

# Unusual behaviour of binary mixtures of ferroelectric and antiferroelectric liquid crystals with three chiral centres

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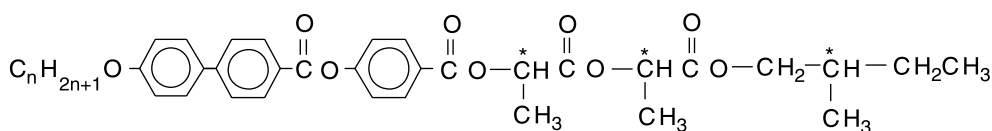
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Two binary mixtures have been studied of homologues from a series derived from 4-alkoxybiphenyl-4'-carboxylic acid with three chiral centres exhibiting ferroelectric (FE), antiferroelectric (AF) and tilted hexatic phases. One homologue exhibits a re-entrant  $SmC^*$  ( $SmC^*_{re}$ ) phase, which is miscible with the  $SmC^*$  phase. The phase diagrams of the studied mixtures exhibit a close pocket of the  $SmC^*_A$  phase. The  $SmC^*_{re}$  phase is induced even in the mixtures composed of homologues without this phase. Dielectric spectroscopy reveals the Goldstone mode in both ferroelectric  $SmC^*$  and the  $SmC^*_{re}$  phases, this mode being stronger when increasing concentration of the antiferroelectric homologue. In the  $SmC^*_A$  phase a relaxation mode is detected with the relaxation frequency three orders higher, which exhibits critical slowing down when approaching the  $SmC^*_{re}$  phase. This mode, which can be attributed to the anti-phase mode, is responsible for the appearance of the  $SmC^*_{re}$  phase. In mixtures exhibiting the  $SmC^*_A$  phase a helix twist inversion occurs in the vicinity of the low temperature border of the AF phase.

**Keywords:** binary mixture, ferroelectric phase, antiferroelectric phase, re-entrant ferroelectric phase, dielectric spectroscopy, soft anti-phase mode.

## 1. Introduction

Recently a series has been synthesised derived from 4-alkoxybiphenyl-4'-carboxylic acid with three chiral centres of the (S) configuration connected to the core by the ester group [1]. General structure of the series denoted as  $ZLLn^*$  is



Mesomorphic properties of homologues [1] are shown in Table 1. All compounds exhibit  $SmA$ ,  $SmC^*$  and tilted hexatic phases. In  $ZLL7^*$  and  $ZLL8^*$  the AF  $SmC^*_A$  phase occurs. The existence of the re-entrant FE,  $SmC^*_{re}$ , phase below the AF phase in  $ZLL7^*$  is a very rare phenomenon. Besides this compound, it has been reported in only one other series so far [2]. As for the hexatic phases, they are FE even in the  $ZLL8^*$  compound, where the hexatic phase exists below the AF  $SmC^*_A$  phase. In homologue  $ZLL6^*$ , a low temperature smectic phase occurs, while the others crystallise just below the hexatic phase [1].

A strong discrimination of FE or AF properties upon lengthening of a non-chiral terminal chain takes place also in other materials [3]. For the next homologues exclusively the FE phase or both FE and AF phases may be observed. As the next homologues differ only in the  $CH_2$  group, their energies cannot strongly differ in the same temperature region. Therefore, the next-neighbouring-layer interac-

tion term, which is positive or negative for AF or FE phases [4], respectively, must be near zero. It means that the correlations of the azimuthal tilt angle of the next-neighbouring layers are very weak and may become still weaker when mixing both homologues. Such situation could bring about phenomenon of frustration which was discovered in Ref. 5.

The aim of this work is to study stabilisation of the  $SmC^*_A$  and  $SmC^*_{re}$  phases in binary mixtures  $ZLL6^*/ZLL7^*$  and  $ZLL6^*/ZLL8^*$ . In the mixtures, dielectric spectroscopy study and pitch, spontaneous polarisation and spontaneous tilt angle measurements have been accomplished. The helix handedness has been inferred from the optical rotatory power study on free-standing films.

