Smectic-A^*–smectic-C^* transition in a ferroelectric liquid crystal without smectic layer shrinkage

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The smectic layer spacing of a nonfluorinated ferroelectric liquid crystal (FLC) compound with almost no shrinkage and only minor tendency to form zigzag defects was characterized by small angle x-ray diffraction. The material lacks a nematic phase. The smectic-A^*–smectic-C^* phase transition was studied by measuring the thermal and electric field response of the optical tilt and the electric polarization. These properties are described very well by a Landau expansion even without introduction of a higher-order Θ^6 term. This result suggests a pure second-order phase transition far from tricriticality and differs considerably from the typical behavior of the A^*-C^* transition in most FLC materials. [S1063-651X(99)01907-8]

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I. INTRODUCTION

In most ferroelectric liquid crystals (FLC's), the molecular tilt Θ implies a shrinkage of the smectic layer spacing beginning at the smectic-A^*–smectic-C^* phase transition (A^*-C^* transition) and leading to the formation of chevrons which are a folding instability of the smectic layer structure where domains of opposite fold direction are separated by zigzag defects (Fig. 1) [1]. The zigzag defects and the reduced effective switching angle in the chevron configuration considerably degrade the quality of surface stabilized ferroelectric liquid crystal (SSFLC) devices. A promising approach to avoid these problems is to select smectic-C^* (Sm-C^*) materials without smectic layer shrinkage. Since 1989, naphtalene-based liquid crystals [2] and partially fluorinated phenylbenzoates [3] were reported to exhibit little or no shrinkage of the smectic layer spacing in the smectic-C^* state. These materials are of great interest for the application in future SSFLC devices.

From the scientific point of view, the existence of smectic-C materials without smectic layer shrinkage concerns the old question of understanding the meaning of the director tilt Θ in terms of any molecular model. So far, basically two models may be contemplated: The first mechanism proposed by de Vries in 1977 [4] assumes the molecules to be tilted both in the smectic-C (Sm-C) and in the smectic-A (Sm-A) state. While the molecular tilt direction is randomly distributed in the uniaxial Sm-A state, it becomes ordered below the A-C transition, leading to the biaxial Sm-C state with the optic axis (director) tilted with respect to the smectic layer plane. The second model proposes a compensation of the smectic layer reduction by conformational changes of the molecule, i.e., by an ordering of flexible alkyl tails, or by changes in the interdigitation of molecules in adjacent smectic layers. Recently, these assumptions were supported by dielectric investigations [5]. A more elaborate treatment of nonchevron structures can be found in Ref. [6].

Recently, a new series of ferroelectric liquid crystals with three ester linkages in the mesogenic core and an (S)-lactic acid ester as chiral unit has been synthesized [7]. Due to the introduction of four ester linkages, an increased molecular

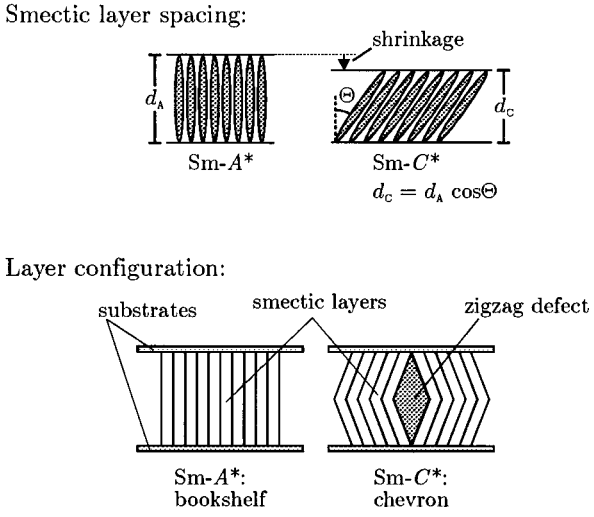

FIG. 1. In a regular smectic-A^*–smectic-C^* material, the director tilt Θ induces a shrinkage of the smectic layer spacing beginning at the transition into the Sm-C^* phase, here illustrated in the extreme case of rigid rodlike molecules. In the surface stabilized state, a Sm-A^* sample with bookshelf configuration of the smectic layers transforms into a chevron configuration when entering the Sm-C^* phase; conserving the anchoring of the Sm-A^* state, the shrinkage involves a folding of the smectic layers. Opposite fold directions are separated by zigzag defects.

