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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Critical Behavior of Chiral Smectic Liquid Crystals

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Version of record first published: 24 Sep 2006

To cite this article: I. Muševič, M. Šarabo, M. Conradi, R. Blinc, G. Heppke & H. T. Nguyen (2001): Critical Behavior of Chiral Smectic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 358:1, 53-72

To link to this article: http://dx.doi.org/10.1080/10587250108028270

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Mol. Cryst. and Liq. Cryst., 2001, Vol. 358, pp. 53-72
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Critical Behavior of Chiral Smectic Liquid Crystals

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(In final form April 27, 2000)

The phase transitions from the *smectic – A* phase to the ferroelectric *smectic – C**, the antiferroelectric *smectic – C^*_A* and the incommensurate *smectic – C^*_α* phase are of the three dimensional (3D) XY universality class, where the soft mode condenses either at the edge, at the boundary or at a general point of the smectic Brillouin zone. High-resolution optical polarimetry and linear electro-optic response have been used to determine the temperature dependence of the order parameter in the antiferroelectric liquid crystals MHPOBC, MHP8CBC, EHPOBC, MHP10CBC and 10OTBBB1M7. The conclusions are: *(i)* In the *smectic- A* phase antiferroelectric liquid crystals exhibit unusually large tilt fluctuations. *(ii)* In most antiferroelectric liquid crystals, the critical exponents for tilt fluctuations are neither pure 3D XY nor Gaussian, but somewhat in between *(iii)* The "reconstructive" phase transitions between incommensurate, ferro-, ferri- and antiferroelectric phases are of first order. *(iv)* The discrete "clock" Landau model explains well the observed discontinuities. *(v)* The results of the resonant X-ray scattering experiment and optical polarimetry on 3 and 4-layer "clock" smectic phases are inconsistent.

Keywords: antiferroelectric liquid crystals; optics; critical behavior

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INTRODUCTION

Recently, there has been a significant advancement in our understanding of phases formed by antiferroelectric liquid crystals. The resonant X-ray scattering experiment performed by Mach et al. allowed for the first direct measurement of the orientational molecular ordering on the molecular level in different tilted smectic phases [1]. Nearly simultaneously, high-resolution optical experiments on bulk intermediate smectic phases have also been performed [2] that gave us substantial information on the macroscopic properties of these phases.

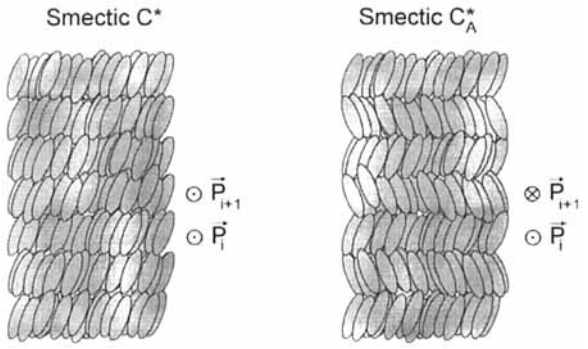

FIGURE 1. In the ferroelectric $smectic-C^*$ phase, the tilt is sinclinic in neighboring layers and there is ferroelectric order of dipoles. In the antiferroelectric $smectic-C^*_A$ phase, tilt shows anticlinic order and the dipolar order is antiferroelectric.

Following the experimental results, it is clear that we have to accept many new and surprising facts about the ordering of director and polarization fields in polar chiral smectics in general. For example, we know from the experiments on bow-shaped molecules [3] that in tilted, polar and chiral smectics there is in general a delicate interplay of sinclinic and anticlinic ordering of both tilt and polarization. The

traditional ferroelectric $smectic-C^*$ and the antiferroelectric $smectic-C_A^*$ phases are only two extreme and simple examples of such structures (see Fig.1.).

In this contribution, we discuss open problems in the characterization of the structure of intermediate smectic phases. We briefly review the proposed theories and discuss their relevance. We compare the results of the resonant X-ray scattering and optical experiments and show an apparent disagreement. Finally, we present new studies of critical behavior of tilted smectic phases, which show antiferroelectric ordering.

1D ISING OR 3D-XY (CLOCK) MODEL OF ANTIFERROELECTRIC LIQUID CRYSTALS?

