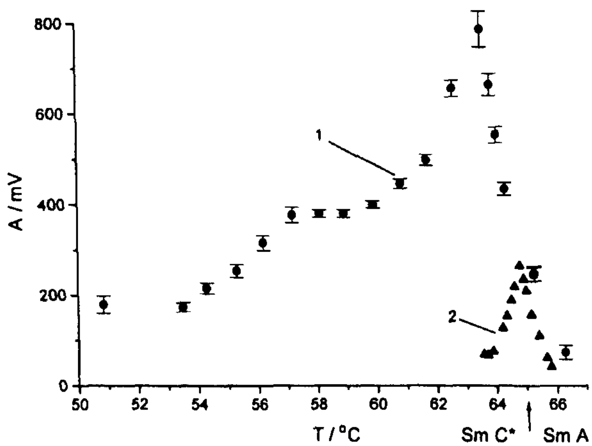


FIGURE 2 Temperature dependence of the oscillation amplitude at the constant external mechanical stress of 320 ± 4 N/m^2 (1) and at the weak internal stress (2) for the mixture 4. The arrow indicates the phase transition temperature for undisturbed FLC.

ternal mechanical stress takes place, the oscillations of small amplitude can be observed in a narrow temperature range near the phase transition (curve 2). The temperature dependence of the oscillation amplitude is symmetrical with respect to the phase transition point. Just such type of the oscillations was observed in all previous investigations [1–7].

A constant external mechanical stress of about 10^2 N/m^2 results in significant increasing of the oscillation amplitude and expansion of the temperature range of oscillation existence at least by 15 – 20°C towards SmC* phase. In contrast, in the SmA phase, the influence of the external mechanical stress is insignificant. Moreover, one can see that the oscillations reach their maximum amplitude at different temperatures depending on the amount of the external mechanical stress. It was supposed in previous works [1,4] that the maximum is associated with the phase transition point. So, the shift of the maximum signifies either the oscillation maximum shift with respect to the phase transition point or that of the phase transition point itself. We consider the second assumption is valid, namely the external mechanical stress changes the temperature of the phase transition at least by 1.5°C at 320 N/m^2. It is similar to the mechanical pressure influence on the phase transition temperature in liquid crystalline elastomers [16].

It was noted at the investigation of the uniform bookshelf texture that the decreasing of the oscillation amplitude with cooling is accompanied by the appearance of typical chevron disclinations [5]. It is remarkable that the application of the mechanical stress results in the disappearance of these disclinations and the reappearance of the oscillations and resonance response of the FLC. We consider that the mechanical stress application results in a change of the molecule tilt angle that causes the shift of the phase transition point and transformation of the chevron texture to the uniform bookshelf one.

Two different types of sound frequency resonances were discerned in the electric response on fast field reversal in a FLC [1,7]. The first one consists of mechanical resonances of bending modes of the cell glass plates. Frequencies of these resonances do not depend on external parameters (temperature, electric field strength). The second type resonance, that of electric oscillations, shows a continuous dependence of all parameters on temperature, electric field strength and mechanical stress, thus allowing us to suppose that this resonance is the texture one.

We have studied the interaction between the texture resonance and the bending modes of the plates for the mixture **5**. The oscillation frequency has been found to be changing during the response period (Figure 3). Oscillations on the texture mode are excited immediately

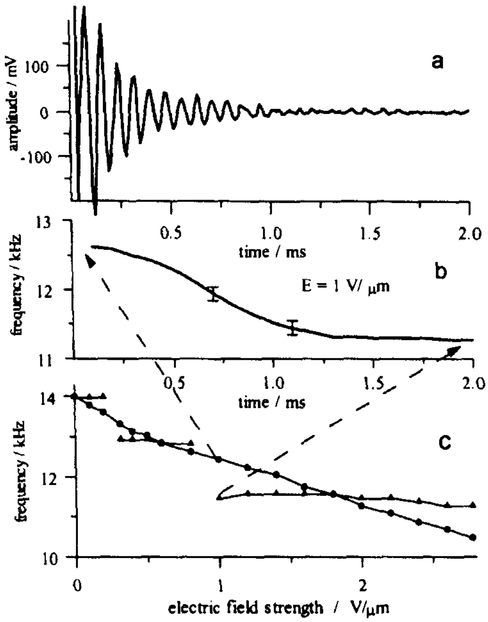


Figure 3 Electric resonance response (a) and the frequency change therein (b) for the mixture **5**. Dependence of the oscillation frequency at the start of the response (circles) and at its end (triangles) versus electric field strength (c).

after the field is reversed, since the excitation time of that mode is short due to its relatively low quality. 1 – 1.5 ms later, oscillations on the nearest bending mode are excited due to interactions of these modes; in other words, the texture resonance is synchronised with the nearest bending mode.

CONCLUSION

The principal factor of the resonance mode origination is the strong pretransitional fluctuations near the second order SmA – SmC* phase transition and the presence of the mechanical stress directed perpendicularly to the smectic layers (*along* the cell plates) in the FLC texture. This mechanical stress either is caused by some internal texture perturbations when there are some regions with a different director alignment, or is made by an external pressure on the upper cell plate in the required direction. This mechanical stress results in a change of the molecule tilt angle and the phase transition temperature and causes the chevron texture to transform to the uniform bookshelf one. An interaction between the texture resonance mode and bending modes of glass cell plates and the synchronization effect have been illustrated.

Acknowledgments
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