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

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F. Gouda[a]; T. Carlsson[a]; G. Andersson[a]; S. T. Lagerwall[a]; B. Stebler[a]
[a] Physics Department, Chalmers University of Technology, Göteborg, Sweden

To cite this Article Gouda, F. , Carlsson, T. , Andersson, G. , Lagerwall, S. T. and Stebler, B.(1994) 'Manifestation of biquadratic coupling in the smectic C* phase soft mode dielectric response', Liquid Crystals, 16: 2, 315 — 322
To link to this Article: DOI: 10.1080/02678299408029155
URL: http://dx.doi.org/10.1080/02678299408029155

LIQUID CRYSTALS, 1994, VOL. 16, NO. 2, 315–322

Manifestation of biquadratic coupling in the smectic C* phase soft mode dielectric response

by F. GOUDA*, T. CARLSSON, G. ANDERSSON, S. T. LAGERWALL
and B. STEBLER
Physics Department, Chalmers University of Technology,
S-412 96, Göteborg, Sweden

(*Received 14 June 1993; accepted 25 August 1993*)

The soft mode dielectric response of three ferroelectric chiral smectic C* substances is studied in the vicinity of the smectic C*–smectic A* phase transition. For some substances the soft mode dielectric strength exhibits a pronounced anomaly in the C* phase just below the phase transition. We show how this anomaly can be systematically correlated with a corresponding anomaly in the experimentally determined ratio of spontaneous polarization over tilt. By comparing the experimental results with the theoretical predictions of an extended Landau model, we demonstrate how the crossover behaviour of the system can be interpreted as being the consequence of the presence of a biquadratic coupling between tilt and polarization in the Landau free-energy of the system.

1. Introduction

Ferroelectric smectic C* (C*) liquid crystals [1] are layered structures for which the molecules are tilted on average with respect to the layer normal. Furthermore, due to the chirality of the system, the tilt direction of the molecules slightly rotates from one layer to another and a helicoidal structure with wavevector q is formed. Some of the most important basic thermodynamic quantities characterizing the C* phase are the tilt, θ, of the molecules with respect to the layer normal, the spontaneous polarization, P, and the pitch, $p=2\pi/q$, of the system.

One important quantity probing the thermodynamic behaviour of the system is the dielectric susceptibility χ [2, 3]. In the C* phase, two mechanisms related to director fluctuations are contributing to χ. Thus the dielectric response of the system, neglecting the high frequency polarization modes [4], generally consists of two modes [3, 4], the soft mode which is due to the tilt fluctuations and the Goldstone mode, which is due to the phase fluctuations of the director. In the smectic A* (A*) phase, because of the disappearance of the helical structure and the tilt, the dielectric response exhibits a contribution from the soft mode only.

Experimentally, the ratio P/θ is observed [5] to be approximately temperature independent throughout most of the C* phase range, except close to the transition to the A* phase where it drops to a lower value in a narrow temperature interval. The experimental behaviour of the pitch is generally observed [6] to show a monotonous increase with temperature at lower temperatures. A few degrees below the transition to the A* phase, the pitch adopts a maximum and then drops sharply to a finite value at T_C. The measured dielectric susceptibility [2, 3] exhibits a small anomaly at T_C, increasing abruptly in a narrow temperature interval when entering the C* phase, and showing a broad maximum a few degrees below T_C. The discussion above demonstrates

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* Author for correspondence.

that the thermodynamic quantities exhibit a crossover behaviour in the C* phase a few degrees below T_C. This behaviour is due to the presence of a biquadratic coupling [7–9] between tilt and polarization in the free energy density of the system. The purpose of this paper is to present experimental evidence that the diquadratic coupling also influences the soft mode dielectric response which, for some compounds, is found to exhibit a crossover behaviour a few degrees below T_C in the C* phase. We will also show how the crossover behaviour of the quantities discussed above are intercorrelated and that essentially only one parameter, which is a measure of the strength of the biquadratic coupling between tilt and polarization in the free-energy density of the system, is needed to quantify how pronounced this crossover behaviour will be.