It was known from the very beginning of the experimental work on antiferroelectric liquid crystals [4] that the continuum Landau theory couldn't explain the structure of all tilted smectic phases, which are observed in these materials. The continuum Landau theory implies expansion of the free energy density in terms of ferroelectric and antiferroelectric order parameters and can reproduce only three structures: *(i)* The chiral ferroelectric $smectic-C^*$ phase, with sinclinic ordering in tilt and ferroelectric ordering of dipoles, *(ii)* The chiral antiferroelectric $smectic-C_A^*$ phase with anticlinic ordering in tilt and antiferroelectric ordering of dipoles, and *(iii)* The ferrielectric $smectic-C_\gamma^*$ phase, where the directions of both tilt and polarization are neither sinclinic and anticlinic, but somewhat in between. This approach does not explain the structure of the $smectic-C_a^*$ phase and the existence of more than one ferrielectric (i.e. intermediate) phase.

The problem of the structure of the $smectic-C_a$ phase and the existence of more than one ferrielectric phase have initiated the

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development of several discrete phenomenological models for the description of intermediate phases. Within these models, one considers the Landau theory for a single smectic layer and includes the interactions of a given smectic layer with its neighbors. There are several discrete models, which can be classified into two categories: *(i)* One-dimensional Ising models [5] and *(ii)* Three-dimensional discrete XY models [6].

In the one-dimensional Ising model of tilted and polar smectics, a single scalar quantity σ is used to describe the orientation of the molecules in a single smectic layer. For example, $\sigma = +1$ is ascribed to the molecules, which are tilted in the plane of the paper in the right direction and $\sigma = -1$ denotes smectic layer where the molecules tilt in the left direction. The Ising models of the intermediate phase can at least qualitatively describe the properties of intermediate phases on the macroscopic scale, as they reproduce a variety of intermediate phases. For example, Fig.2a. shows the antiferroelectric $smectic - C_A^*$ and the ferrielectric $smectic - C_\gamma^*$ phases, respectively. They are denoted with a symbol $q = 1/2$ and $q = 1/3$, which denotes the fraction of ferroelectric order in a unit cell, which is in this case composed of 2 and 3 smectic layers, respectively. Ising models can explain only qualitatively the phase transitions between the intermediate phases, as the direction of the long axis of the molecules is artificially constrained to a single plane.

The constraint of keeping the directions of the molecular tilt in a single plane has been released in the XY mean-field discrete theories, first introduced by Sun, Orihara and Ishibashi [6] and later developed by different authors (Čepič and Žekš, 1995; Lorman et al., 1994,1995; Roy and Madhusudana, 1996; Lorman 1996, see Ref. 6). In these models, the tilt directions of the molecules in the neighboring layers are allowed to make arbitrary angles as one moves from one smectic layer to another. Whereas the original discrete model of Sun et al. [6] only reproduces three structures that are also obtained within the continuous Landau model, the "clock" model of Čepič and Žekš reproduces a variety of

intermediate phases, which are all of the 3D X-Y character, as shown in Fig.2b.

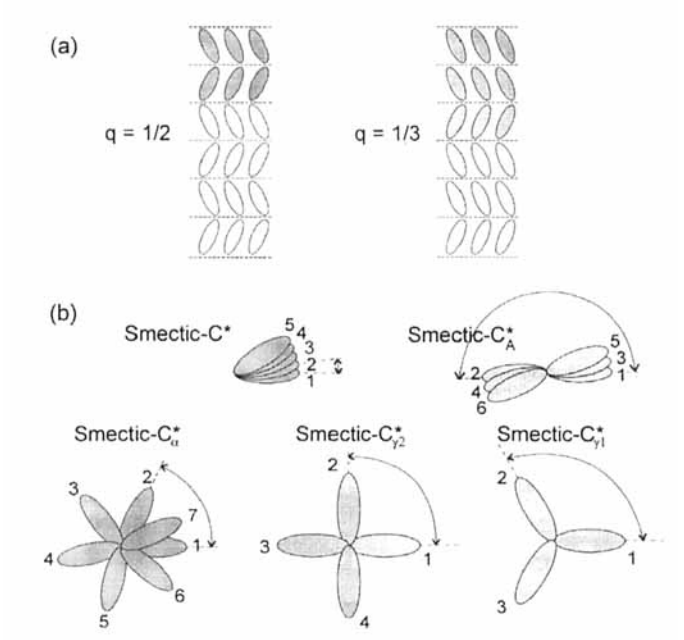

FIGURE 2. (a) Within the 1D Ising model of intermediate phases, the molecular orientation is constrained to a single plane. In this plane, the molecules can obtain two different orientations. A scalar variable σ obtains value $\sigma = +1$ for the molecules, which are tilted into the right direction and $\sigma = -1$ for those tilted in the opposite direction. (b) The "clock" model releases the constraint of keeping molecules in a plane and they spread along the circle of a cone, forming many different tilted polar phases. Molecules are therefore rotated for the phase angle α, as we move to the next layer. In the $smectic - C^*$ phase the phase angle is very small and in it is nearly 180° in the $smectic - C_A^*$ phase.