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Table 1. Phase sequences and transition temperatures between phases of materials used in mixtures, hex is a hexatic phase either SmI\* or SmF\*; • the phase exists, — the phase does not exist.

	Hex	$T_H(^{\circ}\text{C})$	SmC* <sub>re</sub>	$T_H(^{\circ}\text{C})$	SmC* <sub>A</sub>	$T_H(^{\circ}\text{C})$	SmC*	$T_C(^{\circ}\text{C})$	SmA	$T_H(^{\circ}\text{C})$	ISO
ZLL 6/*	•	76	—		—		•	97	•	141	•
ZLL 7/*	•	65	•	71	•	98	•	104	•	129	•
ZLL 8/*	•	58	—		•	99	•	102	•	126	•

## 2. Experimental

Cells for measurements consisted of glass plates coated with indium tin oxide (ITO) transparent electrodes of the area  $5 \times 5 \text{ mm}^2$  and parallel rubbed polyimide layer, which ensured a planar (book-shelf) alignment. The cells with a  $25\text{-}\mu\text{m}$  gap were filled by a capillary action in the isotropic phase. The sample alignment and textures were observed using a polarising microscope. In all measurements temperature stability was better than  $0.1 \text{ K}$ .

The frequency dispersion of the complex permittivity  $\epsilon^*(\omega) = \epsilon' - i\epsilon''$  was measured in a range from  $10 \text{ Hz}$  to  $1 \text{ MHz}$  at stabilised temperatures. Besides,  $\epsilon'$  was recorded at  $100 \text{ Hz}$  on cooling runs at a rate  $1 \text{ K/min}$ . The spontaneous polarisation was determined from the hysteresis loop detected during the sample switching. The spontaneous tilt was determined from an angle difference between minimum transmission (extinction) positions measured under opposite dc electric fields on a planar sample placed between crossed polarisers. A good sample alignment necessary for optical studies was obtained by applying a low frequency electric field of about  $40 \text{ kV/cm}$  for about  $30 \text{ min}$  in the SmC\* phase.

The helical pitch was measured by diffraction of the He-Ne laser light on samples with planar alignment. This method can be used for the measurement of the helical pitch of a limited length. For pitch shorter than  $0.8 \mu\text{m}$  the diffraction ring is diffused or completely disappears. If the equilibrium pitch is longer than a few  $\mu\text{m}$  the helix may become non-regular or is completely unwound by surface anchoring.

Free-standing films (without a glass support) were used for the optical rotatory power measurement. This method yields information on relative changes of the molecular spiralling along the helical axis with the temperature, but the absolute value of the pitch length cannot be evaluated. In free-standing films, the pitch length in the range of the visible wavelength range can be evaluated from the selective reflection of a definite light colour.

## 3. Results

### 3.1. Phase diagrams

The phase diagrams of binary mixtures ZLL6/\*–ZLL7/\* and ZLL6/\*–ZLL8/\* are shown in Figs. 1(a) and 1(b). The phase transition temperatures were determined from the

changes of textures observed in a polarising microscope and were compared with positions of jumps on the temperature dependence of the real part of permittivity  $\epsilon'(T)$  detected on cooling. The FE and AF SmC\* phases, non-distinguishable by textures, were identified according to the value of  $\epsilon'$ , which is about 4 in the AF phase but typically 2 orders higher in the FE phase.