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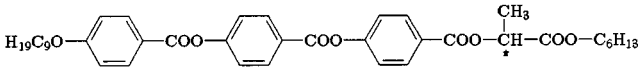
flexibility may be expected for these compounds. Indeed, a number of them show pronounced anomalies of the smectic-C^* layer spacing and minor tendency to form chevrons and zigzag defects. In this paper, we will focus on the characteristics of the smectic A^*-C^* transition for one of these compounds and ask whether the thermodynamics of the A^*-C^* transition without smectic layer shrinkage differ from the regular case. In order to clarify this question, the Landau expansion coefficients which, in the mean field limit, characterize the material properties were experimentally determined and compared to values of a conventional FLC material.

II. EXPERIMENT

The investigations were carried out on the (*S*)-hexyl-lactate



abbrevated as 9HL in [7]. This nonfluorinated compound lacks a nematic phase. In a 4 μm liquid crystal cell (EHC Co. Ltd., Tokyo, Japan) with ITO electrodes and parallel rubbed polyimide coating the phase transition temperatures were observed to be

$$\text{Cry} \overset{40^\circ\text{C}}{\longleftrightarrow} \text{Sm-}C^* \overset{64^\circ\text{C}}{\longleftrightarrow} \text{Sm-}A^* \overset{138^\circ\text{C}}{\longleftrightarrow} I$$

The smectic layer spacing was measured by small angle x-ray diffraction using Cu-K_α radiation, a Kratky-compact camera, and a one-dimensional electronic detector (M. Braun GmbH, Garching, Germany).

The Landau expansion coefficients are experimentally accessible by measuring the thermal and electric field response of the Sm-C^* order parameters (tilt Θ, polarization P) as shown in Ref. [8], where theoretical considerations, experimental techniques, and the data evaluation are described. The measurements on 9HL were performed on heating a well-aligned sample in the vicinity of the A^*-C^* transition ($-8\ \text{K} \leqslant T - T_c^* \leqslant +4\ \text{K}$). At every temperature selected, tilt angles Θ were measured by electro-optical switching at four different amplitudes $E = 1$, 2, 3, and 4 MV m^{-1} of an electric square wave field with a frequency of 108 Hz. The total polarization P was determined by its reversal current using the same frequency and amplitudes of a triangular wave. In order to exclude dispersion effects [9], the electro-optic response was detected at an optical wavelength of $\lambda = 546$ nm. After completing each tilt and polarization measurements the temperature was increased to the next value.

III. RESULTS AND DISCUSSION

The x-ray results on the smectic layer spacing d of 9HL are shown in Fig. 2. They clearly indicate a pronounced anomaly of the layer spacing remaining essentially constant at the A^*-C^* transition: The Sm-A^* spacing of about 4.25 nm fits well to a single molecular length of about 4.5–4.6 nm, estimated from simple molecular models (Fig. 3). In the vicinity of the A^*-C^* transition the smectic layer spacing

