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## Experimental Observation of a Transition between Two Uniaxial Nematic Liquid-Crystal Phases

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The experimental observation of a phase transition between two uniaxial nematic liquid-crystalline phases is reported. High-resolution x-ray scattering and ac calorimetric studies on binary mixtures of octyl- and decyloxyphenyl-nitrobenzoyloxy benzoates show evidence of a first-order transition between two nematic phases with different types of short-range smectic order. This transition is observed in the vicinity of the termination of the smectic- $A_d$ -smectic- $A_1$  phase boundary, in accordance with theoretical predictions.

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Nematic liquid crystals are orientationally ordered fluids [1]. The nematic phase of rodlike molecules is optically uniaxial. However, when the shape of molecules or molecular aggregates is altered, a biaxial nematic phase can result [2–4]. While phase transitions between uniaxial and biaxial nematic phases have indeed been reported in lyotropic as well as thermotropic liquid crystals [2,4], the transition between two uniaxial nematic phases has never been seen experimentally although theoretically it is expected to occur in the vicinity of smectic- $A$ -smectic- $A$ -type critical points [5].

The quasi-long-range order in both partial bilayer smectic- $A_d$  ( $Sm-A_d$ ) and monolayer smectic- $A_1$  ( $Sm-A_1$ ) phases can be described by one-dimensional density modulations with spatial periodicity  $L$  for the  $Sm-A_1$  phase, where  $L$  is approximately equal to the molecular length, and  $L'$  for  $Sm-A_d$ , where  $L < L' < 2L$ . A mean-field theory that takes into account the competition between ordering at the two different length scales  $L$  and  $L'$  predicts that due to the identical symmetries of the two phases, the first-order  $Sm-A_d$ - $Sm-A_1$  transition line can terminate at a critical point, beyond which the two phases evolve continuously into each other [6]. A subsequent fluctuation-corrected model of dislocation loops predicts a different scenario [5]. At the critical point the smectic-layer compressibility vanishes. This causes a dramatic reduction in the energy of dislocation loops which then unbind and the smectic melts into a nematic phase. The smectic-smectic critical point is thus replaced by the remarkable topology of an isolated reentrant nematic “lake” and an associated liquid-gas-like critical point between two uniaxial nematics, denoted as  $N_d$  and  $N_1$ , that are characterized by a  $Sm-A_d$  and a  $Sm-A_1$  type of short-range order, respectively. The nematic lake can often merge with the usual nematic domain (nematic “sea”) to form a nematic “estuary” of the kind shown in Fig. 1.

Although several experiments have observed a nematic lake at the terminus of the  $Sm-A_d$ - $Sm-A_1$  phase boundary [7–9], a transition between the two uniaxial nematic phases has never been seen. In this Letter, we report the first observation of such a nematic-nematic transition. High-resolution x-ray scattering and ac calorimetric studies on binary mixtures of strongly polar homologs show that the transition is first order with pronounced discontinuous jumps in the susceptibility and the correlation lengths associated with short-range smectic fluctuations. We also show that the topology of the phase diagram is in accordance with the theoretical predictions.

The materials studied are the long-core (three-ring), polar liquid-crystal homologs octyloxyphenyl-nitrobenzoyloxy benzoate ( $DB_8ONO_2$ ) and decyloxyphenyl-nitrobenzoyloxy benzoate ( $DB_{10}ONO_2$ ). They exhibit

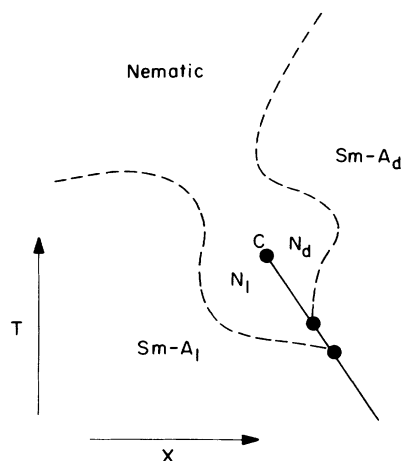


FIG. 1. Theoretical phase diagram from Ref. [5].  $C$  is the critical point at the end of the first-order  $N_d$ - $N_1$  transition line. Dashed curves indicate continuous phase transitions and solid lines indicate first-order transitions.

