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Evidence of a first-order smectic-A–smectic-C^* transition and its approach to tricritical behavior

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Evidence of a first-order smectic-A–smectic-C^* (SmA-SmC^*) transition is presented. Detailed x-ray studies on 4-(3-methyl-2-chloropentanoyloxy)4′-heptyloxybiphenyl show that the SmA-SmC^* transition in this material is characterized by a discontinuous jump in the layer spacing (and hence in the tilt angle) and by a narrow two-phase region in which the density modulations due to the smectic-A and the smectic-C^* phases coexist. Addition of a second compound drives the SmA-SmC^* transition towards second order.

Smectic-A (SmA) and smectic-C (SmC) liquid crystals can be characterized as orientationally ordered fluids with a one-dimensional mass density wave: in the A phase the wave vector of this density wave is along the director and in C it is at an angle. When the molecules are optically active, a chiral smectic-C (or -C^*) phase[1] is observed which exhibits ferroelectric properties.[2] Experimental evidence indicates that the SmA-SmC^* transition is mainly driven by intermolecular forces producing the C phase and not by a ferroelectric coupling between permanent dipoles.[3] The spontaneous polarization of the C^* phase is thus a secondary order parameter while the tilt angle is (as in the case of the nonchiral C phase) the primary order parameter. Thus, the basic physics of the SmC^*-SmA transition may be expected to be the same as that of the SmC-SmA transition.

Experimentally, the SmA-SmC (or SmA-SmC^*) transition is generally found to be second order. Although it was initially proposed that this transition might exhibit heliumlike critical behavior[4] subsequent studies have clearly shown that the SmA-SmC as well as the SmA-SmC^* transition is mean-field-like with a sixth-order term in the Landau free-energy expansion.[5-8] Recently, Lien and Huang[9] predicted that the SmC-SmA transition can be driven to become first-order by large fluctuations of a nearby SmA-isotropic transition. However, the existence of a first-order SmA-SmC (or SmA-SmC^*) transition does not appear to have been established experimentally so far.

Recently, several new ferroelectric liquid crystals exhibiting SmA and SmC^* phases were found[10,11] which showed very high values of the spontaneous polarization. Investigation of their behavior in external electric fields as well as preliminary x-ray and differential scanning calorimetry (DSC) studies indicated that the SmA-SmC^* transition in some of these compounds is likely to be first order.[12] In this Communication we present the results of our high-resolution x-ray measurements on 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl or C7 which show that the SmA-SmC^* transition in this material is clearly first order and characterized by a two-phase region in which the density modulations of the SmA and the SmC^* phases coexist. We also present preliminary studies on mixtures of C7 with another material, 4-heptyloxy-4′-decyloxybenzoate (70 PDOB) which indicate the existence of a tricritical point for the SmA-SmC^* transition.

The experiments have been conducted using a computer-controlled Guinier diffractometer (Huber 644) described earlier.[13] Copper $K\alpha_1$ and $K\alpha_2$ lines were separated and only the former was used for the experiments. An aligned SmA phase was obtained by cooling the sample at a very slow rate (~300 mK/h) from the isotropic to the SmA phase in the presence of a 2.4-T magnetic field. The aligned sample was then transferred along with the temperature controlled oven to the goniometer head of the diffractometer. The accuracy in the determination of the wave vector in the SmA and SmC^* phases was 2×10^{-4} Å^{-1} while the resolution in the equatorial direction (also the scanning direction) was 3×10^{-3} Å^{-1}. The temperature was maintained to a constancy of 5 mK during each measurement.

Figure 1 shows the diffractometer scans taken in the

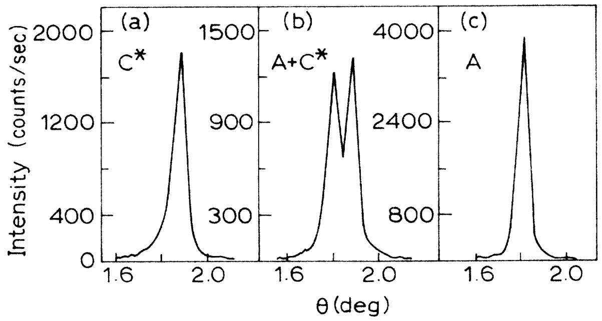

FIG. 1. Raw diffractometer traces taken along the equatorial direction in the (a) SmC^* (53.9 °C), (b) two-phase region (54.0 °C) and (c) SmA (54.06 °C) of 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (C7). The coexistence of two density modulations in the two-phase region signifies that the smectic-A–smectic-C^* transition is first order.

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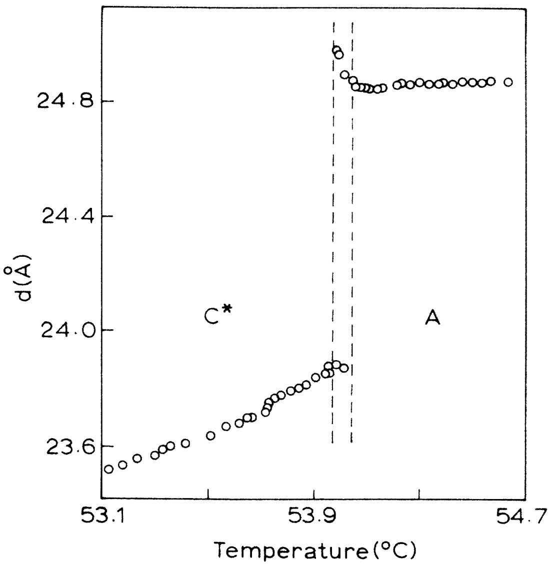