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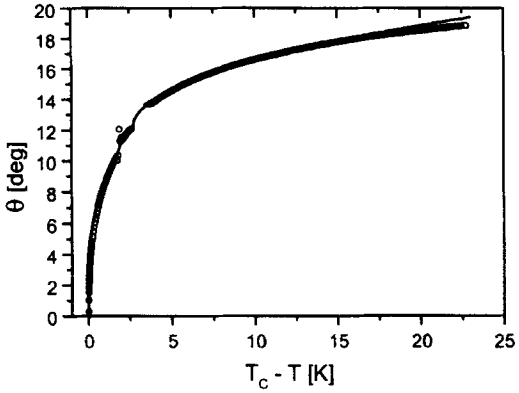

FIGURE 3. The temperature dependence of the tilt angle in MHPOBC (open circles) calculated from the high-resolution birefringence data [2]. The solid line is the best fit to the "clock" model.

Both theoretical models have been tested with resonant X-ray experiment and high-resolution optical methods. These experiments have shown that the intermediate phases are indeed of the 3D X-Y type, as a tilted director field, which is not constrained to a single plane, characterizes them. For example, the "clock" model of Čepič and Žekš has been quantitatively tested with high-resolution tilt angle measurements, performed in the sequence of phase transitions in the antiferroelectric liquid crystal MHPOBC [2]. The result of the fit of the temperature dependence of the tilt angle, which is the order parameter in these systems, is given in Fig.3. and shows remarkably good agreement between the theory and experiment. The optical experiment for the first time clearly showed that the $smectic - C_a^*$ phase is a tilted phase with nearly zero optical rotation. This implies a very short period of helical modulation. The optical experiment suggests that the periodicity of this phase should be smaller than ≈ 50 smectic layers. The phase transition from the $smectic - A$ is of second order, but close to the tricritical point,

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so that sixth order terms have to be included in the free energy expansion. The "reconstructive" phase transitions between the intermediate phases are of first order.

Soon after this experiment, Mach et al has reported a resonant X-ray scattering experiment in 10OTBBB1M7. Whereas normal X-ray scattering is insensitive to the molecular direction, resonant X-ray scattering is orientation-sensitive due to the tensorial nature of the scattering cross-section when the energy of the X-rays is tuned to the absorption edge of an atom in the liquid crystalline molecule. The structures of intermediate phases, as deduced from the resonant X-ray scattering experiment of Mach et al. are listed in Fig.4. and are as follows:

(i) In the chiral ferroelectric $smectic - C^*$, the length of a unit cell of a crystal a is equal to a single smectic layer of thickness, $a = d$. The molecules are tilted at a tilt angle θ with respect to the layer normal and the spontaneous polarization appears perpendicular to the plane of the tilt. The molecular direction precesses, as we move along the smectic normal. The period of this helical arrangement is 1000 times larger than the length of a unit cell and therefore represents only a small chiral perturbation to the system.

(ii) In the chiral antiferroelectric liquid crystalline $smectic - C_A^*$ phase, the molecules are tilted in opposite directions in neighboring smectic layers. The unit cell of this phase therefore consists of two anticlinic smectic layers and is of length $a = 2d$. The alternation of the tilt direction of the molecular orientation in neighboring layers is accompanied by the alternation of the direction of spontaneous polarization. Two neighboring layers thus form an antiferroelectric unit cell with two nearly antiparallel electric dipoles and a very small value of the equilibrium electric

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polarization $\vec{P}_o(\vec{r}) = \vec{P}_i + \vec{P}_{i+1} \approx 0$. Because of chirality, the directions of the spontaneous tilt and the in-plane polarization slowly precess around the layer normal as one moves along the direction perpendicular to the smectic plane. This causes a small deviation from the 180° alternation in the tilt between two consecutive layers and the formation of a modulated, helicoidal structure.

