PHYSICAL REVIEW A VOLUME 42, NUMBER 4 15 AUGUST 1990

Temperature range of the smectic-A phase and its effect on the smectic-A–smectic-C transition

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(Received 19 June 1990)

X-ray studies on a material whose constituent molecules have a weak transverse dipole moment provide clear evidence of a first-order smectic-A–smectic-C transition. In addition, results on materials belonging to the *same* homologous series of compounds show that this transition can be driven from second order to first order simply by reducing the temperature range of the smectic-A phase.

Smectic-A (Sm-A) and smectic-C (Sm-C) liquid-crystalline phases are characterized by a one-dimensional mass density wave whose vector is along the director (Sm-A) or inclined to it (Sm-C). If the constituent molecules are optically active, the chiral smectic-C (Sm-C^*) phase with ferroelectric properties is observed.[1] Experimental results suggest that for both Sm-A–Sm-C and Sm-A–Sm-C^* transitions, the tilt angle plays the role of the primary order parameter, while the spontaneous polarization in the Sm-C^* plays a secondary role for the Sm-A–Sm-C^* transition.[2] Although the Sm-A–Sm-C transition was expected to be heliumlike, studies have shown that the experimental data can be very well described by a mean-field energy expression including a sixth-order term.[3,4] Recent x-ray studies[5] have established the existence of a first-order Sm-A–Sm-C^* transition. Subsequently[6] a crossover from a first-order Sm-A–Sm-C^* transition to a second-order one and a consequent tricritical point was reported. However, the crucial factor that drives this transition to first order is still not quite clear.

Although earlier studies on a number of compounds[7] indicated the possibility of observing a first-order Sm-A–Sm-C transition by shrinking the temperature range of the Sm-A phase, Liu *et al.*[8] have argued in a recent paper that the Sm-A–Sm-C (or Sm-C^*) transition may not become first order by reducing the Sm-A phase temperature range alone. These authors have also concluded that the magnitude of the transverse dipole moment of the constituent molecules has a strong effect on the nature of the transition. In this Rapid Communication, we present results that are at variance with this argument. High-resolution x-ray measurements conducted on a material having a weak transverse dipole moment,[9] viz., the tenth homolog of the series terepthal-bis-alkylaniline (TBDA —$n=10$), provides clear evidence of a first-order Sm-A–Sm-C transition. Furthermore, results obtained on a lower homolog (TBOA—$n=8$) and an intermediate mixture of $n=8$ and 10 confirm that the crossover from second-order to first-order Sm-A–Sm-C transition does not depend on the magnitude of the transverse dipole moment, but occurs purely due to a reduction in the temperature range of the Sm-A phase.

The experiments have been conducted using an aligned Sm-A phase obtained by cooling the sample at a slow rate ($\sim 1\,^\circ$C/h) from the isotropic phase in the presence of an *in situ* 0.8 T magnetic field provided by a pair of samarium cobalt magnet pieces. The x-ray setup was essentially identical to the one described earlier[10] with some modifications. A Ge monochromator having a much larger focal length and a linear position sensitive detector (PSD-Braun OED50) in conjunction with a multichannel analyzer (Braun MCA 3/1) were used in the present setup, instead of the quartz monochromator and scintillation counter used previously. The precision in the determination of the wave vector was 2×10^{-4} Å^{-1} while the resolution in the equatorial direction was 1×10^{-3} Å^{-1} half-width at half maximum (HWHM). The temperature was maintained to a constancy of 10 mK during each measurement.

Figure 1 shows PSD scans taken in the immediate proximity of the Sm-A–Sm-C transition in TBDA. The onset of the transition is characterized by the x-ray diffraction pattern [Fig. 1(b)] consisting of two quasi-Bragg peaks, at wave vectors corresponding to both Sm-A and Sm-C

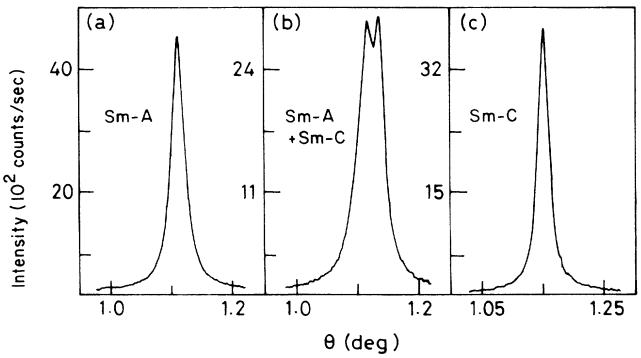

FIG. 1. Raw PSD scans taken along the equatorial direction in the (a) Sm-A phase, (b) two-phase region, and (c) Sm-C phase of TBDA.

phases, signifying a two-phase region. This is exactly as is expected, and indeed seen earlier for a first-order transition between two smectic phases having different layer periodicities.[5,11,12]

The temperature variation of the layer spacing d across the Sm-A-Sm-C transition is plotted in Fig. 2, which shows characteristic features of a first-order phase transition, viz., a jump in the layer spacing accompanied by a two-phase region in which the d values corresponding to both the phases coexist. As already mentioned, the order parameter for the Sm-A-Sm-C transition is the tilt angle ϕ of the director with respect to the layer normal. We have calculated ϕ using the expression,

$$\phi = \cos^{-1}(d_{\text{Sm-}C}/d_{\text{Sm-}A})$$

where $d_{\text{Sm-}A}$ and $d_{\text{Sm-}C}$ are the layer spacing values in the Sm-A and Sm-C phases, respectively, $d_{\text{Sm-}A}$ being the value measured at the commencement of the transition. The variation of tilt angle as a function of temperature is plotted in Fig. 3 which, as for a first-order transition, shows a discontinuous jump. It may be mentioned here that although previous x-ray studies[13,14] had indicated the occurrence of a first-order Sm-A-Sm-C transition in substances with weak transverse dipole moments, the data were not of sufficiently high resolution—as the authors themselves point out[14]—to yield conclusive results. Thus, we have observed clear evidence of the existence of a first-order Sm-A-Sm-C transition in such materials.

