Behavior of Susceptibility and Polarization near a Smectic-*A* –Ferroelectric-Smectic-*C* Tricritical Point

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A binary liquid-crystal system possessing a tricritical point in its smectic-*A*–ferroelectric-smectic-*C* phase boundary is studied. The electroclinic tilt susceptibility and the spontaneous polarization are measured on both the first-order and the second-order side of the tricritical point. The experimental results are compared with predictions of a simple Landau model. Good agreement with mean-field behavior is found.

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Smectic-*A* (Sm*A*) and smectic-*C* (Sm*C*) liquid-crystal phases are orientationally ordered fluids possessing a one-dimensional density wave. The director (i.e., the average direction of the long molecular axes) is either parallel (Sm*A*) or tilted by an angle θ (Sm*C*) with respect to the density wave vector. If these phases are composed of chiral molecules, the reduced symmetry of the material leads to a (basically linear) coupling between the tilt angle θ and the electric polarization, resulting in a ferroelectric spontaneous polarization in the Sm*C* phase[1] and quasipiezoelectric behavior (electroclinic effect)[2] in the Sm*A* phase which becomes tilted in an external electric field. As a further consequence of the molecular chirality the tilt direction in the ferroelectric-Sm*C* phase spirals around the density wave vector, thereby building up a helical superstructure with a periodicity of usually several microns. However, the phase transition from Sm*A* to ferroelectric Sm*C* in chiral compounds is driven by the same tilt-producing molecular interactions as the Sm*A*-Sm*C* transition in nonchiral substances, the tilt angle θ corresponding in both cases to the primary order parameter.

The nature of the Sm*A*-Sm*C* transition is of considerable interest. Generally, Sm*A*-Sm*C* and Sm*A*-ferroelectric-Sm*C* transitions are observed to be of the second-order type describable by an extended mean-field model.[3] Since 1986, however, examples of a first-order Sm*A*-Sm*C* transition were found in some ferroelectric liquid crystals exhibiting high values of the spontaneous polarization.[4] Several factors, such as the width of the Sm*A* phase range,[3(a)] the amount of spontaneous polarization,[5] and the value of the molecular dipole moment,[6(a)] may influence the nature of the transition, resulting in a large variety of experimentally observable behaviors.[6]

Binary systems consisting of a first-order Sm*A*-Sm*C* compound and a second-order Sm*A*-Sm*C* compound exhibit a tricritical point (TCP) in their Sm*A*-Sm*C* phase boundary where the nature of the transition changes from first order to second order.[4(b)] The investigations of these tricritical systems are of interest with respect to the origin of the first-order Sm*A*-Sm*C* behavior and will contribute to the understanding of tricritical phenomena in general. Recently, Shashidhar *et al.*[7] have reported a high-resolution study of the tilt angle near a Sm*A*-Sm*C* TCP. They found a crossover from mean-field to mean-field-tricritical behavior on approaching the TCP from the second-order side. Also, a detailed calorimetric study[8] of a Sm*A*-Sm*C* TCP has been presented.

In this Letter, we present the first study of the electroclinic tilt susceptibility (which is a good approximation to the generalized susceptibility of the Sm*A*-Sm*C* transition) and of the spontaneous polarization in the vicinity of a Sm*A*-ferroelectric-Sm*C* TCP. The experimental results indicate a mean-field-like behavior describable by a simple Landau model.

Our binary system consists of the compound (*S*,*S*)-4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (abbreviated as C7), which shows a first-order Sm*A*-Sm*C* phase transition,[4(b)] and the compound 4-butyloxyphenyl-4′-decyloxybenzoate (abbreviated as 10.O.4), which shows a second-order Sm*A*-Sm*C* transition. We have prepared ten binary mixtures in the composition range between 0 and 20 mole% 10.O.4. In an earlier study[9] we have shown that the 20% mixture shows a second-order Sm*A*-Sm*C* transition; the results described below indicate that the TCP is in the composition range between 10 and 11 mole% 10.O.4. The samples fill a conductively coated glass cell (thickness 10 μm, electrode area 16 mm^2) with planar orienting surfaces. The cell is placed into a two-stage oven providing a temperature resolution better than 10 mK. The oven allows for the optical observation of about 1 mm^2 of the sample area and is placed under a polarizing microscope between crossed polarizers.