Another aspect, which distinguishes between the FE and AF phases is the value of the quasi-static threshold field  $E_{th}$ . This is a lowest d.c. field in which one can see changes in birefringence or in texture in planar samples. In

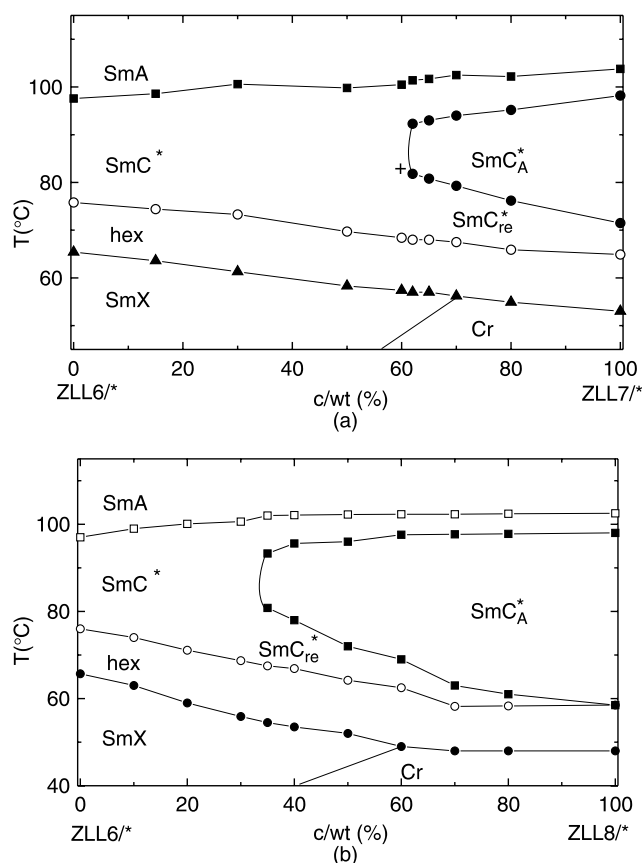


Fig. 1. Phase diagrams for binary mixtures: (a) ZLL6/\* – ZLL7/\*, (b) ZLL6/\* – ZLL8/\* . On the x-axes the concentration of (a) ZLL7/\* and (b) ZLL8/\* in weight % is shown. SmX denotes a low temperature ordered smectic phase, Cr is the crystal phase. The isolated cross in (a) indicates the lowest concentration with the inversion of the helix handedness. Other inversion points in both (a) and (b) coexist with the SmC\*<sub>A</sub> – SmC\*<sub>re</sub> transitions.

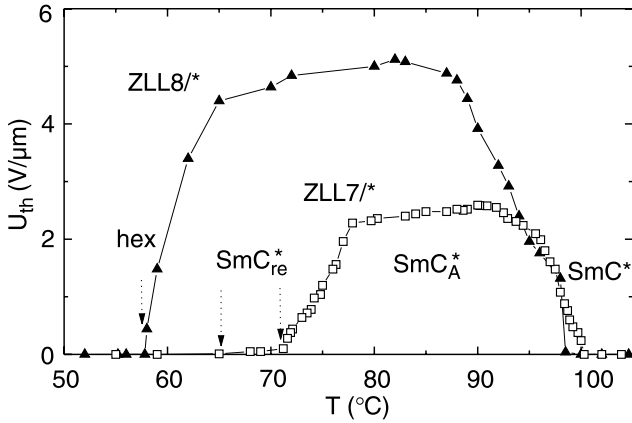


Fig. 2. The quasi-static threshold field in dependence of temperature for ZLL7/\* and ZLL8/\*. The threshold field is much higher in the AF SmC\*\_A phase than in the SmC\*, SmC\*\_re and hex phases.

the FE phases,  $E_{th} \approx 0$  and it is significantly higher in the AF phases. This experiment helps to identify the re-entrant FE phase which exhibits as low  $E_{th}$  as the SmC\* phase (see Fig. 2).

The binary mixture ZLL6/\* – ZLL7/\* [Fig. 1(a)] exhibits a closed pocket of the AF phase surrounded by the FE phase. This fact confirms the existence of the re-entrant SmC\*\_re phase miscible with the upper SmC\* phase. The binary mixture ZLL6/\* – ZLL8/\* exhibits also a closed pocket of the AF phase surrounded by the FE phase despite the fact that the SmC\*\_re phase is not present in either starting compound. The SmC\*\_re phase is induced in mixtures of the concentrations  $c$  of the ZLL8/\* homologue down to 35 weight %. With the binary systems studied the phase transitions that occur with both starting compounds shift nearly linearly with the concentration.

