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Onset and evolution of the tilted smectic antiphase in a polar liquid-crystal binary mixture

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(Received 27 November 1995)

High-resolution x-ray diffraction studies of a binary mixture of the n=8 and n=10 homologs of alkoxyphe- 
nyl nitrobenzoyloxy benzoate DB8ONO2 (52.6 mole % DB8ONO2) have been performed at the onset of the 
tilted smectic antiphase (Sm-tilde) upon cooling from the smectic-A1 phase. Fluctuations of the two competing 
smectic orders are found to be related to monolayer and partial bilayer ordering. With decreasing temperature, 
the period of the antiphase in-plane modulation increases while the smectic layer normal tilts at an angle of 
\pm 7° with respect to the director. This tilt partially recovers upon the transition to the smectic-A2 phase.

PACS number(s): 61.30.-v, 68.55.Jk, 78.20.Ci

The classical picture of the smectic-A (Sm-A) liquid- 
crystal phase is that of a stack of two-dimensional liquid 
layers of rodlike molecules. The order can be described by 
a one-dimensional mass density modulation in the direction of 
the layer normal. This picture is dramatically altered by the 
introduction of longitudinal molecular dipoles. The formation 
of antiferroelectric pairs becomes energetically favor- 
able and this can induce a one-dimensional polarization 
modulation. Three distinct polymorphic smectic-A phases 
can thus be formed, namely, the monolayer Sm-A1, the bi- 
layer Sm-A2, and the partial bilayer Sm-Af. Although all 
three possess the same symmetry, they differ in the relative 
amplitudes and periods of the two modulations. For the Sm- 
A1 phase, the net periodicity \(d=L\) (the molecular 
length), for Sm-A2, \(d=2L\) and for Sm-Af, \(d=L'\) where 
\(L<L'<2L\).

A remarkable property of several polar smectic systems is 
the repeated symmetry breaking and recovery (as a function 
of temperature or composition), due to the appearance of 
reentrant nematic phases N\(\perp\), the smectic antiphase Sm-A, 
or the tilted smectic antiphase Sm-tilde, as intermediate yet 
thermodynamically stable states between the polymorphic 
smectic-A phases. A phenomenological mean-field theory [1] 
based on the competition between two fundamental incom- 
mensurate length scales, i.e., the molecular length \(L\) and the 
antiferroelectric dimer length \(L'\), has been very successful in 
describing the polymorphism of polar smectics. The nematic 
reentrance phenomena has been explained as a means of es-
caping antiferroelectric frustration by the onset of positional 
disorder. The occurrence of smectic antiphases [Sm-A and 
Sm-tilde] is a consequence of the development of an in-plane 
density modulation, to escape imminent incommensurability.

The reentrances of the nematic phase in frustrated smectic 
systems have been studied extensively and fluctuations of 
competing periodicities have been found to play a very 
important role [2]. Fluctuations are also responsible for exotic 
behavior within the reentrant range such as the theoretically 
predicted phase transition between two uniaxial nematics 
characterized by strong monolayer and bilayer correlations. 
This transition was recently observed [3] experimentally. 
While the transition from Sm-A1 to the antiphase Sm-A has 
been studied in detail [4], the onset of the Sm-tilde phase has 
not. In this paper we present a high-resolution x-ray diffraction 
study of the Sm-A1–Sm-tilde phase transition. We find that 
the competition between the two incommensurate [mono-
layer and partial bilayer] smectic order fluctuations plays an 
important role at this weakly first order transition. Our re- 
results on the binary mixture of the n=8 and n=10 homologs 
of DB8ONO2 (52.6 mole % DB10ONO2) demonstrate that 
the diffraction peaks at the Sm-A1–Sm-tilde phase transition 
condense into two pairs of off-axis quasi-Bragg peaks in the 
Sm-tilde phase. The period of the antiphase modulation in-
creases gradually as the incommensurability between the two 
density waves decreases and discontinuously becomes infi-
nite at the transition to the Sm-A2 phase. The normal to 
different sections of smectic layers in the antiphase is tilted 
alternatingly at 7° in opposite directions with respect to the 
director defined by an external magnetic field.