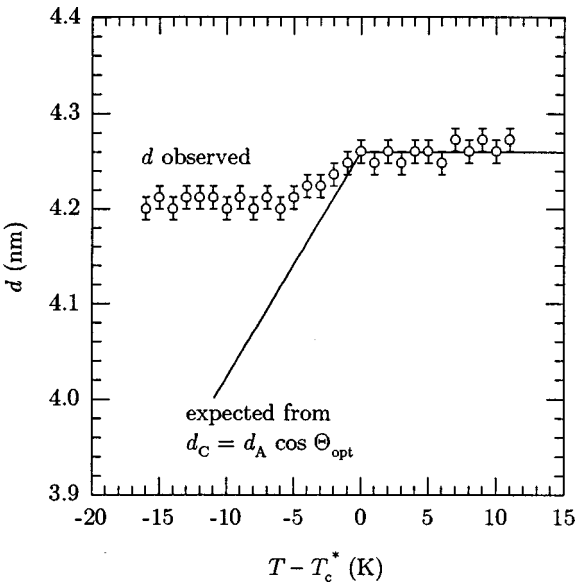


FIG. 2. Smectic layer spacing d as measured in the Sm-A^* and Sm-C^* phases of 9HL by x-ray diffraction. The solid line corresponds to the rigid rod value estimated from the optical tilt angle Θ by $d_C = d_A \cos \Theta$. Error bars indicate an experimental accuracy of ± 1 channel number of the electronic detector.

slightly decreases from $d \approx 4.25$ nm to 4.05 nm. At lower temperatures the Sm-C^* layer spacing remains even constant at $d \approx 4.05$ nm instead of a decreasing smectic layer spacing as expected from the optical tilt Θ in the regular case (solid line in Fig. 2).

The results of polarization and optical tilt measurements are plotted in Figs. 4 and 5, respectively. The polarization P is almost linearily coupled to the tilt Θ (Fig. 4), indicating only minor importance of biquadratic coupling effects for 9HL. The optical tilt angle Θ (Fig. 5) reflects a typical second-order phase transition and strongly depends on the electric field strength, illustrating the electroclinic effect [10]. Due to the large electroclinic coefficient, the second-order A^*-C^* transition in 9HL is considerably smoothed out in an electric field, even at the lowest field amplitude applied ($1\ \text{V}\ \mu\text{m}^{-1}$ in Fig. 5).

Both the polarization-tilt coupling (Fig. 4) and the thermal and electric field response of the optical tilt (Fig. 5), are well described by the generalized Landau expansion of the smectic A^*-C^* transition (solid lines in Figs. 4 and 5). In the framework of this Landau model proposed by Žekš in 1984 [11] the nonsingular part of the free energy f-f_0 is given in the vicinity of the A^*-C^* transition by a power series expansion in terms of the primary (Θ) and secondary (P) order parameters, according to the Sm-A^*/Sm-C^* symmetry invariants

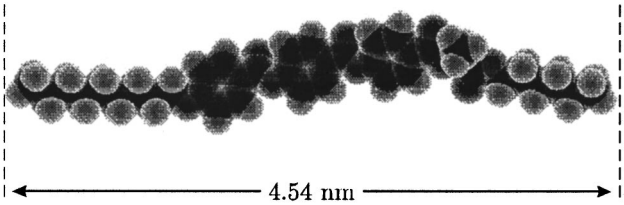


FIG. 3. Simple molecular models of 9HL suggest a molecular length of 4.5 – 4.6 nm, depending on the conformation assumed.

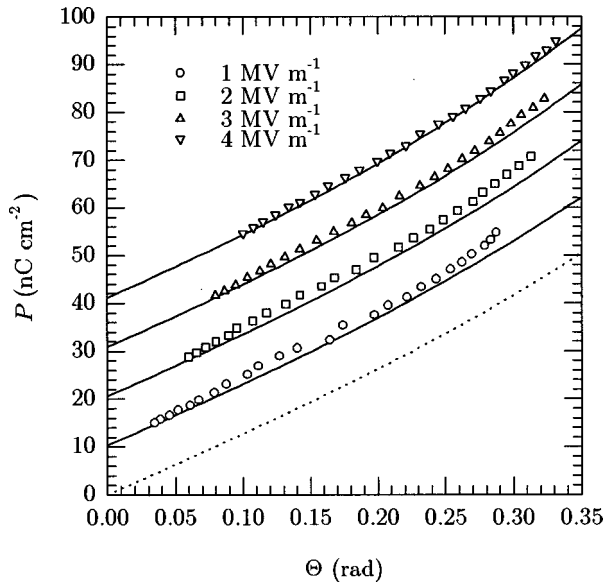


FIG. 4. Polarization (P)-tilt (Θ) coupling in 9HL at various electric field strength E. Solid lines depict the best fit according to the Landau model with coefficients listed in Table I. The zero field polarization is indicated by the dotted line.

