Critical behavior of birefringence in the smectic-*A* phase of chiral smectic liquid crystals

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Using a high resolution polarimeter, we have measured the temperature dependence of birefringence in the vicinity of smectic-*A*–smectic-C^*, smectic-*A*–smectic-C_α^*, and smectic-*A*–smectic-C_A^* phase transitions of chiral smectics. We have observed a large pretransitional decrease of the birefringence in materials exhibiting smectic-C_α^* and smectic-C_A^* phases, indicating unusually large pretransitional fluctuations of the tilt angle. These fluctuations show a clear power-law behavior over more than two decades of temperature.
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Recently, Ema *et al.* have reported a series of high-resolution measurements of the heat capacity in chiral smectics that exhibit the antiferroelectric smectic-C_A^* and incommensurate smectic-C_α^* phase [1]. The experiments reported critical pretransitional behavior of the heat capacity close to the phase transition between the smectic-*A* and tilted phases. In some materials, the heat-capacity critical exponent α was found to be consistent either with a Gaussian tricritical behavior [2], or showed a crossover from the three-dimensional (3D) *XY* to tricritical behavior [3]. Gaussian-like deviations from the extended mean-field Landau model have also been observed in heat-capacity experiments by Reed *et al.* [4], performed close to the smectic-*A*–smectic-*C* transition.

Recent experiments have definitely shown that both the smectic-C_α^* [5] and antiferroelectric smectic-C_A^* [6] are tilted smectic phases. The order parameter of these transitions is therefore a two component tilt vector, introduced by de Gennes [7]. In the antiferroelectric smectic-C_A^* phase the tilt direction is opposite for neighboring smectic layers and this unit cell precesses as we move along the layer normal. The structure of the smectic-C_α^* phase was determined only recently in a resonant x-ray scattering experiment performed by P. Mach *et al.* [8]. The smectic-C_α^* phase was found to be a truly incommensurate, short-period ferroelectriclike structure, as predicted by the model of Čepič and Žekš [9]. The phase transitions from the smectic-*A* phase to the ferroelectric, smectic-C_α^* and the antiferroelectric phase are therefore of the 3D *XY* universality class, where the soft mode condenses either at the center, the edge, or at a general point of the smectic Brillouin zone. However, a truly critical region, dominated by order parameter fluctuations, is rarely observed in phase transitions involving tilted phases. This can be explained by a rather large bare coherence length of these transitions, which reduce the width of the critical region to experimentally unobservable small values [10] of $(T-T_c)/T_c \approx 10^{-5}$. The dilemma of whether the critical behavior was or was not observed in the experiments close to the phase transitions to tilted smectics was a topic of many discussions in the past [11]. This was partially due to the fact that the interpretation of experimental results in tilted smectics is complicated, as these transitions are very often close to the tricritical point [12]. It was also stressed that different physical quantities are influenced in a different manner by critical fluctuations. The fluctuation effects are, for example, far more pronounced in the ultrasonic experiments than in the specific heat experiments [11]. The observation of a truly critical behavior at the phase transition into the tilted smectic phase is therefore of particular relevance.

In this Rapid Communication, we present the results of high-resolution birefringence measurements on chiral tilted smectic materials that exhibit a direct phase transition from the smectic-*A* phase to either the ferroelectric phase (CE-8), the antiferroelectric phase (EHPOCBC) or the smectic-C_α^* phase (MHPOBC, MHP8CBC). In the experiment, we have measured the optical birefringence Δn, which is in the smectic-*A* phase directly related to the mean-square fluctuations of the tilt angle $\Delta n = \Delta n_0(1-\frac{3}{2}\langle \delta\theta^2\rangle)$ [13]. Close to the transition into the tilted phase, we observe in all cases a critical suppression of the birefringence, which is due to pretransitional fluctuations of the order parameter. The amplitudes of these fluctuations are considerably larger in materials that exhibit antiferroelectric and smectic-C_α^* phases. The values of the critical exponents, as obtained in our experiments are neither pure 3D *XY* nor Gaussian, but somewhat in between. This resembles the *N*–smectic-*A* transition, where the coupling between the nematic and smectic order parameter results in nonuniversal ''effective'' values of the critical exponents [14].