2. A theoretical model of the A*–C* phase transition

2.1. *The classical Landau model*

Early phenomenological descriptions of the C* phase were given by Meyer [10] and in particular by Pikin and Indenbom [11]. Their model consists of a Landau expansion employing two order parameters which for our purpose can be considered to be the tilt θ and the spontaneous polarization P. The polarization dependent part of the free-energy density in this 'classical' model can, if we presently restrict our discussion to the study of an unwound, homogeneously ordered sample, be written as

$$g_P^{cl}=\frac{1}{2\varepsilon}P^2-CP\theta. \tag{1}$$

In this expansion, ε corresponds to the high temperature dielectric permittivity in the A* phase, while C denotes the piezoelectric bilinear coupling coefficient. Minimizing the free energy with respect to P gives

$$\frac{P}{\theta}=\varepsilon C \tag{2}$$

and thus the ratio P/θ in the classical model is predicted to be temperature independent, in contrast to what is observed experimentally [5]. Moreover, a detailed survey of the classical model shows that the pitch as well as the Goldstone mode dielectric susceptibility are predicted to be temperature independent. These predictions are also in contrast to the experimental facts [4–6]. The conclusion is therefore that the classical Landau model of the chiral ferroelectric C* phase is too simple to describe the thermodynamic behaviour of the system correctly.

2.2. *The extended Landau model*

A theoretical model describing the experimental behaviour of the C* phase in a better way than the classical model has been developed by Zeks *et al.* [4, 7–9]. In their extended model, the biquadratic coupling betwen tilt and polarization has been included in the Landau energy. That this biquadratic coupling is important has been verified by NMR measurements [12, 13] and can also be understood [9] from sterical reasoning.

If we again restrict the discussion to the study of an unwound, homogeneously ordered sample, the polarization dependent part of the free-energy density in the extended model is given by

$$g_P=\frac{1}{2\varepsilon}P^2-CP\theta-\tfrac{1}{2}\Omega P^2\theta^2+\tfrac{1}{4}\eta P^4, \tag{3}$$

where Ω is the coefficient of the biquadratic coupling term and the fourth term with $\eta > 0$ has been added to stabilize the system. It is easy to see how this expression will lead to a crossover behaviour of the system. Close to T_C, where P and θ are small, the two last terms in equation (3) can be neglected and the extended model is equivalent to the classical one. Away from T_C, on the other hand, it is obvious that the biquadratic coupling term cannot be neglected. One quantity characterizing how important the biquadratic coupling will be [4, 8, 9] for a specific compound is the dimensionless parameter β given by

$$\beta = \frac{\varepsilon \eta^{1/2} C}{|\Omega|^{1/2}}. \qquad (4)$$

This parameter measures how important the biquadratic coupling between tilt and polarization is compared with the bilinear coupling, i.e. the smaller β, the more important is the biquadratic coupling. Typical values of β seem to be of the order of $\beta \approx 0{\cdot}5$, while $\beta = 1$ corresponds to the classical limit [4].

2.3. *Influence of the biquadratic coupling. The connection between the behaviour of P/θ and the soft mode dielectric susceptibility*

In figure 1, we show how the ratio P/θ calculated by the use of the extended Landau energy (equation (3)) varies with the value of the parameter β. As mentioned above the value of $\beta = 1$ corresponds to the classical limit, leading to a temperature independent P/θ, while decreasing β gradually takes the curves into more realistic values. It can be shown [8, 14] that the ratio of the value which P/θ adopts at T_C with the corresponding saturated low temperature value equals β, i.e.

$$\beta = \frac{\lim\limits_{T_C - T \to 0} (P/\theta)}{\lim\limits_{T_C - T \to \infty} (P/\theta)}. \qquad (5)$$

Calculating the dielectric contribution of the soft mode, $\Delta\varepsilon_S$, as a function of β we arrive at the result of figure 2. Where $\Delta\varepsilon_S$ is the difference between the soft mode dielectric permittivity measured at low $\varepsilon(0)$ and high $\varepsilon(\infty)$ frequency. We notice from the upper part of the figure that for a small enough β, $\Delta\varepsilon_S$ exhibits a small secondary maximum a

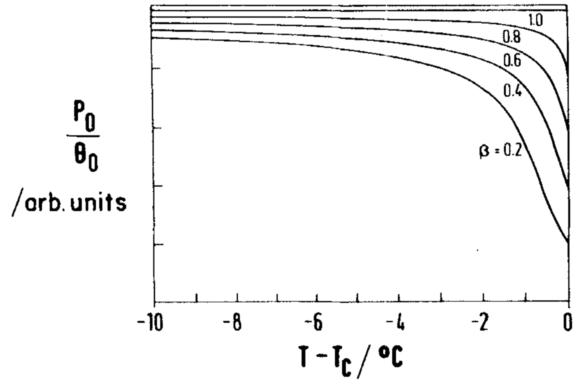


Figure 1. Temperature dependence of the ratio between tilt and polarization, P/θ, calculated [4] by the extended Landau model. The parameter β, being equal to unity in the classical limit, is a measure of how important the biquadratic coupling between tilt and polarization is compared with the bilinear one.