a temperature- ( $T$ -) mole percent concentration ( $X$ ) phase diagram that has a rich variety of liquid-crystal phases with multiple nematic and smectic reentrances [10–12]. We investigated the  $\text{DB}_8\text{ONO}_2 + \text{DB}_{10}\text{ONO}_2$  phase diagram in the very narrow concentration range  $51 < X < 54$  where a first-order  $\text{Sm-A}_d$ – $\text{Sm-A}_1$  transition line ends and the existence of a reentrant nematic phase ( $N_{re}$ ) is well established.

The ac calorimetric technique has been described elsewhere [13]. For the x-ray studies, we used the Cu  $K\alpha$  line from a Rigaku RU-300 rotating anode source operating at 15 kW [14]. We used a pair of Ge (111) single crystals as monochromator and analyzer, which gave a longitudinal in-plane resolution of  $4 \times 10^{-4} \text{ \AA}^{-1}$  half width at half maximum (HWHM). An *in situ* 6.5 kG permanent magnet was used to align the sample in the high-temperature nematic phase at  $T > 200 \text{ }^\circ\text{C}$ . One mixture with  $X = 52.6$  was investigated. Approximately 150 mg of this sample was placed between two  $10 \mu\text{m}$  thick Mylar sheets and mounted in an oven that provided a temperature stability of  $\pm 1 \text{ mK}$ . Sealed in this manner, the sample was found to be extremely stable. Over a period of 6 d, no drifts in transition temperatures due to thermal deterioration were observed. This was very important for the success of the x-ray experiment and made possible to reproduce the data presented here on several different runs.

The  $C_p$  data for four different concentrations of  $\text{DB}_{10}\text{ONO}_2$  in the mixture are presented in Fig. 2. Starting at the lowest concentration  $X = 51.33$ , two  $C_p$  peaks are observed at 126.85 and 126.0  $^\circ\text{C}$ , consistent with the phase sequence  $\text{Sm-A}_d$ – $N_{re}$ – $\text{Sm-A}_1$ . The relative magnitudes of the peaks are in good agreement with the frustrated spin-gas model [15]. Previous analysis of

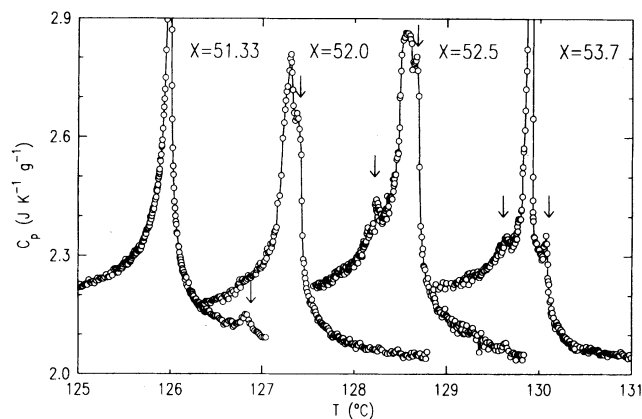


FIG. 2. Detailed view of  $C_p$  variation for  $\text{DB}_8\text{ONO}_2 + \text{DB}_{10}\text{ONO}_2$  mixtures with  $X = 51.33$  (Ref. [7]), 52.0, 52.5, and 53.7 (Ref. [8]). The temperature scale is valid for the  $X = 51.33$  sample. Data have been shifted by  $1.2 \text{ }^\circ\text{C}$  for  $X = 52.0$ , by  $2.4 \text{ }^\circ\text{C}$  for  $X = 52.5$ , and by  $4.2 \text{ }^\circ\text{C}$  for the  $X = 53.7$  sample. The maximum  $C_p$  value lies off scale at  $3.3 \text{ J K}^{-1} \text{ g}^{-1}$  for  $X = 51.33$  and  $4.4 \text{ J K}^{-1} \text{ g}^{-1}$  for  $X = 53.7$ . The arrows indicate the satellite peaks to the main  $C_p$  anomaly.