$$f-f_0=\frac{1}{2}\alpha(T-T_c)\Theta^2+\frac{1}{4}b\Theta^4+\frac{1}{6}c\Theta^6-CP\Theta+\frac{1}{2\chi\varepsilon_0}P^2 - \frac{1}{2}\Omega P^2\Theta^2+\frac{1}{4}\eta P^4-PE. \quad (1)$$

The first three terms represent the free energy of the nonchiral Sm-C phase with Landau coefficients α, b, and c. The polarization-tilt coupling is reflected by the bilinear ($-CP\Theta$) and biquadratic ($-\Omega P^2\Theta^2/2$) coupling terms, introducing the coefficients C and Ω. The $P^2/2\chi\varepsilon_0$ term is entropic in origin, related to the decrease in entropy due to polar ordering in the material. In the case of 9HL, as in most other cases (see, e.g., Ref. [8]), the $\eta P^4/4$ term is not necessary to obtain a sufficient description of experimental data and, hence, is omitted in the further treatment. The last term in Eq. (1), finally, describes the contribution due to a nonzero electric field.

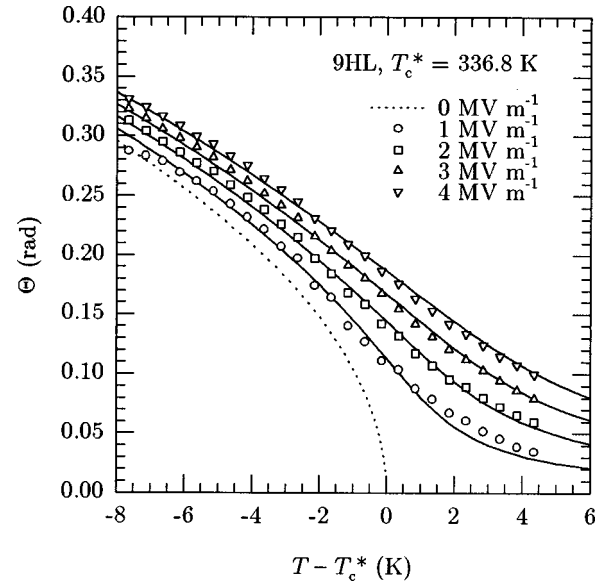


FIG. 5. Smectic-A^*–smectic-C^* transition in the studied FLC material without smectic layer shrinkage: optical tilt angle Θ of 9HL vs temperature T at various electric field strength E. Solid lines depict the best fit to the Landau model with coefficients listed in Table I. The dotted line is the optical tilt at zero electric field, extrapolated from the Landau model.

TABLE I. Landau expansion coefficients obtained for 9HL in comparison to reference values for FLC 6430. The values of T_c^* are obtained by polarization microscopy and T_c is calculated by $T_c = T_c^* - \chi\varepsilon_0 C^2/\alpha$ [8].

	9HL	FLC 6430
T_c^* (K)	336.8	331.4
T_c (K)	335.0	330.5
α (10^3 J m^{-3} K^{-1})	11	45
b (10^6 J m^{-3})	1.0	0.61
c (10^6 J m^{-3})	≈ 0	10
χ	11.4	3.3
C (10^6 V m^{-1})	13.9	37
Ω (10^6 V m C^{-1})	9	49

While the Landau expansion relies on basic considerations of symmetry and, hence, universally applies to any second-order A^*-C^* transition, the individual properties of a certain FLC material are reflected by its Landau expansion coefficients, i.e., α, b, c, C, χ, and Ω in Eq. (1). Following the treatment in Ref. [8], these coefficients can be obtained from a careful analysis of the tilt and polarization data depicted in Figs. 4 and 5. The Landau expansion coefficients obtained for 9HL are listed in Table I. For reasons of comparison, coefficients are also listed for the FLC material FLC 6430 from Hoffmann-La Roche, Basle, Switzerland. The optical tilt data for FLC 6430 are plotted in Fig. 6 to the same scale as used for 9HL in Fig. 5. Data for FLC 6430 are taken from Ref. [8].