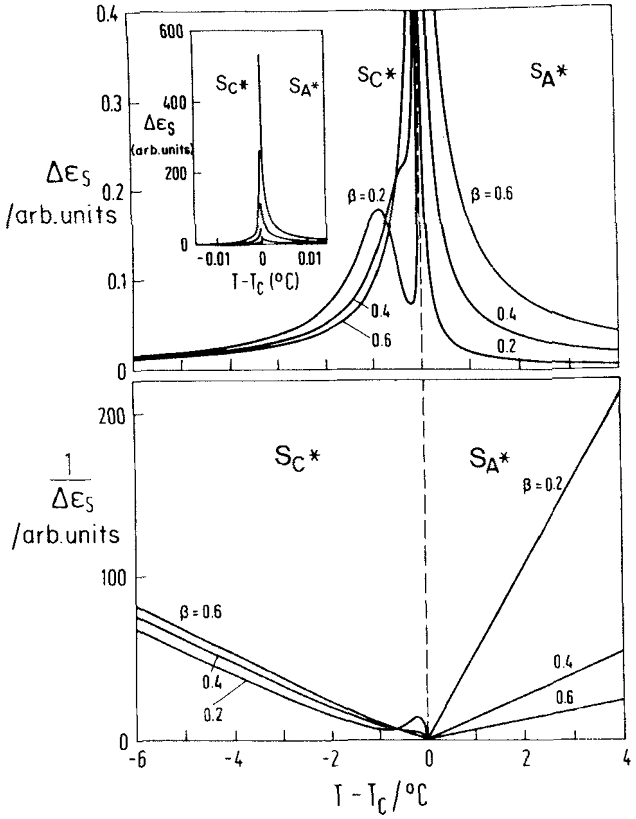


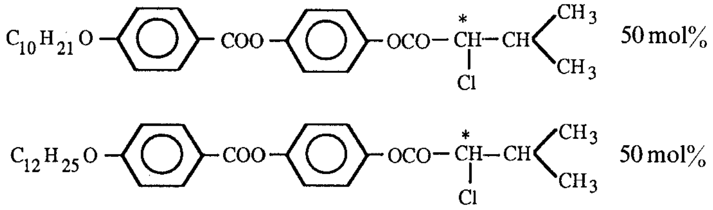
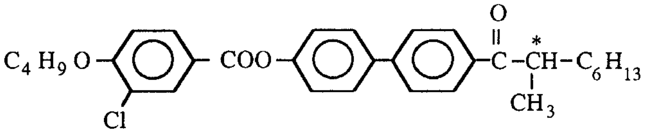
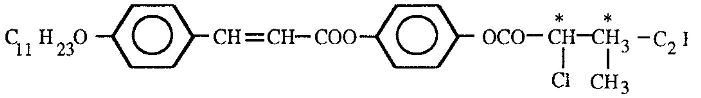
Figure 2. Temperature dependence of the soft mode dielectric strength $\Delta\varepsilon_S$ (upper figure) and its inverse $1/\Delta\varepsilon_S$ (lower figure) in the S_A^* and S_C^* phases, calculated [4] by the extended Landau model.

few degrees below T_C. From a theoretical point of view, the existence of this maximum can be understood, because it appears in the temperature interval where the ratio P/θ shows a very sharp increase with $T_C - T$, an increase which is more pronounced the stronger the biquadratic coupling (c.f. figure 1). By plotting $1/\Delta\varepsilon_S$ versus temperature, as done in the lower part of figure 2, we see that for a strong biquadratic coupling we get one linear behaviour close to T_C and another one far from T_C. By extrapolating this last line, we see that it will not cross the corresponding line obtained in the A* phase at $T = T_C$ for a small finite value of $1/\Delta\varepsilon_S$, as is the case in the classical limit, but crossing of the lines will occur for $T < T_C$ and a negative value of $1/\Delta\varepsilon_S$. We will show in the next section how this behaviour of the soft mode dielectric response has actually been observed and how it can be correlated to the strength in the crossover behaviour of the temperature dependence of P/θ.