the  $N_{re}$ – $\text{Sm-A}_1$  data revealed a tricritical  $C_p$  exponent  $\alpha = 0.50$  [12]. This result is unexpected since the usual nematic ( $N$ )– $\text{Sm-A}$  tricritical point occurs due to coupling between nematic and smectic order parameters when the isotropic ( $I$ )– $N$  transition temperature ( $T_{I-N}$ ) is close to the  $N$ – $\text{Sm-A}$  transition temperature ( $T_{N-A}$ ). However, in this case  $T_{I-N}$  is 95 K above the  $N_{re}$ – $\text{Sm-A}_1$  transition. We will discuss later how the existence of this tricritical point can be understood in terms of the associated  $N_d$ – $N_1$  transition. In the case of the  $X = 52.0$  mixture two  $C_p$  peaks are also observed at  $T = 126.18$  and  $126.11 \text{ }^\circ\text{C}$ . Neither of them exhibits anomalous behavior in the ac phase shift measurements that would indicate a first-order transition [13].

For the  $X = 52.5$  sample a new picture emerges. The  $C_p$  measurements reveal three peaks. The central peak at  $126.13 \text{ }^\circ\text{C}$  is the main feature with two subsidiary peaks at  $126.27$  and  $125.82 \text{ }^\circ\text{C}$ . The existence of three  $C_p$  peaks strongly suggests the phase sequence  $\text{Sm-A}_d$ – $N_d$ – $N_1$ – $\text{Sm-A}_1$ . The main peak is rounded and no clear evidence of two-phase coexistence could be detected for any of the three  $C_p$  anomalies. The  $C_p$  results for the  $X = 53.7$  mixture are consistent with those for  $X = 52.5$ . Once again three distinct  $C_p$  peaks are found. The central peak at  $T = 125.71 \text{ }^\circ\text{C}$  is a sharp, first-order anomaly [12]. The character of the transitions associated with the two satellite peaks at  $125.87$  and  $125.60 \text{ }^\circ\text{C}$  could not be determined. Because of the narrow temperature ranges between the various  $C_p$  peaks, no critical power-law analysis can be convincingly performed for the data on the 52.0, 52.5, and 53.7 mixtures. It should be noted that optical microscopy studies of the same mixtures failed to detect the  $N_d$ – $N_1$  transition.

We now turn to the results from high-resolution x-ray scattering. Starting in the  $\text{Sm-A}_d$  phase close to  $\text{Sm-A}_d$ – $N_{re}$  boundary and cooling until the  $\text{Sm-A}_1$  phase was entered, longitudinal (parallel to the layer normal) and transverse scans were performed at a series of constant temperatures. For each temperature we found two x-ray peaks corresponding to the partial bilayer and monolayer ordering. For each peak, the pair of longitudinal and transverse scans at a given temperature was analyzed via the following expression for the structure factor:

$$S(\mathbf{q}) = \sigma / [1 + \xi_{\parallel}^2 (q_{\parallel} - q_0)^2 + \xi_{\perp}^2 q_{\perp}^2 + c \xi_{\perp}^4 q_{\perp}^4],$$

convoluted with the resolution function. Here  $\sigma$  is the smectic susceptibility and  $\xi_{\parallel}$ ,  $\xi_{\perp}$  are the longitudinal and transverse correlation lengths.