### 3.2. Dielectric properties

Frequency dependencies of the complex permittivity show a single relaxation process in the whole temperature range studied, dc conductivity contribution  $\sigma$ , being significant. The dielectric spectra were analysed using the Cole-Cole formula for the frequency dependent complex permittivity  $\epsilon^*(f)$

$$\epsilon^* - \epsilon_\infty = \frac{\Delta\epsilon}{1 + (if/f_r)^{(1-\alpha)}} - i \frac{\sigma}{2\pi\epsilon_0 f}$$

where  $f_r$  is the relaxation frequency,  $\Delta\epsilon$  is the dielectric strength of the mode,  $\epsilon_\infty$  is the high frequency permittivity, and  $\epsilon_0$  is the permittivity of the vacuum. The distribution parameter  $0 \leq \alpha \leq 1$  is zero for the pure Debye relaxation, higher values of  $\alpha$  characterise broadening of relaxation due to non-homogeneity in the structure and/or temperature, or due to defects. In our study  $\alpha < 0.1$  except the temperature range less than 1 K just below the SmA – SmC\* phase transition, where  $\alpha \sim 0.3$ . All these quantities were

determined by fitting the formula given above to the experimental data.

For selected ZLL6/\*–ZLL7/\* mixtures temperature dependencies of fitted  $f_r$  and  $\Delta\epsilon$  are shown in Figs. 3(a) and 3(b), respectively. For the other system the same results are shown in Figs. 4(a) and 4(b). In the SmC\* and SmC\*\_re phases  $f_r$  is a few hundreds of Hz, nearly temperature independent, in the hexatic phase  $f_r$  is still lower with a slight anomaly near the upper temperature limit of this phase. The transition to the hexatic phase is described in detail in Ref. 6. In the SmA phase nearly linear softening of  $f_r$  is seen for both studied systems as well as in the SmC\*\_A phase. Dielectric strength is very high in both SmC\* and SmC\*\_re phases and is nearly two orders lower in the SmC\*\_A phase. In the hexatic phase it has an intermediate value.

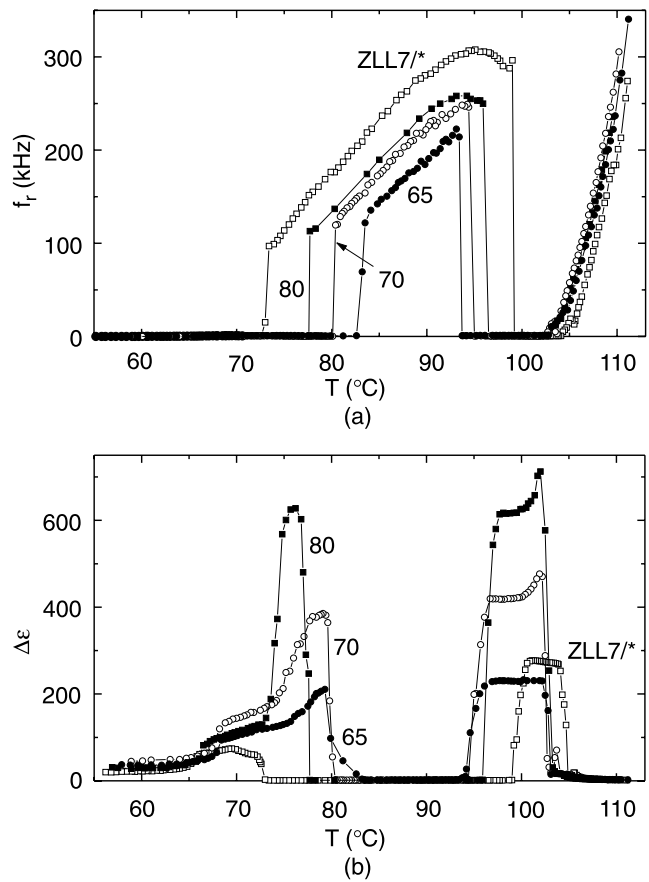


Fig. 3. Temperature dependence of relaxation frequency (a), dielectric strength (b) for pure ZLL7/\* and mixtures ZLL6/\*–ZLL7/\* of indicated concentrations of ZLL7/\*.