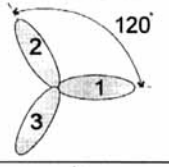
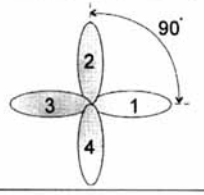
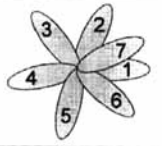
Symbol	Type	Unit cell	Top view of a unit cell
$smectic - C^*$	ferroelectric	one smectic layer	
$smectic - C^*_A$	antiferroelectric	two smectic layers	
$smectic - C^*_{FI1}$ ($\equiv smectic - C^*_\gamma$)	ferrielectric 1	three smectic layers	
$smectic - C^*_{FI2}$	ferrielectric 2	four smectic layers	
$smectic - C^*_\alpha$	presumably incommensurate	none	

FIGURE 4. List of tilted smectic phases, as determined from the resonant X-ray experiment [1].

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(iii) In the chiral ferrielectric I. $smectic-C^*_{\gamma 1}$ phase, the angle between the tilt directions in neighboring smectic layers is nearly 120°. This phase is equivalent to the $smectic-C^*_{\gamma}$ phase of MHPOBC (Nguyen et al., 1994). The unit cell of this phase therefore consists of three smectic layers. The length of a unit cell is $a = 3d$ and the tilt angle is uniform throughout the crystal. The spontaneous polarization in the three neighboring layers nearly cancels and results in a very small value, $\vec{P}_\circ(\vec{r}) = \vec{P}_i + \vec{P}_{i+1} + \vec{P}_{i+2} \approx 0$. Because of chirality, this unit cell precesses as a whole, as we move along the smectic layer normal. The period of this modulation is again much larger than the length of a unit cell. This structure can be considered also as a combination of three helical structures, gearing into each other at an angle of 120°. Optically, this structure should be equivalent to the $smectic-A$ phase with very small optical rotation.

(iv) In the chiral ferrielectric II. $smectic-C^*_{\gamma 2}$ phase, the angle between the tilt directions in neighboring smectic layers is nearly 90°. The unit cell of this phase therefore consists of four smectic layers. The length of a unit cell is $a = 4d$ and the tilt angle is uniform throughout the crystal. The spontaneous polarization in the four neighboring layers nearly cancels and results in a very small value, $\vec{P}_\circ(\vec{r}) = \vec{P}_i + \vec{P}_{i+1} + \vec{P}_{i+2} + \vec{P}_{i+3} \approx 0$. Because of chirality, this unit cell precesses as a whole, as we move along the smectic layer normal. The period of this modulation is again much larger than the length of a unit cell. This structure can be considered as a combination of two antiferroelectric helical structures, gearing into each other at an angle of 90°. Optically, this structure should be equivalent to the $smectic-A$ phase with very small optical rotation.

(v) In the chiral alpha phase, $smectic - C_\alpha^*$, the angle between the directions of the tilt in the neighboring layers is smaller than 90°. For example, the resonant X-ray scattering in the $smectic - C_\alpha^*$ phase of 10OTBBB1M7, indicates that this angle is close to 60°. The unit cell is very close to six molecular layers and changes with temperature, which is an indication of the incommensurate structure of this phase.

We expect that the intermediate phases with three- and four-layers unit cells should show very small optical rotation (i.e. smaller than $smectic - C_\alpha^*$ phase) if the phase angle between molecules in neighboring layers is 120° and 90°, respectively. The spontaneous polarization of a unit cell of such phases should also be very small, i.e. comparable to the spontaneous polarization of the antiferroelectric $smectic - C_A^*$ and $smectic - C_\alpha^*$ phases. This means that dielectric or linear electro-optic response of such "perfect" phases is expected to be very small.

This assumption was tested in our optical experiment in 10OTBBB1M7 and MHP10CBC, where we have measured the temperature dependence of linear electro-optic response, birefringence and optical rotation of linearly polarized light. Birefringence and optical rotation measurements were performed with a high-resolution polarimeter based on a photoelastic modulator [2]. The birefringence of the sample was measured for light propagating at an angle with respect to the optical axis, whereas the optical rotation of the sample was measured for light propagating along the normal to the smectic layers. Red and green lasers with the wavelength $\lambda_1 = 632.8\,nm$ and $\lambda_1 = 532\,nm$ were used for measurements. The relative accuracy for both types of measurements was 0.01 deg. Linear electro-optic response was measured at a constant frequency of the measuring electric field. It has been shown that this method is an optical analogue of dielectric

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spectroscopy [7]. The linear electro-optic response at low frequency of the measuring electric field is therefore proportional to the dielectric strength $\Delta\varepsilon$.