3. Experimental results and discussion

In this work, we have investigated the soft mode dielectric response of three different ferroelectric C* substances, comparing the results obtained with the corresponding behaviour of P/θ in view of the extended Landau model. The chemical formulae [15] and the transition temperatures of the substances investigated, denoted by us as **LC 1**, **LC 2** and **LC 3**, respectively, are listed in the table. A description of the

Chemical formulae of the three substances. The first substance (abbreviated **LC 1**) was a binary mixture made by the Halle group [15 (a)], the second substance (**LC 2**) was synthesized by the Nippon Mining Co., Limited, Japan, and the third substance was synthesized by the Bordeaux group [15 (c)].

Chemical formulae and transition temperatures	Abbreviation
 Crystal–8°C–Smectic C*–43·1°C–Smectic A*–70°C–Cholesteric–71·0°C–Isotropic	**LC 1**
 Crystal–8°C–Smectic C*–64·10°C–Smectic A*–105·0°C–Isotropic	**LC 2**
 Crystal–55°C–Smectic C*–78·2°C–Smectic A*–99·0°C–Isotropic	**LC 3**

experimental details for dielectric [16], polarization and tilt angle [17] measurements has been published by us elsewhere. In figure 3 is depicted the temperature dependence of the ratio P/θ for the three substances. While **LC 1** exhibits an almost classical behaviour, corresponding to a value $\beta_1 \sim 0{\cdot}8$, the ratio P/θ exhibits a pronounced decrease close to T_C for **LC 2** and an even larger drop for **LC 3**. Typical values of β_2 and β_3 would, in view of equation (5), correspond to $\beta_2, \beta_3 \sim 0{\cdot}2$–$0{\cdot}4$. We do not attempt to give any exact estimation of the values of the parameter β for the three substances, but conclude from figure 3 that the following inequality holds

$$\beta_3 < \beta_2 < \beta_1. \qquad (6)$$

Figure 4 shows the temperature dependence of the inverse $1/\Delta\varepsilon_S$ of the soft mode dielectric strength. As mentioned earlier, the director fluctuations contribute to two director modes in the C* phase, the Goldstone mode and the soft mode. The dielectric strength of the Goldstone mode is, except in the very vicinity of T_C, larger than that of the soft mode by two orders of magnitude [3, 11]. Thus it is a non-trivial task to resolve the soft mode dielectric response for that of the Goldstone mode except in a very narrow temperature interval below T_C ($T_C - T \approx 0{\cdot}2$°C). One way to overcome this problem is to apply a bias electric field over the sample in order to unwind the helix, thus suppressing the Goldstone mode dielectric response. By doing so, we have been able to study the soft mode in temperature intervals of 3°C, 8°C and 4°C below T_C for the three substances **LC 1**, **LC 2** and **LC 3**, respectively. As is seen from figure 4, except