### 3.3. Spontaneous quantities

Temperature dependencies of the spontaneous polarisation,  $P_S$ , and of the tilt angle,  $\theta_S$ , for the ZLL6/\* – ZLL7/\* mixtures are shown in Fig. 5 in the temperature range of all smectic-C\* phases and in the hexatic phase. The values show a typical increase in cooling across all smectic-C\* phases. No anomalies are seen at the transition to the

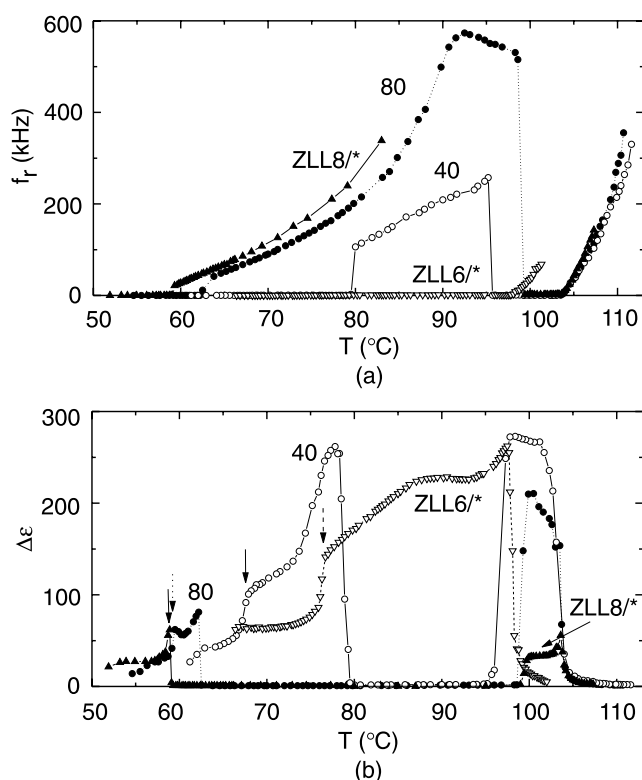


Fig. 4. Temperature dependence of relaxation frequency (a), dielectric strength (b) for pure ZLL6/\* and ZLL8/\* and for mixtures ZLL6/\*-ZLL8/\* of indicated concentrations of ZLL8/\* . Vertical arrows in (b) indicate the transition to the hexatic phase.

$\text{SmC}^*_A$  or to the  $\text{SmC}^*_{re}$  phases. In saturation, the  $\theta_s$  values change continuously with concentration. On entering the hexatic phase both  $P_s$  and  $\theta_s$  start to decrease. Let us point out that for other compounds exhibiting either  $\text{SmC}^*$  – hex or the  $\text{SmC}^*_A$  – hex phase transition and studied so far, both  $P_s$  and  $\theta_s$  increase on entering the hexatic phase [7,8].

### 3.4. Helicoidal properties

In compounds, which exhibit the AF phase the helicoidal pitch  $p$  is constant in the  $\text{SmC}^*$  phase and makes a low jump up when entering the AF phase. Before reaching the transition to the  $\text{SmC}^*_{re}$  phase the helix becomes spontaneously unwound. The unwinding is seen as disappearance of dechiralisation lines, which are linear defects spaced by  $p$ . In the hexatic phase the helix pitch is much shorter than  $1 \mu\text{m}$ . In this phase the helical pitch cannot be measured by diffraction of the laser light. The dechiralisation lines are not seen, because they are very dense. In compounds without the AF phase  $p$  is nearly constant within the  $\text{SmC}^*$  phase except for the low temperature side of this phase, where it continuously decreases on cooling.