The smectic mosaic of the partial bilayer peak in the  $\text{Sm-A}_d$  and  $\text{Sm-A}_1$  phases was  $2.4^\circ$  HWHM. Because the mosaicity was temperature independent over the narrow temperature range that was studied, no corrections for it were applied in the line-shape analysis. The x-ray results are summarized in Figs. 3 and 4. Data for the smectic susceptibilities  $\sigma$  and the smectic-layer thickness  $L$  (for monolayer) and  $L'$  (for partial bilayer) are presented in

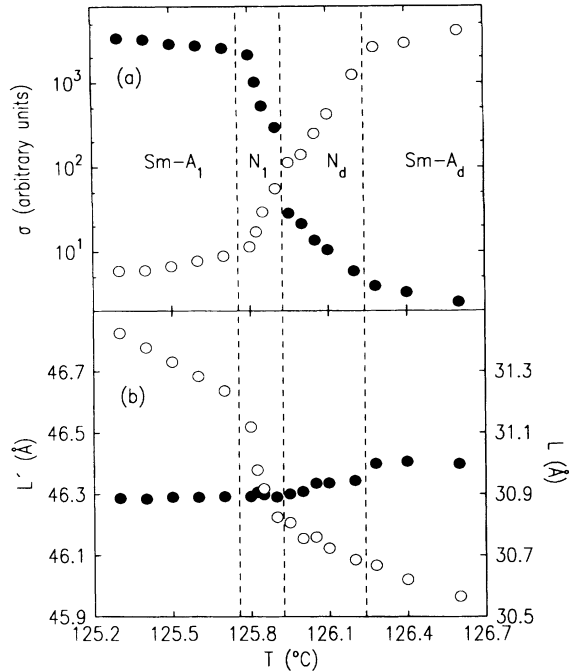


FIG. 3. Temperature dependence of (a) the smectic susceptibility  $\sigma$ , and (b) the smectic-layer thickness  $L$  (right axis) and  $L'$  (left axis) for the  $X = 52.6$  sample. Open symbols refer to the partial bilayer and filled symbols to the monolayer peak. The dashed lines indicate the transition temperatures.

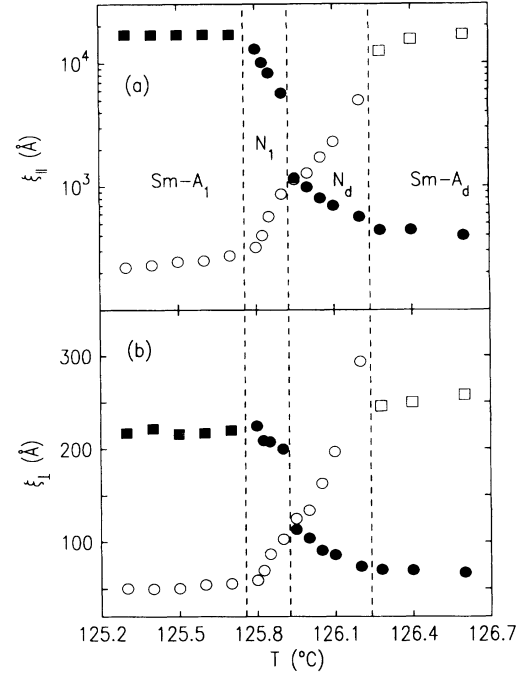


FIG. 4. Temperature dependence of the correlation lengths (a) parallel  $\xi_{\parallel}$  and (b) perpendicular  $\xi_{\perp}$  to the layer normal. Open symbols correspond to the partial bilayer and filled to the monolayer peak. The squares in (a) indicate resolution-limited and in (b) mosaic-limited x-ray peaks. The dashed lines mark the transition temperatures.

Fig. 3. Data for the correlation lengths  $\xi_{\parallel}$  and  $\xi_{\perp}$  are given in Fig. 4.