Special attention was paid to the temperature stabilization of the sample. The sample was placed in a double stage temperature controlled oven with a temperature control better than $5mK$. The temperature dependence of the birefringence Δn, optical rotation Ψ and dielectric strength $\Delta\varepsilon$ were measured by slowly and continuously decreasing the temperature of the sample at a rate of $20mK$ per minute. Homeotropically aligned samples of $120\mu m$ thickness were prepared between two clean glass plates treated with DMOAP. For the linear electro-optic experiments, one of the glass plates was covered with ITO electrodes, separated by a $1.2mm$ wide gap. An AC voltage was applied across the ITO electrodes thus creating a nearly homogenous electric field at the measuring spot in the middle of the gap between the electrodes.

The results in Figs.5. and 6. show the temperature dependencies of optical rotation, dielectric strength and birefringence in MHP10CBC and 10OTBB1M7. In the $smectic-A$ phases of both materials we observe zero optical rotation (see Fig.5a and 6a) and pretransitional increase of the dielectric strength, which is due to the coupling to the soft mode (Fig.5c and 6c). The dielectric strength reaches a finite value at the phase transition into the $smectic-C_\alpha^*$ phase, which reflects the fact that this is a phase transition into a spatially modulated phase. The temperature dependencies of the birefringence (Figs5b and 6b) is continuous across the $smectic-A$ - $smectic-C_\alpha^*$ phase transitions, which indicates that this transition is of the second order in both substances.

In the $smectic-C_\alpha^*$ phases of both substances we observe zero optical rotation, significant dielectric response and significant decrease of the birefringence. This indicates that the $smectic-C_\alpha^*$ phase is tilted and helically modulated, which results in a decrease of the birefringence

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[2]. Nearly zero optical rotation in the $smectic-C^*_\alpha$ phases of MHP10CBC and 10OTBB1M7 is in agreement with the results of the resonant X-ray experiment in 10OTBB1M7: Optical rotation of a helical phase with a length of the helical period equal to 6-8 smectic layers and a tilt angle of $\approx 10\,\mathrm{deg}$ is expected to be of the order of $0.1\,\mathrm{deg}/mm$. For a sample thickness of $0.1mm$, this is at the experimental limit of our set-up.

In the ferroelectric $smectic-C^*$ phase of both substances we observe a significant optical rotation of several deg/mm (Figs.5b and 6b). In MHP10CBC the dielectric response is larger in the ferroelectric phase than in the $smectic-C^*_\alpha$ phase, whereas in 10OTBB1M7 it is smaller for some unknown reason.

In the ferrielectric $smectic-C^*_{\gamma 2}$ phases of both substances we observe an optical rotation of the same order of magnitude as in the ferroelectric phases. However, the dielectric response is here in both substances significantly smaller and is similar to the dielectric response of the antiferroelectric $smectic-C^*_A$ phase.

In the ferrielectric $smectic-C^*_{\gamma 1}$ phases of both substances we observe significant optical rotation (Fig.5a and 6a) and also significant dielectric response (Fig.5c and 6c). It should be stressed that ***it is nearly impossible to align this phase***. This is ***in sharp contrast with other tilted phases***, which all show very good alignment on silanated surfaces. Under a microscope, a network of disclination lines is usually observed in $smectic-C^*_{\gamma 1}$ phase, which is in this sense equal to the $smectic-C^*_\gamma$ phase of MHPOBC. The birefringence of this phase could not be measured very accurately and also the data on the dielectric strength have to be taken with some precaution. It seems to us that the linear response of the $smectic-C^*_{\gamma 1}$ phase is mostly a result of the movement of disclination lines under an applied electric field, because the corresponding relaxation rates are extremely low, i.e. of the order of $1Hz$ or less.