Comparing 9HL to FLC 6430, the most striking difference is that the A^*-C^* transition in 9HL can be described over a temperature range of, at least, 12 K *without* consideration of a sixth-order term $c\Theta^6/6$ in Eq. (1), i.e., $c\approx 0$ in Table I. Normally a large sixth-order term has to be introduced reflecting the fact that the A^*-C^* transition in most FLC materials comes close to the tricritical transition [12,13] which defines the crossover from a second-order to a first-order phase transition [14]. With $c\approx 0$, the A^*-C^* transition in 9HL is a very pure second-order phase transition far from tricriticality. In this respect, the phase transition in 9HL differs considerably from most FLC materials.

Comparing Figs. 5 and 6, the difference in the phase transition between 9HL and FLC 6430 becomes obvious: Passing the A^*-C^* transition, the change in the optical tilt is considerably larger for FLC 6430 and reflects the proximity of a first-order transition with a much faster change in the tilt as a function of temperature. The reverse is true for the tilt as a function of the electric field: Except for the very close vicinity of the A^*-C^* transition it is seen that the electroclinic effect (the dependence of the tilt on the electric field)

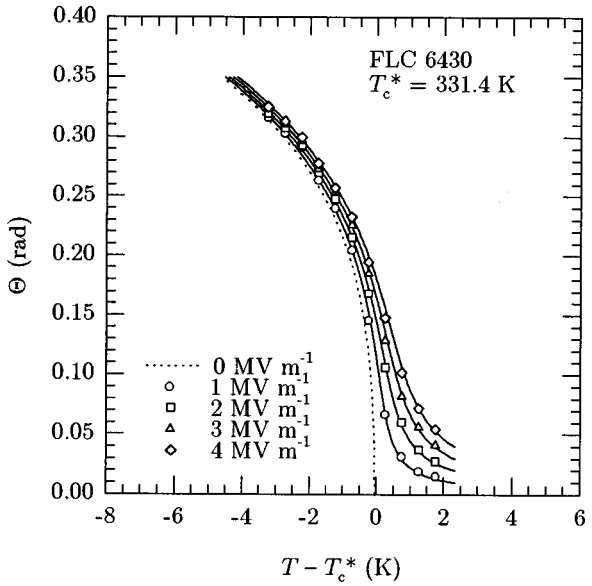


FIG. 6. Smectic-A*–smectic-C* transition in a regular FLC material (from Ref. [8]): optical tilt angle Θ of FLC 6430 vs temperature T at various electric field strength E. For solid and dotted lines, see the caption to Fig. 5.

is much more pronounced in the case of 9HL (Figs. 5 and 7) than for FLC 6430 (Figs. 6 and 8). The same holds for the nonlinearity of the electroclinic effect (Figs. 7 and 8). Both observations are related to the small α coefficient of 9HL which is about one fourth of typical values, e.g., for FLC 6430 (Table I).

In conclusion, there are three basic results of this study concerning the A*-C* transition in the hexyl-lactate 9HL.

(1) Anomalous smectic layer spacing (no layer shrinkage).