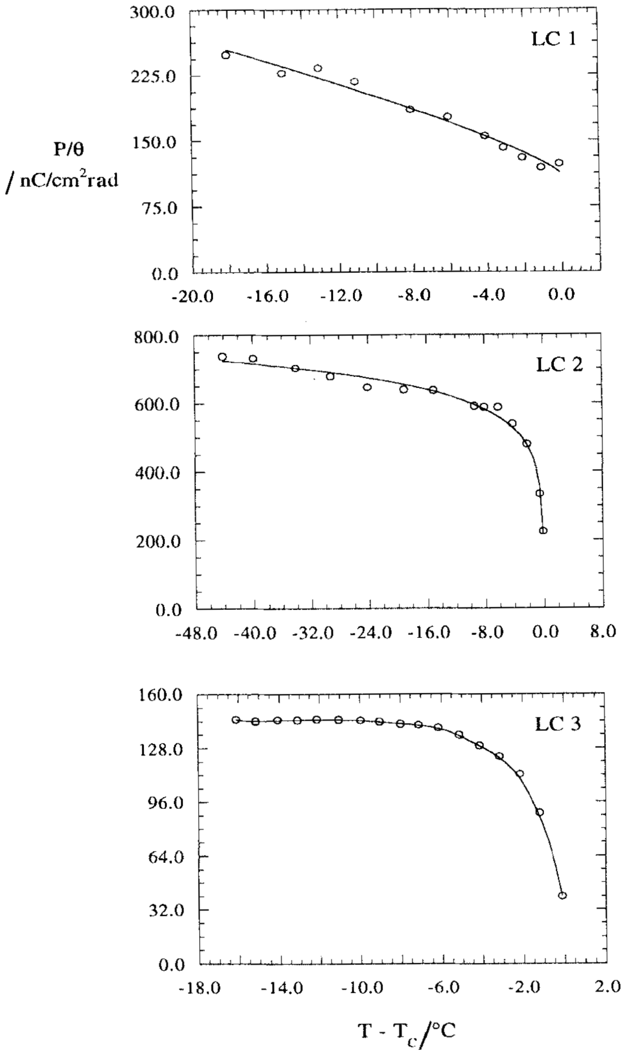


Figure 3. Temperature dependence of the experimentally determined ratio P/θ for the three liquid crystal materials.

for temperatures in the vicinity of T_C, the values of $1/\Delta\varepsilon_S$ increase linearly with decreasing temperature. The deviation from the linear behaviour in the case of **LC 2** and **LC 3** close to T_C has a two-fold origin. First of all, we do not expect a linear behaviour of $1/\Delta\varepsilon_S$ in the whole temperature range of the C* phase due to the crossover behaviour which the system exhibits if the biquadratic coupling is strong enough. Secondly, the bias field affects the measurements in the vicinity of T_C, a point which has been investigated in detail by us elswhere [18]. We have not tried to resolve these two effects from each others. Anyhow, we can determine whether or not the soft mode dielectric response exhibits any crossover in the C* phase by investigating the extrapolated low temperature values of $1/\Delta\varepsilon_S$ in that phase, where the bias field does not influence the measurements. In the case of **LC 1**, we notice that the C* branch of $1/\Delta\varepsilon_S$ intersects that of the A* phase at T_C, within the experimental accuracy. The soft mode dielectric reponse of this substance thus exhibits an almost classical behaviour, a

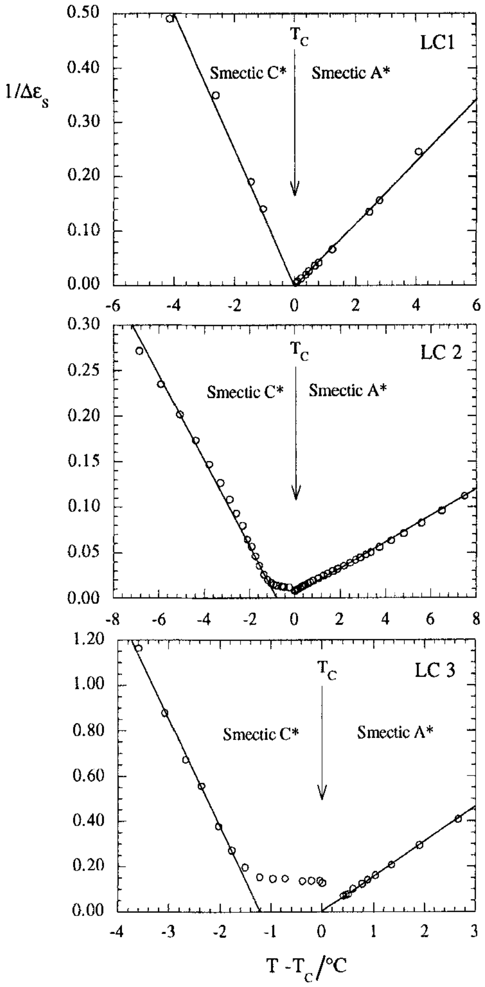


Figure 4. Temperature dependence of the inverse of the soft mode dielectric strength $1/\Delta\varepsilon_S$ in the A* and C* phases for the three liquid crystal materials.

fact which goes well together with the corresponding behaviour of P/θ. However, in the case of **LC 2** and **LC 3**, the extrapolated soft mode branch of $1/\Delta\varepsilon_S$ in the C* phase goes to zero at $T_C-T=0{\cdot}8$°C and $T_C-T=1{\cdot}2$°C, respectively. Thus these two substances exhibit a crossover behaviour which is more pronounced for **LC 3** than for **LC 2**. In the language of the extended model, the biquadratic coupling is thus larger for **LC 3** than for **LC 2**, corresponding to $\beta_3<\beta_2$. This is in accordance with the conclusion (c.f. equation (4)) drawn from the experimental behaviour of P/θ depicted in figure 3.

