RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 46, NUMBER 10 15 NOVEMBER 1992

Continuous thermodynamic path between three smectic-A phases of the same symmetry

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(Received 14 February 1992)

Observation of a continuous thermodynamic path between smectic-A_1 and smectic-A_2 phases is reported. This path follows a continuous evolution from smectic-A_1 to smectic-A_d in the vicinity of a closed-loop nematic domain and then from smectic-A_d to smectic-A_2 in the neighborhood of a smectic-A_d–smectic-A_2 critical point.

PACS number(s): 64.70.Md, 61.10.Lx

Smectic-A liquid crystals are orientationally ordered fluids with a one-dimensional density modulation along the preferred direction [1]. It has been established that the smectic-A (Sm-A) phase of terminally polar substituted molecules exhibits three polymorphic forms: monolayer Sm-A_1, bilayer Sm-A_2, and partial bilayer Sm-A_d [2]. They are distinguished by the periodicity of the density modulation along the director, i.e., the smectic-layer spacing d relative to the length l of the constituent molecules. In case of the Sm-A_1 phase, d is of the order of l, while d is of the order of $2l$ in the Sm-A_2 phase. For the Sm-A_d phase, d has values in between l and $2l$. The occurrence of these polymorphic phases has been explained on the basis of a phenomenological theory in terms of two competing length scales which are related to the molecular length and to the length of an antiparallel associated pair of molecules, respectively [3–6].

Phase transitions between these three polymorphic forms of the Sm-A phase are of considerable interest since they constitute transitions between phases with one-dimensional quasi-long-range positional order along the director. It has been argued theoretically [7] that there can only be a first-order phase transition between Sm-A_d and Sm-A_2 as well as between Sm-A_d and Sm-A_1. Under certain circumstances, the Sm-A_d–Sm-A_2 phase boundary can terminate at a critical point beyond which Sm-A_d continuously evolves into Sm-A_2 (supercritical evolution) without a phase transition [8]. In the case of the Sm-A_d–Sm-A_1 transition, two different situations have been dealt with theoretically [9]. The first-order phase boundary can either terminate at a critical point (as in the case of the Sm-A_d–Sm-A_2 transition), or can lead to a closed-loop nematic domain depending on whether the compressive elastic constant goes to zero or to a finite minimum value. Beyond the critical point or the nematic domain as the case may be, Sm-A_d evolves continuously into Sm-A_1. On the experimental side, the Sm-A_d–Sm-A_2 critical point and the concomitant first-order transitions as well as supercritical evolutions between the two phases have been observed [10–12]. Also, the closed-loop nematic domain at the termination of the first-order Sm-A_d–Sm-A_1 boundary as well as continuous evolutions between Sm-A_d and Sm-A_1 have been observed [13–15]. The predicted critical point for this phase boundary is yet to be established.

The situation regarding the Sm-A_1–Sm-A_2 transition is different. Although Sm-A_1 and Sm-A_2 have the same global symmetry, there can be a second-order transition as well as a first-order transition between them. The former possibility is due to the exact doubling of the layer periodicity at the phase transition. Experimentally both first- and second-order Sm-A_1–Sm-A_2 phase transitions have been observed [16,17]. To our knowledge, both theoretically calculated as well as experimentally observed phase diagrams have always involved phase transitions on going from Sm-A_1 to Sm-A_2. The possibility of a continuous path between Sm-A_1 and Sm-A_2 via Sm-A_d by a continuous variation of d has been theoretically discussed, and a "possible" theoretical phase diagram schematically combines the different thermodynamic paths between the three polymorphic smectic-A phases [8]. Experimentally the continuous path has not been observed. We report in this Rapid Communication the observation of a continuous thermodynamic path between Sm-A_1 and Sm-A_2 phases. X-ray and optical studies show that this path, which is observed in the temperature-concentration (T,x) diagram of a binary liquid-crystal system, follows continuous evolutions from Sm-A_1 to Sm-A_d and from Sm-A_d to Sm-A_2.

The compounds studied are 4-n-decyloxy-(4′-isothiocyanatophenyl)-benzoate or 10·O·NCS [17] and 4-n-undecyloxyphenyl-4′-(4″-cyanobenzyloxy)-benzoate or

11OPCBOB [18]. 10·O·NCS shows a Sm-A_1 phase while the Sm-A phase of 11OPCBOB has been shown to evolve continuously from Sm-A_d to Sm-A_2 on cooling [19]. Mixing these two compounds leads to a rich variety of phases and phase transitions over a certain range of the temperature-concentration (T,x) phase diagram (Fig. 1). (Here x is the mole fraction of 11OPCBOB). The phases were identified by optical microscopy in conjunction with x-ray diffraction studies on aligned samples. For probing the transitions between Sm-A phases, two types of x-ray investigations were carried out. For the Sm-A_d-Sm-A_1 transition which involves a large change in the layer spacing, a photographic setup was used. In this case, the relative variation of d was determined to ± 0.2 Å, the temperature accuracy being ± 25 mK. In the case of the Sm-A_d-Sm-A_2 transition where the change in d is known to be much smaller, the measurements were carried out using a computer-controlled Guinier diffractometer (Huber 644). In this case, the precision in the determination of the wave vector $(2\pi/d)$ was 1×10^{-3} Å^{-1} while the temperature was maintained to ± 5 mK [20].