In the  $\text{Sm-}A_d$  phase, at  $126.60^\circ\text{C}$  two x-ray peaks were found, centered at  $q'_0 = (0, 0, 0.1367)$  corresponding to partial bilayer thickness  $L' = 45.96 \text{ \AA}$  and at  $q_0 = (0, 0, 0.2027)$  corresponding to monolayer thickness  $L = 31.0 \text{ \AA}$ . The peak at  $q'_0$  is resolution limited while that at  $q_0$  is diffuse. When the  $\text{Sm-}A_d$ -nematic transition line is crossed, on cooling from  $126.28$  to  $126.20^\circ\text{C}$ , the  $q'_0$  peak becomes diffuse with  $\xi_{\parallel} = 5000 \text{ \AA}$ . The smectic-mosaic features also disappear from the transverse scans of this peak, which makes the transverse profile sharper [Fig. 4(b)]. The peak at  $q_0$  remains diffuse. As the data of Figs. 3 and 4 demonstrate, short-range partial bilayer ( $A_d$ ) fluctuations are dominant in the high-temperature region of the nematic phase. At  $126.20^\circ\text{C}$ , the value of  $\sigma$  for the  $q'_0$  peak is  $\sim 220$  times larger than for  $q_0$  and the correlation volume  $\xi_{\parallel}\xi_{\perp}^2$  associated with  $A_d$  fluctuations is 150 times larger than for monolayer ( $A_1$ ). This region of the nematic phase is denoted as  $N_d$ .

At  $125.95^\circ\text{C}$  the correlation volumes for  $A_d$  and  $A_1$  fluctuations are about equal while  $\sigma$  is still  $\sim 4$  times larger for the  $q'_0$  peak. Upon cooling to  $T = 125.90^\circ\text{C}$ ,  $q_0$  becomes the dominant feature of the scattering profile after discontinuous jumps in  $\sigma$ ,  $\xi_{\parallel}$ , and  $\xi_{\perp}$  ( $\sigma$  for  $q_0$  is now  $\sim 7$  times larger than for  $q'_0$  and the  $A_1$  correlation volume is  $\sim 25$  times larger). This low-temperature

region of the nematic phase primarily characterized by short-range monolayer ( $A_1$ ) fluctuations is denoted as  $N_1$ . Between  $125.95$  and  $125.90^\circ\text{C}$  a transition between the two uniaxial nematic phases  $N_d$  and  $N_1$  is clearly observed. The discontinuities in the size and shape of the  $q_0$  peak indicate that this transition is first order. It is remarkable that first-order discontinuities are primarily manifested in the  $A_1$  fluctuations.

The peak at  $q_0$  becomes resolution limited at  $125.70^\circ\text{C}$ . The onset of mosaic structure in the transverse  $q_0$  profile also marks the entrance to the  $\text{Sm-}A_1$  phase. The abrupt change in the temperature dependence of the partial bilayer thickness  $L'$  at the  $N_1$ - $\text{Sm-}A_1$  boundary along with the equally abrupt changes in the  $\sigma$  data for both the  $q'_0$  and the  $q_0$  peaks indicate that the transition may be first order. Worth noticing at this point is the very interesting behavior of the smectic-layer thickness  $L$  and  $L'$ . While  $L = 31.0 \text{ \AA}$  is almost constant throughout the  $\text{Sm-}A_d$ - $N_d$ - $N_1$ - $\text{Sm-}A_1$  phase sequence,  $L'$  shows a distinct temperature dependence from  $45.96 \text{ \AA}$  at  $126.60^\circ\text{C}$  to  $46.83 \text{ \AA}$  at  $125.30^\circ\text{C}$ , that is especially large in the  $N_1$  phase.