In conclusion, we have been able to study the soft mode dielectric response close to the A–C* transition in an unusually large temperature interval due to the unwinding of the helix by the presence of an electric bias field in the C* phase. We have demonstrated how $\Delta\varepsilon_S$ for some substances exhibits varying degree of crossover behaviour just below T_C. The strength of this crossover behaviour can be quantified by the parameter β, defined by equation (4). The substance **LC 1** exhibits an almost classical behaviour ($\beta\rightarrow 1$) without any pronounced drop of P/θ close to T_C and with the branches of $1/\Delta\varepsilon_S$ in the A* and C* phases intersecting at T_C. On the other hand, the two substances **LC 2** and **LC 3** exhibit a clear crossover behaviour where the magnitude of the drop of P/θ

close to T_C is correlated to how pronounced the anomalous behaviour of $1/\Delta\varepsilon_S$ will be in the C* phase. Thus the present investigation demonstrates how the biquadratic coupling influences the behaviour of the soft mode dielectric response in the C* phase and how this can be correlated to the anomalous behaviour of other measurable thermodynamic quantities.

References

[1] Meyer, R. B., Strzelecki, L. L., and Keller, P., 1975, *J. Phys. Lett., Paris*, **30**, 69.

[2] Ostrovski, B. I., Rabinovich, A. Z., Sonin, A. S., and Strukov, B. A., 1978, *Soviet Phys. JETP*, **47**, 912.

[3] Levstik, A., Carlsson, T., Filipic, C., Levstik, I., and Zeks, B., 1987, *Phys. Rev.* A, **35**, 3527.

[4] Carlsson, T., Zeks, B., Filipic, C., and Levstik, A., 1990, *Phys. Rev.* A, **42**, 877.

[5] Dumrongrattarna, S., and Huang, C. C., 1986, *Phys. Rev. Lett.*, **56**, 464.

[6] Musevic, I., Zeks, B., Blinc, R., Jansen, L., Seppen, A., and Wyder, P., 1984, *Ferroelectrics*, **58**, 71.

[7] Zeks, B., 1984, *Molec. Crystals liq. Crystals*, **114**, 259.

[8] Carlsson, T., Zeks, B., Filipic, C., Levstik, A., and Blinc, R., 1988, *Molec. Crystals liq. Crystals*, **163**, 11.

[9] Zeks, B., Filipic, C., and Carlsson, T., 1989, *Physica scripta*, **T25**, 362.

[10] Meyer, R. B., 1977, *Molec. Crystals liq. Crystals*, **40**, 33. Garoff, S., and Meyer, R. B., 1977, *Phys. Rev. Lett.*, **38**, 848.

[11] Indenbom, L. S., Pikin, A., and Loginov, E. B., 1976, *Kristallogafiya*, **21**, 1093 [1976, *Soviet Phys. Crystallogr.*, **21**, 635]. Pikin, S. A., and Indenbom, V. L., 1978, *Usp. Fiz. Nauk*, **125**, 251 [1978, *Soviet Phys. Usp.*, **21**, 487].

[12] Lugar, M., Rutar, V., Zeliger, Z., and Blinc, R., 1984, *Ferroelectrics*, **58**, 115.

[13] Blinc, R., Viltan, M., and Zeliger, Z., 1983, *Bull. Mag. Res.*, **5**, 51.

[14] Zeks, B., Carlsson, T., Filipic, C., and Levstik, A., 1987, *Molec. Crystals liq. Crystals*, **151**, 109.

[15] The references for the compounds investigated, **LC 1**, **LC 2** and **LC 3**, are, respectively: (a) Mohr, K., Köhler, S., Worm, K., Plezl, G., Zaschke, H., Demus, D., Andersson, G., Dahl, I., Lagerwall, S. T., Skarp, K., and Stebler, B., 1987, *Molec. Crystals liq. Crystals*, **146**, 151. (b) The compound **LC 2** was synthesized by Nippon Mining Co., Limited, Japan. (c) Nguyen, H. T., Salleneuve, C., and Destrade, C., 1988, *Ferroelectrics*, **85**, 435.

[16] Gouda, F., Skarp, K., and Lagerwall, S. T., 1991, *Ferroelectrics*, **113**, 165.

[17] Skarp, K., and Andersson, G., 1986, *Ferroelectric Lett.*, **6**, 67.

[18] Gouda, F., Andersson, G., Lagerwall, S. T., Skarp, K., Stebler, B., Carlsson, T., Zeks, B., Filipic, C., and Levstik, A., 1989, *Liq. Crystals*, **6**, 219.