Optical properties of the smectic-*A* phase are described by a uniaxial dielectric tensor, where the largest principal axis ε_3 is directed along the smectic layer normal and the smaller principal axis ε_1 is in the smectic planes. Fluctuations of the director field represent small rotations of this tensor and therefore tend to reduce the difference between the two eigenvalues. For small amplitudes of the fluctuations, the average value of the dielectric tensor of the smectic-*A* phase is

$$\langle \varepsilon(\vec{r},t)\rangle = \begin{bmatrix} \varepsilon_1+\frac{1}{2}(\varepsilon_3-\varepsilon_1)\langle\delta\theta^2\rangle & 0 & 0 \\ 0 & \varepsilon_1+\frac{1}{2}(\varepsilon_3-\varepsilon_1)\langle\delta\theta^2\rangle & 0 \\ 0 & 0 & \varepsilon_3-(\varepsilon_3-\varepsilon_1)\langle\delta\theta^2\rangle \end{bmatrix}. \tag{1}$$

The fluctuations of the local direction of the optical axis therefore tend to *increase* the eigenvalues along the smectic layers and *decrease* the dielectric constant along the layer normal. This corresponds to a slight increase of the ordinary index of refraction and to a slight decrease of the extraordinary index of refrection. In total, thermal fluctuations of the director field tend to decrease the birefringence of the smectic-*A* phase. A straightforward calculation shows that the birefringence of the smectic-*A* phase is

$$\Delta n(T)=\Delta n_0(T)[1-\tfrac{3}{2}\langle\delta\theta^2(T)\rangle]. \tag{2}$$

Here, $\Delta n_0=\sqrt{\varepsilon_3}-\sqrt{\varepsilon_1}$ is the birefringence in the absence of director fluctuations. This is slightly temperature dependent due to the temperature dependence of the nematic order parameter. The term $\langle\delta\theta^2(T)\rangle$ is due to director fluctuations and should therefore represent contributions from the collective director modes, including critical modes.

The critical exponent for the mean-square tilt angle fluctuations is simply related the heat-capacity exponent α [13]

$$\langle\delta\theta^2\rangle\approx t^{1-\alpha}, \tag{3}$$

where $t=(T-T_c)/T_c$. This shows a straightforward comparison between the critical exponents, as obtained from heat-capacity and optical birefringence experiments.

The optical experiments were performed with a high-resolution polarimeter, based on a photoelastic modulator [5]. The absolute sensitivity of this system is 10^{-2} deg of the retardation between the ordinary and extraordinary wave and allows for a very accurate determination of the optical birefringence. Samples were prepared between two DMOAP silane treated glass slides. The thickness of the samples was 120 μm and the quality of the alignment was carefully checked between crossed polarizers. In all of the samples we obtained a high-quality alignment with no visible defects. The sample was put in a double temperature controlled oven where the temperature of the sample was controlled to better that ± 2 mK. The laser beam was slightly focused to a 20 μm-diameter point on the sample, thus reducing the rounding and smearing of the phase transition, due to temperature gradients in the cell. The experiments were performed by slowly cooling the sample from the isotropic phase throughout the smectic-*A* phase and into the tilted smectic phases. A typical experimental run lasted for 24 hours and the width of the temperature scan was typically 30 K.

Figures 1(a) and 1(b) show the measured temperature dependences of birefringence in the smectic-*A* phase of 4-(2′-methybutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate (CE-8) and 4-(1-methyl-heptyloxycarbonyl-phenyl) 4′-octylbiphenyl-4-carboxylate (MHPOBC). After a discontinuity at the first order transition from the isotropic phase, the birefringence in both samples increases due to the increase of the nematic order parameter with decreasing temperature. However, several degrees before the phase transition into the tilted phase, the birefringence starts to behave qualitatively different: it decreases with decreasing temperature. This suppression of birefringence was observed close to the smectic-*A*–smectic-*C* transition by Lim and Ho [13] and is the result of *enhanced order parameter fluctuations*. One can immediately observe that the magnitude of suppression of the birefringence is significantly larger in MHPOBC than in CE-8. We have observed similar enhanced behavior in the other two compounds that show a weakly first-order smectic-*A*–smectic-C_A^* transition [4-(1-ethylheptyloxycarbonyl) phenyl-4′-alkylcarbonyloxy- biphenyl-4-carboxylate (EH-POCBC)] and a second-order smectic-*A*–smectic-C_α^* transition [4-(1-methylheptyloxycarbonyl-phenyl) 4′-octylcarbonyloxybiphenyl-4-carboxylate (MHP8CBC)].