FIG. 2. Variation of the smectic layer spacing (d) with temperature in the vicinity of the smectic-A–smectic-C^* transition in C7. The vertical dashed lines indicate the two-phase region.

neighborhood of the SmA-SmC^* transition in C7. The signature of the SmA-SmC^* transition is a two-phase region whose diffraction pattern consists of the wave vectors corresponding to both the SmA and SmC^* phases. This is exactly as expected and indeed seen earlier for a first-order transition between two smectic phases with different layer periodicities.[14,15]

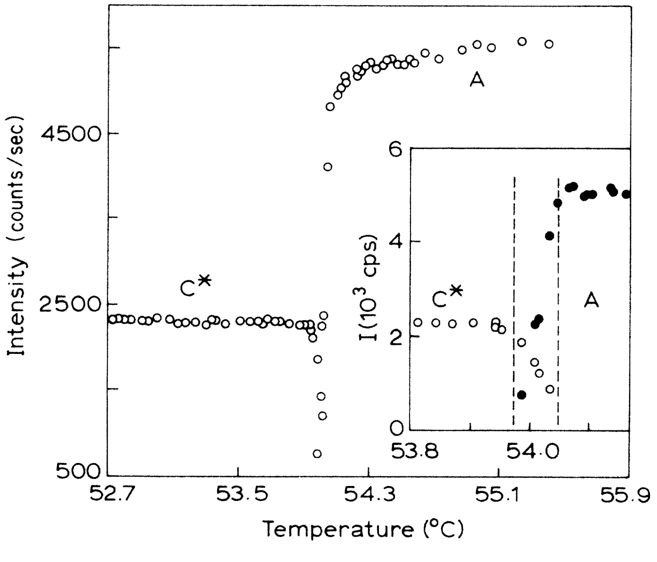

FIG. 3. Variation of the intensity of the x-ray diffraction maxima as a function of temperature for C7. The data in the immediate vicinity of the SmA-SmC^* transition are shown on an enlarged scale in the inset. Solid and open circles in the inset correspond to the density modulations in the SmA and SmC^* phases respectively. A crossover of the intensity is seen in the two-phase region.

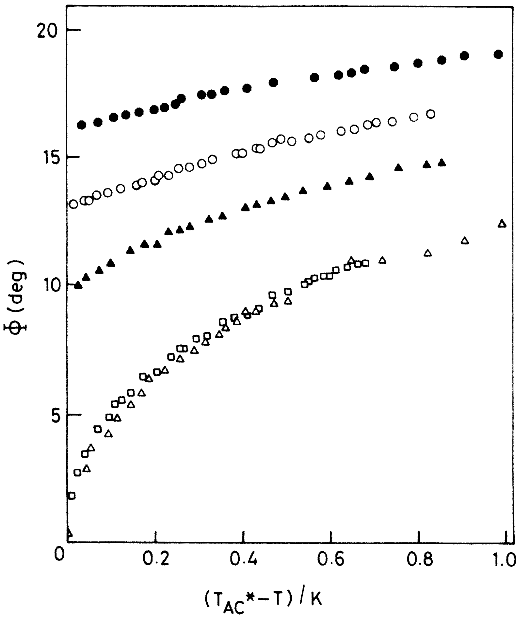

FIG. 4. Variation of the tilt angle ϕ calculated from the layer spacing data as a function of $T_{AC^*}-T$ for C7 and its mixtures with 70PDOB. The concentrations (expressed in mol% of 70PDOB) are ●, 0 (C7); ○, 5.15; ▲, 9.68; □, 15.0; and △, 19.4.

The temperature variation of the layer spacing d and the intensity of the quasi-Bragg peaks in the neighborhood of the SmA-SmC^* transition are plotted in Figs. 2 and 3 respectively. Both the figures show the existence of a two-phase region of about 50 mK. The characteristic features of this two-phase region are the coexistence of the layer spacing corresponding to both the SmA and the SmC^* phases and a crossover of the intensities of the x-ray diffraction peaks, the crossover occurring roughly in the midposition of the two-phase region. We have also evaluated the tilt angle ϕ in the SmC^* phase by the expression $\phi=\arccos(d_{C^*}/d_A)$ where d_A and d_{C^*} are the layer spacings in the SmA and SmC^* phases respectively, d_A being taken as the value as measured just before the commencement of the two-phase region. It may be pointed out that the tilt angle obtained directly from a "four-spot" x-ray diffraction picture (photographic technique[16]) was found to be in agreement with that evaluated from the layer spacing data. These data which are presented in Fig. 4 (closed circles) show that at the SmA-SmC^* transition ϕ exhibits a discontinuous jump ($\sim 15°$). Thus, we have observed for the first time clear evidence of the existence of a first-order SmA-SmC^* transition.

Having observed a first-order SmA-SmC^* transition, it is relevant to ask whether the transition can be driven to second order and hence towards a tricritical point by adding a suitable second component. We have attempted to do this by adding 70PDOB to C7. Preliminary results of the variation of the tilt angle (determined as explained earlier) for a series of mixtures of 70PDOB in C7 are also given in Fig. 4. It is clear that with increasing concentration of the former the jump in ϕ at the SmA-SmC^* transition decreases until finally for mixtures with $x \geq 15$

mol%, the tilt angle continuously goes to zero indicating thereby that the transition has become second order for this mixture. We have therefore shown, albeit somewhat qualitatively, that a tricritical point for the Sm*A*-Sm*C** transition exists for mixtures of C7 with 70PDOB in the concentration range between 10 and 15 mol%. It would be of considerable interest to look in these mixtures for a mean-field-like to tricritical crossover as discussed by Lien and Huang.[9] Such a study would help in a further understanding of the smectic-*A*–smectic-*C** transition.

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