The rotatory power measured on free-standing films shows opposite handedness of the helix in the AF and  $\text{SmC}^*_{re}$  phases. This fact shows that the helix unwinding is accompanied by the change in the helix sense. In mixtures

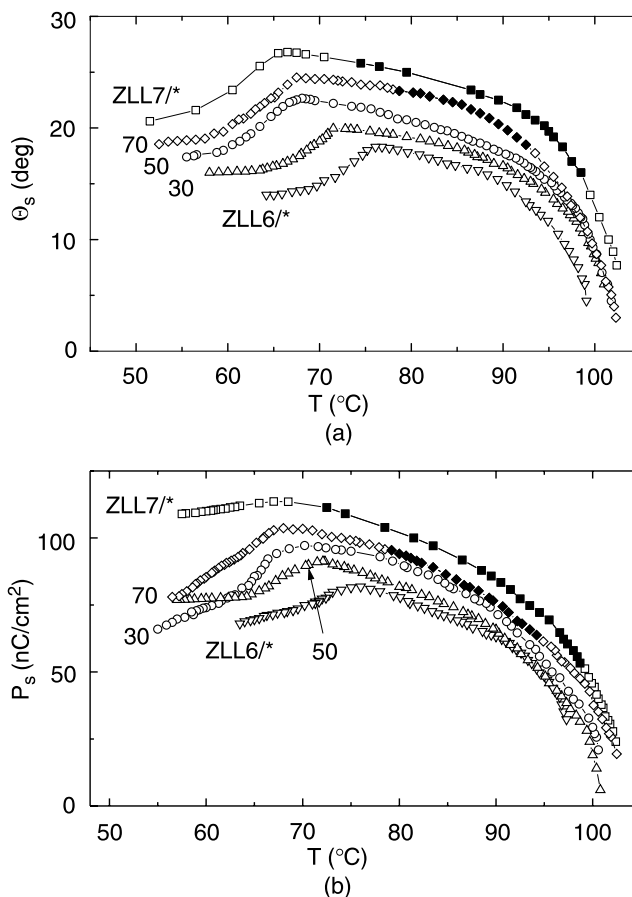


Fig. 5. Temperature dependence of spontaneous tilt angle (a), spontaneous polarisation (b) for pure ZLL6/\* and ZLL7/\* and for their mixtures of indicated concentrations of ZLL7/\* . Full symbols show the values in the AF phase. The decrease in values on cooling indicates the transition to the hexatic phase.

where the AF phase is not present the helix twist inversion is not observed except for the mixture containing 60% of ZLL7/\*, which exhibits the inversion at a temperature of 82°C [see Fig. 1(a)]. One cannot exclude that in this mixture the AF phase exists in free-standing films, but be-

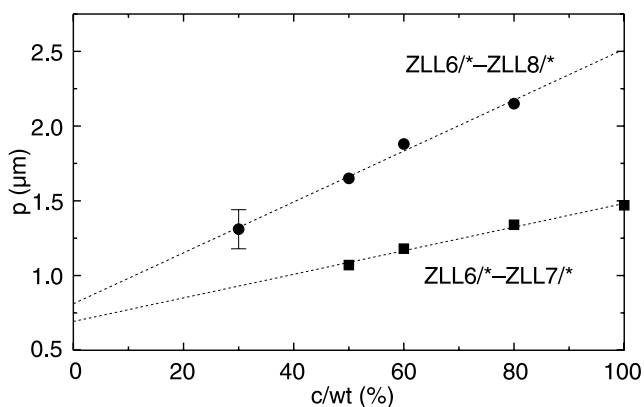


Fig. 6. Concentration dependence of the helix pitch length taken in the  $\text{SmC}^*$  phase. The concentration is expressed in the content of ZLL7/\* or ZLL8/\*.

comes suppressed by surface interactions in planar samples fixed to glass cells.