For all mixtures in the (T,x) diagram (Fig. 1), Sm-A_d is the higher-temperature Sm-A phase, while the lower-

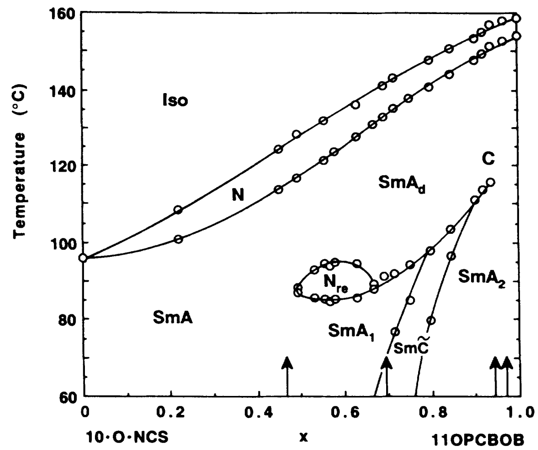

FIG. 1. Temperature-molecular fraction (T,x) phase diagram of the binary 10·O·NCS-11OPCBOB system. The continuous evolution leading from Sm-A_1 to Sm-A_d surrounds the closed-loop reentrant-nematic domain (N_{re}) while the supercritical evolution between Sm-A_d and Sm-A_2 is seen near the Sm-A_d-Sm-A_2 critical point (C). Arrows indicate the concentrations of individual mixtures used for the x-ray experiments.

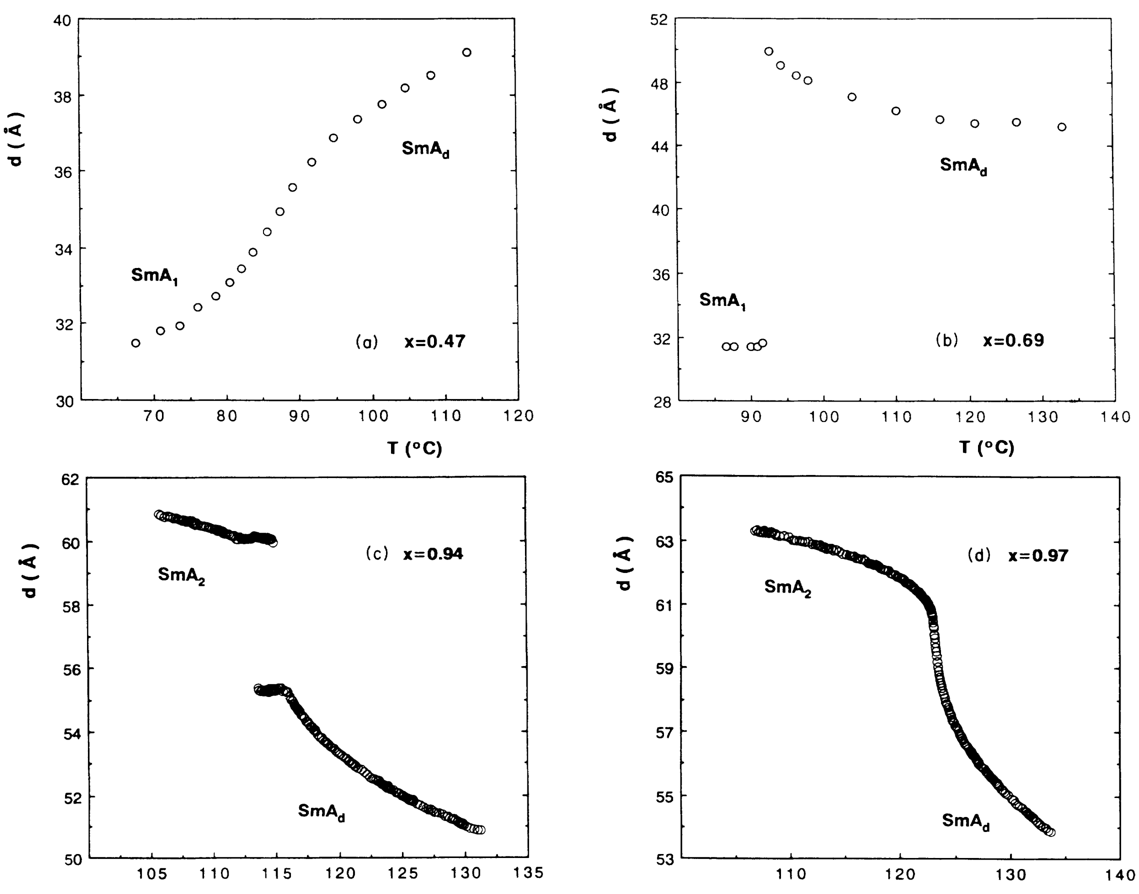

FIG. 2. Temperature dependence of the smectic-layer spacing d for individual mixtures of the 10·O·NCS-11OPCBOB system: (a) $x=0.47$ shows the supercritical evolution between Sm-A_d and Sm-A_1; (b) $x=0.69$ exhibits a first-order Sm-A_d-Sm-A_1 transition with a large jump in d; (c) $x=0.94$ shows the Sm-A_d-Sm-A_2 transition with a small jump in d; (d) $x=0.97$ shows a continuous evolution from Sm-A_d to Sm-A_2.