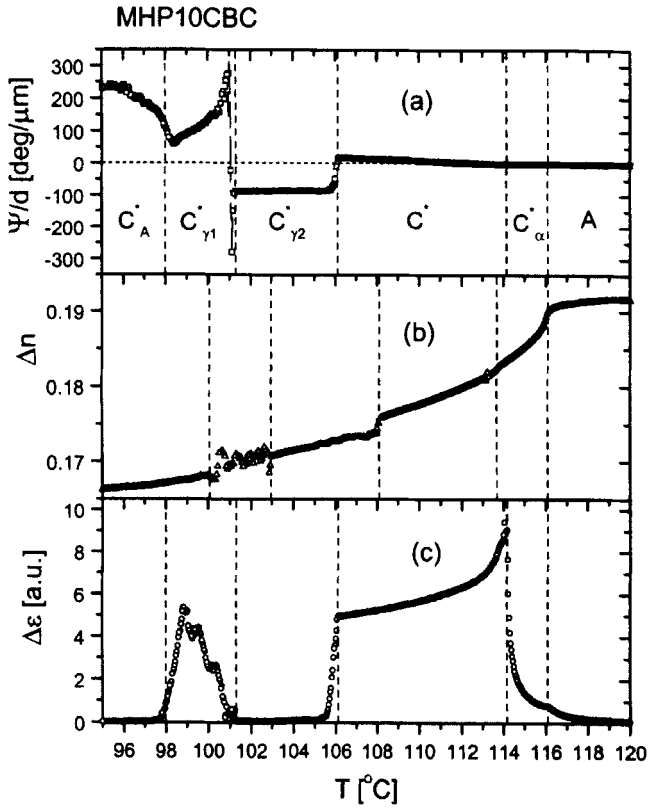

FIGURE 5. The temperature dependence of the optical rotation per unit length Ψ / d (□), birefringence Δn (△) and dielectric strength $\Delta\varepsilon$ (○) in the intermediate phases of MHP10CBC. Ψ / d and $\Delta\varepsilon$ have been measured simultaneously. The measuring field for dielectric strength was of amplitude of $0.1 V / mm$ and the frequency of $8 Hz$.

Finally, in the antiferroelectric $smectic - C_A^*$ phase, we observe significant optical rotation and very small dielectric response. In this sense, the antiferroelectric $smectic - C_A^*$ (two-layer phase) is similar to

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the ferrielectric $smectic - C^*_{\gamma 2}$ (four-layer phase), as we have already pointed before.

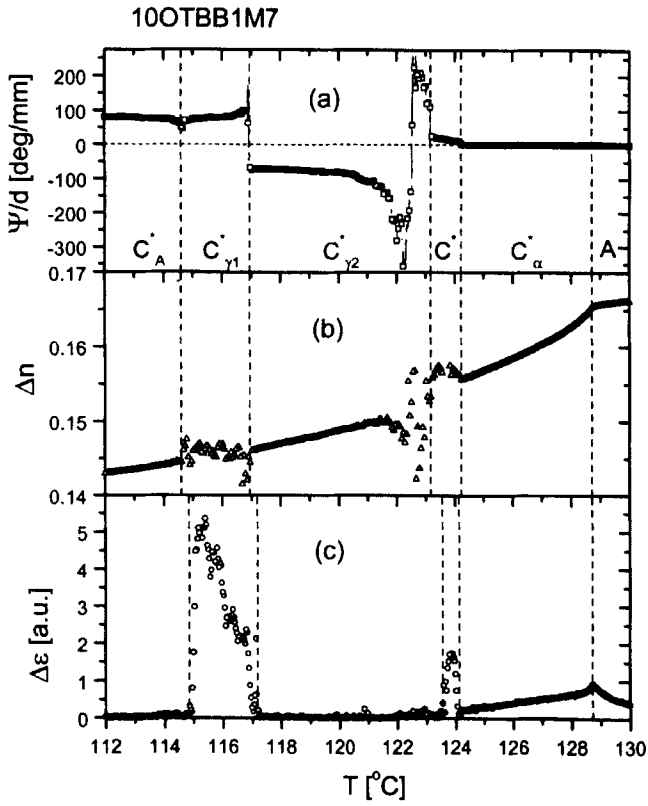

FIGURE 6. The temperature dependence of the optical rotation per unit length Ψ / d (a) (□), birefringence Δn (b) (△) and dielectric strength $\Delta \varepsilon$ (c) (○) in the intermediate phases of 10OTBBB1M7. Ψ / d and Δn have been measured simultaneously. The measuring field for dielectric strength was of amplitude of $0.1 V / mm$ and the frequency of $6 Hz$.