Both binary systems ZLL6/\* – ZLL7/\* and ZLL6/\* – ZLL8/\* behave in a similar way. The main difference lies in the fact that in ZLL6/\* – ZLL8/\* mixtures the existence of the helix inversion is limited to the concentrations where the SmC\*<sub>A</sub> phase exists, while in ZLL6/\* – ZLL7/\* mixtures it is observed even for a slightly lower concentration. Figure 6 shows a concentration dependence of the helical pitch for both studied systems for concentrations where  $p$  was measurable. The extrapolation for the pure ZLL6/\* gives a value between 0.7 and 0.8  $\mu\text{m}$ .

## 5. Discussion and conclusions

In both studied binary systems the SmC\*<sub>re</sub> phase exists in a certain concentration region, even in the ZLL6/\* – ZLL8/\* system composed of materials without this phase. In Ref. 9, where the SmC\*<sub>re</sub> phase was discussed for the first time, its appearance was explained on the basis of increased quadrupolar ordering when temperature is decreased. The quadrupolar ordering facilitates the interlayer molecular penetration, and in this way it promotes the reappearance of the SmC\* phase at lower temperatures [9]. This speculation sounds reasonable.

Our dielectric spectroscopy study revealed a softening of the mode in the AF phase [see Figs. 3 (a) and 4 (a)] on approaching the transition to the SmC\*<sub>re</sub> phase, which can be held as a cause for the SmC\*<sub>A</sub> – SmC\*<sub>re</sub> phase transition. Let us point out that such softening has not been found in the SmC\*<sub>A</sub> phase to date. The soft dielectric relaxation can be interpreted as the anti-phase mode, i.e. the azimuthal director fluctuations that deform the anticlinic ordering. Such a mode was reported in Ref. 10 where it was supposed to be responsible for the increase of permittivity in the vicinity of the ferroelectric – AF phase transition. Quenching of large amplitudes of this mode at the SmC\*<sub>A</sub> – SmC\*<sub>re</sub> phase transition gives the FE (synclinc) order.

The AF soft mode exists also in the ZLL8/\*, where the SmC\*<sub>re</sub> phase does not exist [Fig. 4 (a)]. One can presume that in this compound the SmC\*<sub>re</sub> phase would be stabilised very near below the transition to the hexatic phase. However, this transition has taken place before the softening is completed, so that the SmC\*<sub>re</sub> phase cannot arise. In the ZLL6/\* – ZLL8/\* mixtures the low temperature limit of the SmC\*<sub>A</sub> phase shifts to higher temperatures and SmC\*<sub>re</sub> phase can appear.

In the SmC\* phase the mode which contributes to permittivity is the Goldstone mode, except in the vicinity of the SmA – SmC\* transition, where the contribution from the ferroelectric soft mode is significant. The sum of contribution from both modes in this temperature range is responsible for the increase of  $\Delta\epsilon$  at the SmA – SmC\* transition, which is observed with some compounds [see Figs. 3(b) and 4(b)]. Both modes are not distinguishable in the dielectric spectroscopy as their relaxation frequencies are

rather close. Their coexistence is expressed in the increase of distribution coefficient  $\alpha$  (see Sec. 3.2).

The FE soft mode is the fluctuation of molecular tilt, the Goldstone mode is the fluctuation of the azimuthal molecular orientation in the FE phase [11]. The dielectric strength of the Goldstone mode is a function of the helical pitch  $p$ , and spontaneous quantities  $P_S$ ,  $\theta_S$  as  $\Delta\epsilon_G = (pP_S/\theta_S)^2/(8\pi^2K_{33})$ , where  $K_{33}$  is an elastic constant [12]. In the compounds and mixtures that do not exhibit the AF phase, but only a relatively broad SmC\* phase, the shortening of the helical pitch on cooling (see sec. 3.4) is responsible for the decrease in dielectric strength as observed in Fig. 4(b) for ZLL6/\*. On the other hand it is difficult to understand the non-monotonic dependence of the Goldstone mode contribution to permittivity on the concentration  $\Delta\epsilon_G(c)$ , which is observed for both binary systems studied [Figs. 3(b) and 4 (b)]. The ratio  $P_S/\theta_S$  taken at the temperature 5 K below the SmA – SmC\* phase transition is independent of concentration within the error limits and the concentration changes of  $p$  (Fig. 6) cannot explain this non-monotonic behaviour. One can imagine only an anomalous concentration dependence of the elastic constant  $K_{33}$ , which might account for the non-monotonic  $\Delta\epsilon_G(c)$  dependence.