The experiment was conducted using a four-circle x-ray 
diffractometer with an 18 kW Cu rotating anode source and 
a pair of Ge(111) single crystals as monochromator and ana-
lyzer that gave a longitudinal resolution \(\Delta Q_1=4 \times 10^{-4}\) 
\(\text{Å}^{-1}\). The out-of-plane transverse resolution is \(\Delta Q_2=10^{-2}\) 
\(\text{Å}^{-1}\). Experimental details have been described elsewhere 
[5]. A Siemens X1000 diffractometer equipped with an area 
detector was used to obtain global features of the diffraction 
patterns. Approximately 100 mg of the sample was sealed 
between two 10 \(\mu\)m thick mylar sheets and placed in an oven 
with a temperature stability of \(\pm 0.01\) K. The sample was 
initially aligned in the nematic phase \((T>200 \text{ °C})\) and then 
cycled through the Sm-Af phase and the reentrant nematic 
phase several times in the presence of \(\text{in situ} (6.5 \text{ kG})\) mag- 
etic field produced by a pair of permanent magnets, to en- 
sure good alignment. The two fundamental lengths, \(L'\) and 
\(L\), were determined from the peak positions of the quasi- 
Bragg peaks, \(q'\) in the Sm-Af phase and \(2q_0\) in the Sm-A1 
phase in the proximity of the reentrant N phase, and found to 
be 46.0 \(\text{Å}\) and 30.8 \(\text{Å}\), respectively.

We measured the evolution of the reflections at \(2q_0\) and 
\(q'\) as the Sm-tilde phase was approached on cooling. The 
evolution of the density wave with wave vector \(2q_0\) at the Sm- 
A1–Sm-tilde transition is shown in Fig. 1. The ten iso-intensity
FIG. 1. Evolution of the 2q_0 peak at the Sm-A_1→C phase transition. (a) The 2q_0 peak is resolution limited in the A_1 phase. (b, c) It gradually broadened and moved to higher values of scattering vectors giving a decrease of 0.7% in smectic layer spacing in 5 K with decreasing temperature. (d) The tilted layer segments with ±7 degree layer tilt developed at this transition as evidenced by the growth of two off-axis peaks.

Contours are evenly spaced between the maximum and background intensities. At approximately 5 K above the transition, at 125.50 °C [Fig. 1(a)], the condensed quasi-Bragg peak was located at (0, 0, 0.2040) Å\(^{-1}\) with resolution limited full width at half maximum (FWHM) of 0.0008 Å\(^{-1}\) along Q_⊥. In the transverse direction, the peak was mosaic limited with 0.0053 Å\(^{-1}\) FWHM. The in-plane transverse correlation length was estimated to be at least 380 Å. The transverse width, primarily due to layer undulations that develop upon approaching the Sm-C phase, increased [Figs. 1(b) and 1(c)] at a linear rate of 1.2 °/K with decreasing temperature accompanied by a decrease in the layer spacing at a rate of −0.14%/K. This broadening has been interpreted [6] as evidence that the Sm-A_1→Sm-C transition is mediated by smectic-C-like fluctuations of the orientational order. At T = 120.50 °C, just 10 mK above the transition temperature (T_{A_1→C} = 120.49 °C), the angular peak width and the fractional layer-spacing change (ΔL/L) attained the values of 8° and −0.7%, respectively. At T = 120.48 °C, 10 mK below T_{A_1→C}, two off-axis peaks appeared at (±0.025, 0, 0.2040) Å\(^{-1}\), at ±7° with respect to the monolayer peak (i.e., the director, defined by the direction of the magnetic field). The positions of these two peaks did not change as the temperature was lowered, but they gained intensity at the expense of the on-axis Sm-A_1 peak, Fig. 1(d). The widths of the off-axis peaks in Q_∥ and Q_⊥ directions were comparable to that of the on-axis Sm-A_1 peak (2q_0) at 125.50 °C, Fig. 1(a). The difference in their intensities could be accounted for by the experimental geometry and initial alignment [3]. ω scans of both off-axis peaks were identical [7,8] suggesting that these reflections originated from the same scattering volume. This led us to conclude that the smectic layers attain a zigzag shape at the transition to the antiphase Sm-C with adjacent layer segments making an angle of 14° with each other which is two times the angle of 7° between the local smectic layer normal and the director.

The evolution of the q′ peak at the onset of the antiphase modulation is shown in Fig. 2. In the Sm-A_1 phase, Fig. 2(a), the diffuse q′ peak at (0, 0, 0.1350) Å\(^{-1}\) arose from the Sm-A_d fluctuations [9]. The presence of the antiphase fluctuations are indicated by the two off-axis diffuse peaks at q_1′ and q_2′ which began developing at approximately 124.85 °C, in the Sm-A_1 phase [9]. These peaks gradually moved to a lower value of Q_∥ with increasing intensities as the Sm-A_1→Sm-C transition was approached, Fig. 2(b).