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The most important conclusion of the optical studies of MHP10CBC and 10OTBB1M7 is related to the optical rotation of ferrielectric $smectic-C^*_{\gamma 1}$ and $smectic-C^*_{\gamma 2}$: In both cases these two phases clearly show significant optical rotation, which is of the same order as the optical rotation of ferroelectric $smectic-C^*$ and antiferroelectric $smectic-C^*_A$ phases. This optical rotation is of the order of $10 deg/mm$ and is at least two orders of magnitude larger than the optical rotation of the $smectic-C^*_\alpha$ phase. This is in clear disagreement with the results of the resonant X-ray scattering: If the $smectic-C^*_{\gamma 1}$ and $smectic-C^*_{\gamma 2}$ phases were phases with three- and four-smectic layer "perfect" unit cell (i.e.symmetric, see Fig.7a.), the corresponding optical rotation would be of the same order as the optical rotation of $smectic-C^*_\alpha$. The experiment however shows that this is not the case, which may indicate that the arrangement of the direction of the molecules in the unit cell is not symmetric. One of the possible explanations of the significant rotary power in three- and four-layer phases, is a distorted unit cell arrangement, which is shown in Fig.7b. We should clearly stress that this is ***still pure conjecture and is not based on any physical model***. If the $smectic-C^*_{\gamma 1}$ phase would have a "polar" distorted three-layer unit cell, that would stack onto each other with a small angle of rotation due to chirality, the unit cell would posses a small spontaneous polarization and a small birefringence. Note that this structure would be very similar to the 1/3 structure of 1D Ising model. Stacking of these birefringent unit cells onto each other would lead to an optical rotation due to the macroscopic length of helical modulation. This would explain the linear electro-optic response and the significant optical rotation. Similarly, the "quadrupolar" distortion of the "perfect" four-layer unit cell would lead to zero spontaneous polarization and to a linear response similar to the antiferroelectric phase. At the same time, stacking of these distorted unit cells onto each other, together with a small rotation between neighboring cells would result in a

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significant optical rotation. A calculation shows that such a unit cell should have an optical rotation of the same order as the antiferroelectric $smectic-C_A^*$ phase, if the angle $\alpha < 40-50\,\mathrm{deg}$ (see Fig.7b). This would be in agreement with optical experiment, but in disagreement with X-ray experiment. It should be stressed that quantitative optical features of such distorted phases, such as optical rotation, still have to be calculated. The stability of these distorted structures has also to be estimated within "Clock" model of intermediate phases. We should once again stress that the structures, shown in Fig.7. have to be considered with precaution, as they are based on pure conjecture.

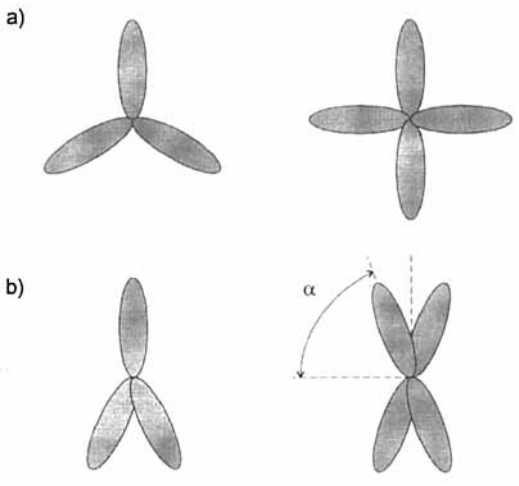

FIGURE 7. (a) The results of the resonant X-ray experiment on 10OTBB1M7 indicate nearly perfectly symmetric 3- and 4-layer structure of $smectic-C_{FI1}^*$ and $smectic-C_{FI2}^*$ phases, respectively. These two structures should have a very small optical rotary power, in disagreement with optical experiments. (b) Optical rotation is significantly increased, if the unit cell is distorted, either in a polar (3-layer structure) or quadrupolar fashion (4-layer structure in (b)).