The temperature dependence of the birefringence was analyzed using the following procedure. A large temperature interval was chosen in the smectic-*A* phase, starting close to the isotropic-smectic transition and ending approximately 10 K above the transition into the tilted phase. The temperature dependence of the birefringence in this temperature region was fitted to the power law, in order to describe the gradual increase of the birefringence due to the increase of the nematic order parameter. This curve was then extrapolated into

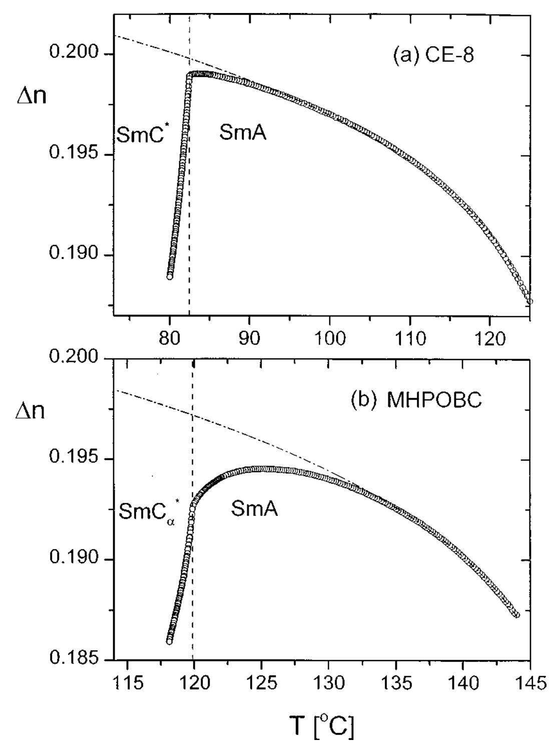

FIG. 1. (a) Temperature dependence of birefringence in the smectic-*A* phase of 4-(2′-methybutyl)phenyl 4′-n-octylbiphenyl-4-carboxylate (CE-8); (b) 4-(1-methyl-heptyloxycarbonyl-phenyl) 4′-octylbiphenyl-4-carboxylate (MHPOBC). The dashed line is a background curve, describing a gradual increase of the birefringence due to increased orientational order.

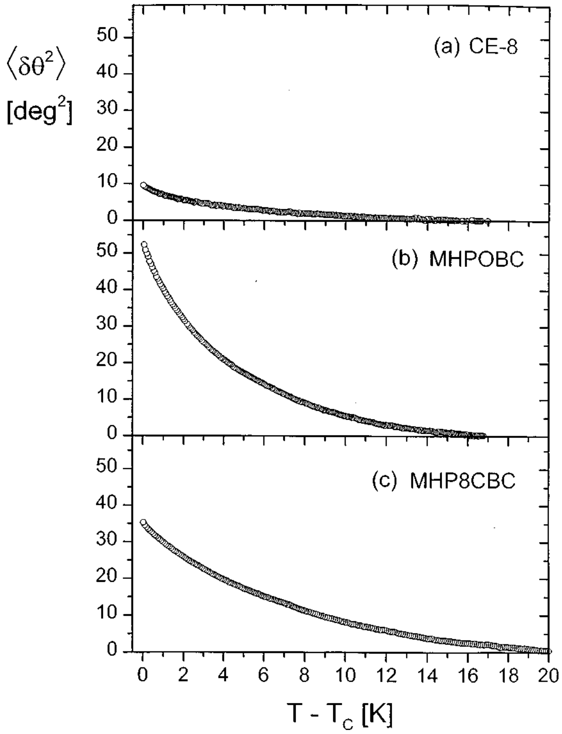

FIG. 2. Temperature dependence of the mean square of the fluctuations of the tilt angle $\langle \delta\theta^2(T)\rangle$ in the smectic-*A* phases of (a) CE-8, (b) MHPOBC, and (c) MHP8CBC.

the region, where we observe a suppression of the birefringence due to critical fluctuations. It was used as a background curve, shown by the dashed lines in Fig. 1. This procedure is analogous to the background correction in the heat-capacity studies. We made sure that the length of the temperature interval, chosen in the smectic-*A* phase, does not significantly influence the values of the critical exponents. This is indeed true for all of our experiments, as the background-correction curve is already quite smooth and saturated in the region far away from the isotropic phase. We have found that different choices of the background correcting curve change the critical exponent by only several percent. The phase transition temperature was determined from the sudden change of the slope in the temperature dependence of the birefringence. We estimate that the phase transition temperature could be located with a precision of 10 mK. This is also a typical width of the rounding region of the phase transitions.