Figure 5 displays the experimental phase diagram constructed from the  $C_p$ , x-ray, and optical microscopy results. Although the number of points is sparse, there is a good correspondence between the topology of this diagram and that of the theoretical phase diagram shown in

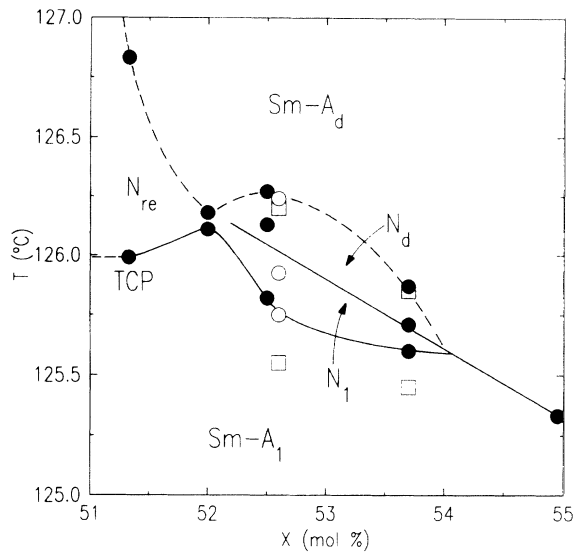


FIG. 5. Detail of the  $X$ - $T$  phase diagram for the  $\text{DB}_8\text{ONO}_2 + \text{DB}_{10}\text{ONO}_2$  binary mixtures for  $51 < X < 55$ . The filled circles are ac calorimetric data from Ref. [7] and the present study. Open circles are the results of x-ray scattering and open squares represent optical microscopy measurements. Dashed curves indicate continuous phase transitions and solid, first-order ones. TCP marks the tricritical point.

Fig. 1. In agreement with theory, we find the  $N_d$ - $N_1$  transition to be first order at  $X = 52.6$  and  $X = 53.7$ . The exact location of the  $N_d$ - $N_1$  critical point is uncertain and to characterize it in terms of universality is a major challenge primarily because of the narrow temperature ranges.

While the theory predicts a continuous  $N_1$ - $\text{Sm-A}_1$  transition, the x-ray data suggest otherwise. As mentioned earlier, from previous calorimetric work [12], it is expected that for  $X > 51.33$  the transition will become first order since a tricritical point exists for  $X = 51.33$ . The theory does not explicitly predict or preclude the existence of such a tricritical point. Tricriticality in the nematic-smectic-A transition is usually the result of strong coupling between the nematic and smectic order parameters whenever the isotropic-nematic transition is close by and the nematic susceptibility  $\chi_S$  is large. In the present system, a large  $\chi_S$  may be attributed to the  $N_d$ - $N_1$  critical point. Although the  $\text{Sm-A}_d$ - $N_d$  transition appears to be second order confirming the theoretical prediction, the possibility that it can be weakly first order has not been thoroughly investigated. A tricritical point may also exist on the  $\text{Sm-A}_d$ - $N_d$  transition line for the same reason it exists on the  $N_1$ - $\text{Sm-A}_1$ .

Earlier calorimetric and x-ray studies of reentrant nematics enclosed between  $\text{Sm-A}_d$  and  $\text{Sm-A}_1$  phases [9,16,17] did not provide any evidence for a  $N_d$ - $N_1$  transition. It is possible that these systems are beyond the  $N_d$ - $N_1$  critical point, in the supercritical regime, where only a continuous  $N_d$ - $N_1$  evolution can be observed, or

that the  $N_d$ - $N_1$  critical point has merged with the  $N_{re}$ - $\text{Sm-A}_1$  phase boundary [18]. Moreover, the topologies observed in the present system are nonuniversal and depend on the particular microscopic characteristics of the investigated system [5].

The  $C_p$  data for the  $X = 52.5$  and  $X = 53.7$  mixtures and the x-ray data for  $X = 52.6$  provide strong evidence that the  $\text{Sm-A}_d$ - $N_d$ - $N_1$ - $\text{Sm-A}_1$  phase sequence occurs in  $\text{DB}_8\text{ONO}_2 + \text{DB}_{10}\text{ONO}_2$  mixtures. In excellent agreement with the dislocation-loop melting theory, the two uniaxial nematic phases  $N_d$  and  $N_1$  are shown to be dominated by short-range smectic fluctuations of partial-bilayer and monolayer ordering, respectively. The exact location of the  $N_d$ - $N_1$  critical point and a detailed study of its nature will be of considerable interest.

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