At the Sm-A_1→Sm-C transition, two pairs, i.e., q_1′, q_1″ and q_2′, q_2″, appeared (Fig. 3) at the same time as the two reflec-
The shaded squares on segment \(a\) were obtained from a low resolution experiment. Representative uncertainties in the value of the scattering vector as shown on one point. This peak moved towards \(2q_0/2\) (big open circle). The vectors represent the positions of the scattering peaks in reciprocal space at 119.00 °C. The contour map is a plot of the Sm-\(C\)-fluctuation measured at 120.5 °C. The dependence on temperature of the peak moved towards \(2q_0\). The double antiphase peaks became diffuse with decreasing temperature. \(q_0\) peak remained stationary. The positions of antiphase peaks were due to the intrinsic structure of the Sm-\(C\) layers which tilt symmetrically in a zigzag manner with respect to the director.

The segments \(a, a', b, b'\) in Fig. 3, depict the locus of the peaks at \(q_{1}', q_{1}''\), and \(q_{2}', q_{2}''\), respectively, with the temperature decreasing from 119.02 to 100.50 °C. The \(2q_0\) scattering profile did not change within the range of the Sm-\(C\) phase.

The projection of the incommensurate wave vector \(q_1\) onto the smectic layer normal was \(2b = q_1'sin\alpha\). Here, \(\alpha (= 22.1°)\) is the angle between \(2q_0 = (-0.025, 0, 0.2040) \text{ Å}^{-1}\) and \(q_{1}' = (0.034, 0, 0.1235) \text{ Å}^{-1}\) at 119.02 °C. The period of the antiphase modulation increased from approximately 130 Å at 119.02 °C to 240 Å at 110.40 °C as evidenced by decreasing \(Q\) components of \(q_1'\) and \(q_1''\). This monotonic change continued and the two reflections appeared to be approaching the lockin position indicated by the large open circle. However, before they could converge at this point, the weakly first order transition to the \(A_2\) phase took place and they jumped to the on-axis \(q_0\) position, shown as open square. At the same time the on-axis \(2q_0\) peak (at the roughly same position as in the Sm-\(A_1\) phase) became much
brighter than the Sm-$\delta$ peaks at $(\pm 0.025, 0, 0.2040)$ Å$^{-1}$. It should be noted that, as shown in Fig. 3, segments $b$ and $b'$ follow a path analogous to that of $a$ and $a'$.

Figure 4 shows the longitudinal and transverse scans through various peaks at the Sm-$\delta$–Sm-$A_2$ transition. In (a) and (a’), at 101.11 °C, the two antiphase peaks were located at $(\pm 0.012, 0, 0.2040)$ Å$^{-1}$ and some diffuse scattering was centered at $(0, 0, 0.0980)$ Å$^{-1}$. In scans (b) and (b’) at 101.00 °C, the antiphase peaks moved closer and towards $(\pm 0.010, 0, 0.1083)$ Å$^{-1}$. At temperatures below 101 °C, a single condensed peak gradually developed at $(0, 0, 0.1025)$ Å$^{-1}$, commensurate with the on-axis $2q_0$ peak at $(0, 0, 0.2050)$ Å$^{-1}$. The commensurate on-axis peaks gained intensity marking the advent of the bilayer Sm-$A_2$ phase. In (c) and (c’), at 100.51 °C, the single condensed peak, located now at $(0, 0, 0.1030)$ Å$^{-1}$, coexisted with the double antiphase peaks at $(\pm 0.008, 0, 0.1065)$ Å$^{-1}$. As shown in (d) and (d’) at 100.31 °C the two antiphase peaks finally disappeared. At the same temperature and after equilibration time of about 10 minutes, the \( \omega \) scans of the peaks at $2q_0 (= 0.2090$ Å$^{-1}$) and $q_0 (= 0.1045$ Å$^{-1}$) peaks were found to be identical. The system eventually crystallized at 87.30 °C.

In summary, we have observed pretransitional effects and studied, in detail, the onset and evolution of the tilted antiphase Sm-$\delta$ in a binary mixture of polar liquid crystal. The in-plane antiphase modulation, in this phase, fully developed approximately at 1.5 K below the transition temperature. The period of antiphase modulation increased monotonically as the incommensurability of the two modulations along the smectic layer normal decreased and eventually became infinite at the transition to the Sm-$A_2$ phase.

The authors thank S. Pfeiffer for synthesizing the compounds, M. Sutton, C.W. Garland, P. Heiney, and A. M. Levelut for helpful discussions, and acknowledge the use of Siemen’s X1000 diffractometer at the Liquid Crystal Institute. This research was supported by the NSF Science and Technology Center ALCOM Grant No. DMR-89-20147.


[9] C.W. Garland, in Geometry and Thermodynamics, edited by J.-C. Toledano (Plenum, New York, 1990), p. 221; the Sm-$A_1$ phase with double off-axis diffuse peaks was defined as the Sm-$A'_1$ phase in this paper.