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CRITICAL FLUCTUATIONS IN ANTIFERROELECTRIC LIQUID CRYSTALS

It has been recently reported [8] that the antiferroelectric liquid crystals show unusually large pretransitional fluctuations at the $smectic-A$-$smectic-C_a^*$ phase transition. These fluctuations can be observed in the temperature dependence of the birefringence, which shows large pretransitional suppression, first observed in ferroelectric liquid crystals by Lim and Ho [9]. Similar phenomenon and unusual softening of the layer compressibility modulus due to fluctuations has been recently reported by Shibahara et al. [10]. The Ginzburg temperature, which is a measure for the relevance of fluctuations near phase transition [11], is for the phase transition into the tilted $smectic-C_a^*$ phase in many antiferroelectric liquid crystals as large as $1K$. This is nearly two orders of magnitude larger than the corresponding Ginzburg temperature in most ferroelectric liquid crystals. This fact has re-opened the question of observability of truly critical behavior at the $smectic-A$-$smectic-C_a^*$ transition in antiferroelectric liquid crystals. High-resolution birefringence measurements have shown [8] that the heat capacity critical exponent α is nonuniversal in MHPOBC, EHPOCBC and MHP8CBC for the reduced temperatures $5\times10^{-5} < t < 10^{-2}$. A typical value of the critical exponent in this range is $\alpha \approx 0.2$, which was in qualitative agreement with the heat-capacity experiments of Ema et al. [12]. This value of the critical index, which is in between the Gaussian value of $\alpha = 0.5$ and 3D-XY value of $\alpha = -0.006$, is similar to the *nematic-smectic-A* transition [13] and may be an indication of a coupling mechanism between density and orientational order in antiferroelectric liquid crystals.

We have performed high resolution birefringence measurements in MHP10CBC and 10OTBB1M7 in order to see, if also these two substances also show enhanced tilt fluctuations at the $smectic-A$-

smectic $-C_\alpha^*$ transition. The mean square of tilt fluctuations was calculated as described elsewhere [2] and is shown in Fig.8. for 10OTBB1M7. The results for MHP10CBC are very similar.

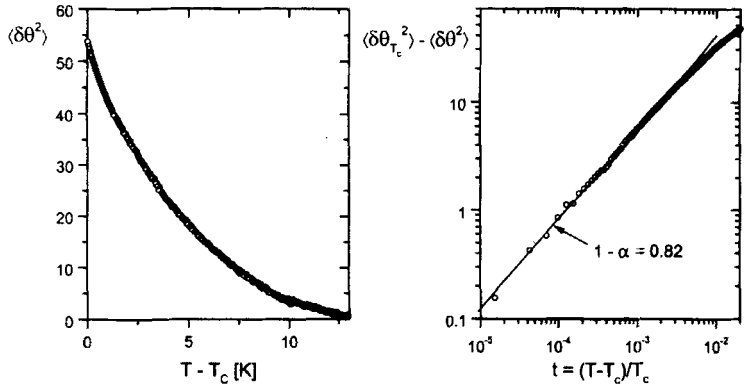

FIGURE 8. (a) Temperature dependence of the mean square of the fluctuations of the tilt angle $\langle \delta\theta^2(T) \rangle$ in the *smectic* $-A$ phase of 10OTBB1M7. (b) Log-log plot of $\langle \delta\theta^2(t=0) \rangle - \langle \delta\theta^2(t) \rangle$ for the same data. The solid line on log-log plot represents best fit to the power-law dependence below reduced temperature $t = 1.5 \times 10^{-3}$. The heat capacity critical exponent is $\alpha = 0.18$.

The magnitude of tilt fluctuations at the *smectic* $-A$ - *smectic* $-C_\alpha^*$ transition is practically the same as in MHPOBC, EHPOCBC and MHP8CBC [2], indicating surprisingly large fluctuations in antiferroelectric materials. The heat capacity critical exponent for the *smectic* $-A$ - *smectic* $-C_\alpha^*$ transition in MHP10CBC and 10OTBB1M7 is $\alpha \approx 0.2$, which is similar to the results obtained in other antiferroelectric materials. One can therefore see, that enhanced tilt

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fluctuations at the phase transition into tilted phases is characteristic for antiferroelectric materials. One of the possible explanations for such large tilt fluctuations is an enhancement of the smectic order, which is characteristic of antiferroelectric materials.

CONCLUSIONS

We have presented an overview of the optical properties of intermediate phases formed by antiferroelectric liquid crystals. The optical rotatory power of 3- and 4-layer smectic structures $smectic - C^*_{\gamma 2}$ and $smectic - C^*_{\gamma 1}$ in 10OTBB1M7 and MHP10CBC is of the same order of magnitude as in the ferroelectric and antiferroelectric phase of these materials. This result is an apparent disagreement with the results of the resonant X-ray scattering experiments on the same material (i.e. 10OTBB1M7) and indicates that a unit cell of these structures may be distorted. However, a quantitative analysis of the optical rotation in 3- and 4-layer distorted smectic structures has to be performed, together with the analysis of thermodynamic stability of these phases within the "clock" model of tilted smectic phases and a further analysis of the resonant X-ray cross-section for the distorted unit cell superstructures.

Acknowledgments

The authors would like to thank M.Čepič and B.Žekš for extensive discussions.

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