Figures 2(a), 2(b), and 2(c) show the temperature dependence of the mean-square fluctuations of the tilt angle $\langle \delta\theta^2(T)\rangle$ in the smectic-*A* phases of CE-8, MHPOBC, and MHP8CBC. This was calculated from the difference between the extrapolated background correcting curve and the experimental birefringence, using the calibration data for the polarimeter. One can clearly see that the magnitude of fluctuations is much larger in MHPOBC and MHP8CBC than in CE-8. The quantitative comparison of the magnitudes is difficult, however, because these depend on the choice of the background correction curve, used in the analysis. It is also difficult to determine these fluctuations in the tilted phases, because there is a very large mean-field contribution due to the molecular tilt. As a consequence, it is not possible to separate the mean field from the fluctuation part below the phase transition.

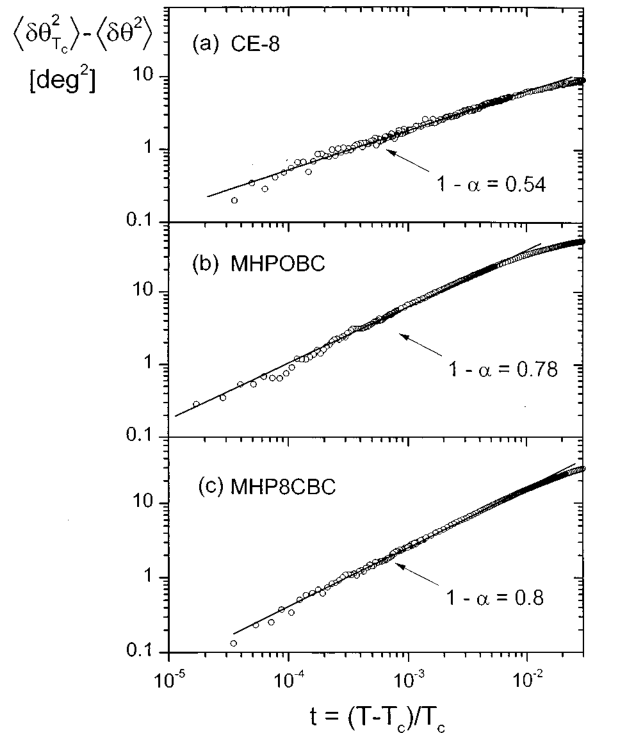

FIG. 3. Log-log plots of $\langle \delta\theta^2(t=0)\rangle - (\delta\theta^2(t))$ for (a) CE-8, (b) MHPOBC, and (c) MHP8CBC. One can clearly see power-law dependence over several decades of the reduced temperature *t*. For these particular measurements, we obtain $\alpha=0.46$ for CE-8, $\alpha=0.22$ for MHPOBC, and $\alpha=0.2$ for MHP8CBC.

The critical part of the fluctuations of the tilt angle is expected to follow the power law $\langle \delta\theta^2\rangle \approx t^{1-\alpha}$. In Fig. 3, we therefore plot $\delta\theta^2_{T_c} - \delta\theta^2(t)$ for CE-8, MHPOBC, and MHP8CBC. One can easily see a clear power-law behavior over nearly three decades of reduced temperature $10^{-5}<t<10^{-2}$. For a given experiment, the critical exponent was determined from these plots for different background correcting curves. We have also performed several experiments on different samples and we find slightly different values of the critical exponents. The average values of these exponents as obtained for different experiments, different experimental runs, and various background correcting curves are summarized in Table I, together with estimated experimental errors.