Having observed a first-order Sm-A-Sm-C transition in TBDA, a material with a Sm-A phase range of $\sim 1.8\,^{\circ}\text{C}$ only, we proceeded to investigate whether the strength and order of this transition is affected by merely increasing the range of the Sm-A phase without changing the basic structure of the constituent molecules. With this in view, we have studied a lower homolog, TBOA, and a binary mixture of 10% TBOA and TBDA (molar concentration). Figure 3 shows the temperature variation of tilt angle and Table I gives the range of the Sm-A phase and the jump in tilt angle at the transition for all the three materials. It is clearly seen that as the range of Sm-A phase decreases, the order of the transition changes from second to first and increases in strength with a further decrease in the range.

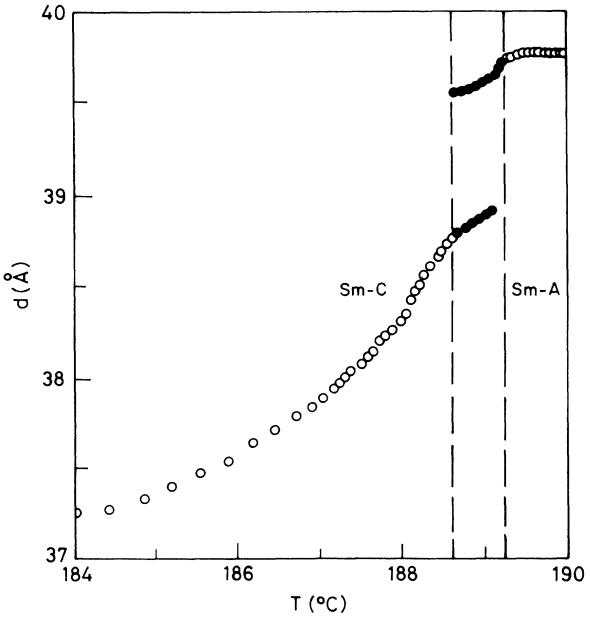

FIG. 2. Temperature variation of the smectic layer spacing (d) in the vicinity of the Sm-A-Sm-C transition of TBDA.

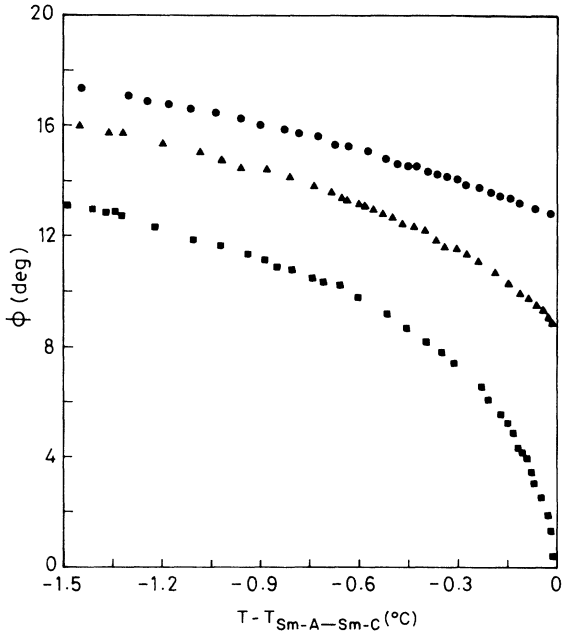

FIG. 3. Variation of the Sm-C tilt angle as a function of reduced temperature for TBDA (●); 10% TBOA+TBDA mixture (▲), and TBOA (■).

Thus, we have shown that even a substance having a weak transverse dipole moment can exhibit a first-order Sm-A-Sm-C transition and that it can become second order by just increasing the range of the Sm-A phase. Perhaps the argument of Liu *et al.*[8] has to be generalized to explain our results: It is possible that if the transverse dipole moment is strong, materials with a large range of Sm-A phase can show a first-order transition, while for materials with weak transverse dipole moment the range has to be much narrower for the same effect to be seen. Evidently systematic investigations on many more materials are needed in this direction.

TABLE I. The temperature range of the Sm-A phase ($T_{I\text{-Sm-}A} - T_{\text{Sm-}A\text{-Sm-}C}$) and the jump in the tilt angle ($\Delta\phi$) at the Sm-A-Sm-C transition for the materials studied (where $T_{I\text{-Sm-}A}$ is the isotropic–smectic-A transition temperature).

Material	$T_{I\text{-Sm-}A} - T_{\text{Sm-}A\text{-Sm-}C}$ (°C)	$\Delta\phi$ (deg)
TBOA	10.0	0
10% TBOA+TBDA	2.9	8.9
TBDA	1.8	12.8

The authors are highly indebted to Professor S. Chandrasekhar for his very keen interest in this work and for many valuable discussions. Thanks are also due to Larry Maurer for his help in the preparation of the compounds. One of us (M.E.N.) acknowledges support from the National Science Foundation Grant No. 8818561.

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