The experimental results show that all the phase transitions in the binary mixtures studied are sharp and divide homogeneous phases. In this way our systems differ from that described in Ref. 5, where a heterogeneous phase composed of FE and AF clusters appeared just below the FE phase in mixtures of a homologue exhibiting both AF and FE phases and a homologue with the FE phase only. The reason for the different behaviour might be in a different temperature dependence of the term describing the interaction of neighbouring smectic layers  $A_1(\bar{\xi}_j \times \bar{\xi}_{j+1})$  in the discrete phenomenological theory [4]. This term reverses its sign from negative to positive when the order is changed from FE to AF. One can imagine that if a smooth temperature change of  $A_1$  takes place and  $A_1 \approx 0$  within the low temperature phase, this phase can be frustrated and thus be composed of clusters of both FE and AF phases as was observed in Ref. 5. On the opposite, when the temperature dependence of the coefficient  $A_1$  is abrupt, a distinct FE – AF phase transition occurs as it is described in the present paper.

The significant decrease in the spontaneous polarisation, spontaneous tilt angle (Fig. 5) and helical pitch (sec. 3.4) when entering the hexatic phase cannot be understood on the basis of the simple theory, which has been worked out recently for the SmC\*–SmI\* (or SmF\*) phase transition [7]. In that model the main parameters describing the full transition sequence SmA–SmC\*–SmI\* (or SmF\*) are tilt  $\theta = \theta_0 \exp[i\varphi_\theta]$ , which becomes soft at the SmA–SmC\* phase transition and bond orientational order (BOO)  $A = A_0 \exp[i6\varphi_A]$ , which is soft at the transition to the hexatic phase. It was supposed that  $\varphi_\theta = \varphi_A$ , which means that BOO adopts the modulation of the tilt and that the spontaneous tilt as well as the helical pitch is not affected

by the phase transition to the hexatic phase. In that case the BOO parameter affects only the values of  $P_S$ .

To explain the anomalies of tilt and helical pitch a new theory [6] has been developed based on that presented in Ref. 7. It takes into account the BOO parameter in the most general form allowed by the symmetry. It is supposed that BOO parameter generally can have a space modulation independent of tilt,  $\varphi_\theta \neq \varphi_A$ . In such a case, gradient BOO parameter terms have to be introduced to the free energy. As a result, the interaction of tilt and BOO makes constraints on the tilt decreasing its magnitude at the transition to the hexatic phase, where BOO strongly increases. Because of the interaction of the tilt and polarisation, a similar decrease can be expected for the spontaneous polarisation as well.

The helical pitch,  $p$ , is defined through the wave vector  $q = 2\pi/p$ . The wave vector for tilt and BOO can be defined as  $q_\theta = d\varphi_\theta/dz$ , and  $q_A = d\varphi_A/dz$ , respectively, where  $z$ -axis is directed along the helix axis. Due to the interaction of the tilt and BOO, a single sinusoidal modulation with the wave vector  $q$  can be set in, differing from both  $q_\theta$  and  $q_A$ . The experiment shows that the helical pitch in the SmC\* phase is much longer than that in the hexatic phase. From it one can infer that the equilibrium wave vector  $q$  obey the condition  $q_A > q > q_\theta$ . Moreover, the higher is the difference  $q_A - q_\theta$ , the higher is the decrease in spontaneous tilt at the transition to the hexatic phase. For still higher difference, the orthogonal SmB phase can appear. The theory will be published in detail elsewhere.

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