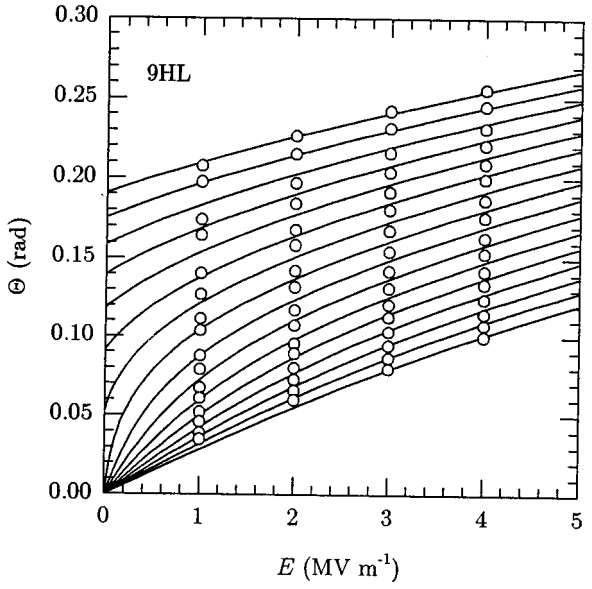


FIG. 7. Electroclinic effect in the studied FLC material without smectic layer shrinkage: optical tilt angle Θ of 9HL vs electric field strength E at various temperatures from $T-T_c^*=+4.35$ K (lower curve) to $T-T_c^*=-4.15$ K (upper curve) in intervals of -0.5 K. The solid lines depict the best fit to the Landau model with coefficients listed in Table I.

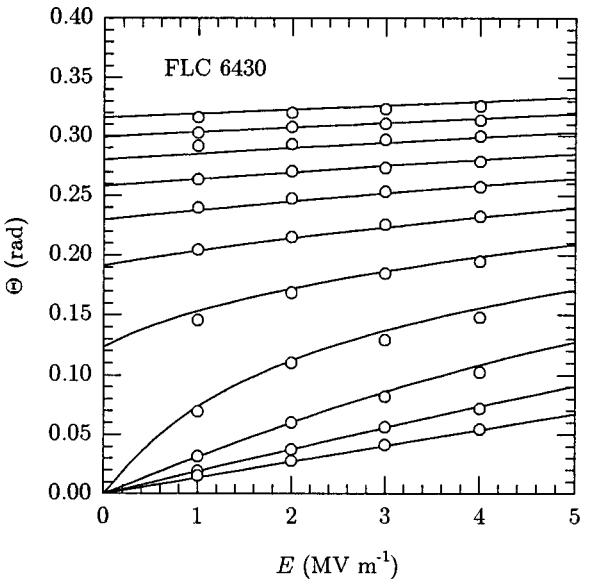


FIG. 8. Electroclinic effect in a regular FLC material (from Ref. [8]): optical tilt angle Θ of FLC 6430 vs electric field strength E at various temperatures from $T-T_C^*=+1.75$ K (lower curve) to $T-T_c^*=-3.25$ K (upper curve) in intervals of -0.5 K. The solid lines depict the best fit to the Landau model with coefficients listed in Table I.

(2) Very large electroclinic effect (small α).

(3) Second-order transition far from tricriticality ($c\approx 0$).

The first point can be explained by a model according to De Vries [4] as well as by changes in the molecular conformation or packing. The second point is closely related to the absence of the smectic layer shrinkage: the resistance to an electroclinic tilt arises from the compression of the smectic layers associated with the induced tilt. If there is no significant change in the smectic layer spacing in spite of an induced tilt, the electroclinic effect can be expected to be large. In addition the tilt can be performed without being accompanied by a striped defect pattern [15]. Convenient materials for the application of the electroclinic effect should therefore be sought from those with little or no layer shrinkage. The third point does not contradict the assumption of a De Vries transition. As in a ferromagnetic material without space quantization of the spin moments, the vectors pointing into the tilt direction of the individual molecules can formally be treated as spins undergoing a Langevin-like ordering below the critical temperature. This leads to a second-order phase transition [16].

Another point which may contribute to the anomaly in the A*-C* transition of 9HL is the coupling between order parameters of succeeding phase transitions: due to the broad Sm-A* phase in 9HL, the second-order A*-C* transition is well separated in temperature from the first-order smectic-A*-isotropic transition. Therefore, order parameters such as the nematic S_2 or the smectic σ are expected to be almost constant in temperature and should not affect the A*-C* transition in the case of 9HL. In most of the regular FLC materials, the A*-C* transition is far less separated in temperature from first-order transitions and a coupling of various order parameters may superimpose effects from these transitions.

Future experiments will show whether the results obtained for 9HL can be generalized for other materials with anomalous layer shrinkage. Detailed x-ray investigations on aligned samples, dielectric spectroscopy, and molecular simulations might improve our understanding of the nature of A^*-C^* transitions with and without smectic layer shrinkage.

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