temperature Sm-A phase is Sm-A_1 for $0<x<0.48$ and Sm-A_2 for $0.8<x<1$. For intermediate x, the ribbon phase Sm-$\tilde{C}$ is seen to intervene. The temperature dependence of the smectic-layer spacing for four different concentrations (marked by arrows in Fig. 1) are given in Figs. 2(a)–2(d). These concentrations have been chosen to illustrate continuous evolutions as well as direct first-order phase transitions between Sm-A_d and Sm-A_1 or between Sm-A_d and Sm-A_2 phases. All these figures only show the data for the first harmonic in both Sm-A_d and Sm-A_2 phases, although a second harmonic was also seen at most temperatures. For $x=0.47$, a continuous evolution between Sm-A_d and Sm-A_1 is seen [Fig. 2(a)], there being a point of inflection around 90 °C. Figure 2(b) shows a clear signature of the first-order Sm-A_d–Sm-A_1 transition for $x=0.69$. The value of d drops from 50 to 32 Å at the phase transition. The $x=0.94$ mixture exhibits a first-order Sm-A_d–Sm-A_2 transition with a two-phase coexistence region in which the density modulations of both Sm-A_d and Sm-A_2 phases are seen [Fig. 2(c)]. A continuous evolution between Sm-A_d and Sm-A_2 is observed for $x=0.97$ [Fig. 2(d)]. It is therefore concluded that the first-order Sm-A_d–Sm-A_2 transition line terminates at a Sm-A_d–Sm-A_2 critical point (C) for $0.94<x<0.97$. It should also be mentioned that the absence of the Sm-$\tilde{C}$ phase between Sm-A_d and Sm-A_2 for $x>0.94$ has been ascertained by careful optical microscopic observations. These studies, carried out by slowly (100 mK/min) cooling a homeotropically aligned sample across the transition, did not show any birefringence characteristic of the onset of the Sm-$\tilde{C}$ phase. A similar experiment, carried out on $x<0.90$ mixtures, clearly showed a narrow region of the Sm-$\tilde{C}$ phase.

Thus the phase diagram given in Fig. 1 shows that there exists a *continuous thermodynamic path between Sm-A_1 and Sm-A_2 phases.* This path is seen to traverse via a Sm-A_d phase, i.e., Sm-A_1 first evolves continuously into Sm-A_d and then into Sm-A_2. Our results thereby show that the global symmetry of Sm-A_1, Sm-A_d, and Sm-A_2 phases is the same.

Another important aspect of the phase diagram is the termination of the phase boundary involving the Sm-A_d phase as the high-temperature phase and the Sm-A_1 or Sm-A_2 as the low-temperature phase. The Sm-A_d–Sm-A_2 part of the phase boundary terminates at the critical point (C) while the Sm-A_d–Sm-A_1 part of the boundary ends as a closed-loop nematic domain. Although the existence of the Sm-A_d–Sm-A_2 critical point as well as the closed nematic domain at the terminus of the Sm-A_d–Sm-A_1 boundary has been predicted theoretically [7–9] and observed experimentally [10–15], the possibility of their existing *together* at the two ends of a phase boundary in a single-phase diagram has not been considered before. Our experimental diagram (Fig. 1) shows the occurrence of such a situation. It is conceivable [21] that combining the appropriate aspects of both the mean-field and the dislocation approaches could in fact lead to a phase diagram of the type seen experimentally. Finally, it should also be mentioned that other features of the experimental phase diagram involving the Sm-$\tilde{C}$ phase are in accordance with a theoretical phase diagram calculated in the framework of extended mean-field theory which introduces adequate order parameters to describe the Sm-$\tilde{A}$ and Sm-$\tilde{C}$ phases in addition to the three polymorphic Sm-A phases (Fig. 6.21 in Ref. [6]).

In conclusion, we have observed an experimental phase diagram with a continuous thermodynamic path between all the three polymorphic forms of the smectic-A phase having the same global symmetry. X-ray studies show that this continuous thermodynamic path follows a continuous evolution from Sm-A_1 to Sm-A_d in the vicinity of a closed-loop nematic domain and then from Sm-A_d to Sm-A_2 in the neighborhood of a Sm-A_d–Sm-A_2 critical point. High-resolution calorimetric studies which are essential for an exact characterization of the critical point as well as the thermodynamic paths in this system are underway.

We thank Dr. B. R. Ratna and Dr. P. Barois for several helpful discussions. The help of Dr. S. Krishna Prasad in the x-ray measurements is thankfully acknowledged. The support of Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335 "Anisotrope Fluide" and Grant No. Pf 239/1-1) and of the Office of Naval Research is also gratefully acknowledged.

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