The experiments on CE-8 [Fig. 3(a)] yield an average value of $\alpha=0.4\pm0.06$, whereas for MHPOBC [Fig. 3(b)] we obtain $\alpha=0.26\pm0.04$. Figure 3(c) shows the mean-square

TABLE I. Note: the exponent α was determined in a reduced temperature interval of $5\times10^{-5}<t<10^{-2}$, which approximately corresponds to 3 K.

Liquid crystal	α
CE-8	0.4 ±0.05
MHPOBC	0.26±0.04
MHP8CBC	0.2 ±0.05
EHPOCBC	0.38±0.04

tilt fluctuation contribution for MHP8CBC. This is a particularly interesting compound because it shows a fluctuation behavior that is closest to the expected 3D *XY* type. We have analyzed the slope of this fluctuation contribution for different widths of the temperature interval. For the reduced temperature interval $t_{\max}=2.5\times10^{-4}$ we obtain $\alpha=0.07$, which is close to the expected value $\alpha_{\mathrm{3D\,XY}}=-0.006$. By taking a larger temperature interval, this exponent than stabilizes at the value of $\alpha=0.20\pm0.05$ for the reduced temperature range of $t_{\max}=10^{-2}$. In all cases we observe the general trend of a further increase of the critical exponent α for data outside a typically reduced temperature interval $t_{\max}=10^{-2}$. This corresponds to temperatures several degrees K above the phase transition into the tilted phase. This resembles the crossover behavior: for small temperature ranges close to the phase transition α seems to approach 3D *XY* values, whereas far away α seems to approach a Gaussian value of $\alpha=0.5$, as predicted by the fluctuation correction of the Landau mean-field theory [15]. The crossover temperatures are several degrees K above T_c in all cases and are of the same order, as those reported by Ema and co-workers [1–3]. It is, however, difficult to directly compare the critical indices, as obtained within this work, with those of Ema and co-workers. They have used a renormalization-group expression, including the corrections-to-scaling terms to the heat-capacity data, which are already quite significant for the reduced temperature interval of $t_{\max}=10^{-2}$. Qualitative comparison is possible, however, for the reduced temperature interval of $t_{\max}\approx10^{-4}$, where the amplitude of the corrections-to-scaling term is expected to be much smaller than the leading term. For this reduced temperature interval we obtain $\alpha=0.07$ for MHP8CBC, which is close to $\alpha=0.04$, reported by Ema *et al.* [3]. The agreement is worse for other substances.

Finally, we would like to point out the correlation between the magnitude of the tilt fluctuations and the corresponding critical exponents that we observe in our experiments. If we compare the results for CE-8 and MHPOBC, we immediately observe that for a given temperature interval the fluctuations are much smaller in CE-8 than in MHPOBC. One would than intuitively expect that the pretransitional behavior in CE-8 is closer to the mean-field regime than the critical one, as the fluctuations are here smaller and less dominant. This is indeed reflected in the corresponding critical exponent α. This exponent is $\alpha\approx0.4$ for CE-8 and is closer to the Gaussian value of $\alpha=0.5$ than the critical exponent $\alpha=0.26$ for MHPOBC. This seems to confirm qualitatively the overall conclusion of this Rapid Communication that fluctuations are dominating the pretransitional thermodynamics of some chiral smectics that exhibit smectic-C_α^* and antiferroelectric smectic-C_A^* phase. Our experiments have also clearly shown that birefringence is very sensitive to the pretransitional fluctuations of tilted smectics. We believe that it is possible to improve experimental conditions to enter the most interesting region of the reduced temperatures $t_{\max}<10^{-4}$ and this will be reported in the future.

In conclusion, we have reported the critical pretransitional behavior of optical birefringence in the smectic-*A* phase of chiral and polar tilted smectics. We have observed a power-law behavior of the mean square of the tilt fluctuations, as deduced from the birefringence. The magnitude of these fluctuations is significant in materials that exhibit the smectic-C_α^* and the antiferroelectric smectic-C_A^* phase. This is reflected in the corresponding critical exponents α that exhibit nonuniversal effective values. In view of similar results that were obtained for the *N*–smectic-*A* transition, we conjecture that some coupling mechanism might be responsible for this nonuniversality. Recently, it was pointed out by Benguigui and Martinoty [11] that a coupling among the molecular tilt, the layer compression, and the density in tilted smectics could result in effective critical exponents that are among the mean-field, Gaussian, or 3D *XY* values.

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