The electroclinic tilt susceptibility $d\theta/dE$ (θ denotes the field-induced tilt, E denotes the applied electric field) in the Sm*A* phase is determined by the lock-in method[10,11] measuring the amplitude of the modulation of transmitted light caused by a tilt-inducing electric field (120-Hz sine wave, 0.02–0.04 V_{rms}). The inset of Fig. 1 shows the temperature dependence of the recipro-

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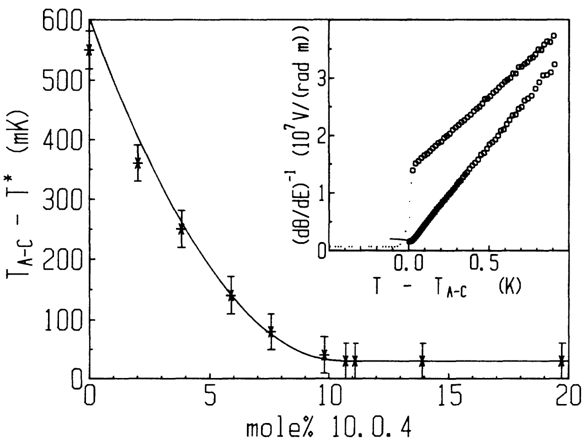

FIG. 1. Variation of the difference between the Sm*A*-Sm*C* transition temperature $T_{A\text{-}C}$ and the extrapolated divergence temperature T^* near the tricritical point at 10.5 mole%. The solid line corresponds to the values calculated by Eq. (3) plus a constant offset of 30 mK (see text). Inset: Temperature dependence of the reciprocal tilt susceptibility in the Sm*A* phase: upper curve, pure C7 (first order); lower curve, 10.7% mixture (close to tricritical).

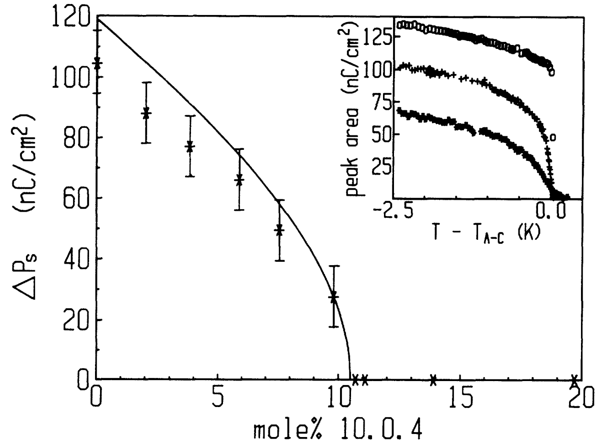

FIG. 2. Variation of the jump of the spontaneous polarization at the phase transitions near the tricritical point at 10.5 mole%. The solid line corresponds to the values calculated by Eq. (4). Inset: Temperature dependence of the area of the polarization current peak. The values are divided by twice the electrode area and correspond to the spontaneous polarization, except very close to the transition (see text). Upper curve: pure C7 compound (first order); middle curve: 10.7% mixture (close to tricritical); lower curve: 19.7% mixture (second order).

cal tilt susceptibility for a first-order and a second-order sample. Obviously, the linear (Curie-Weiss-like) behavior can be described by a simple power law of the form

$$d\theta/dE \propto (T-T^*)^{-\gamma}, \tag{1}$$

with T^* denoting the divergence temperature and the value of the exponent γ being close to 1 in accordance with a recent measurement of another liquid-crystal sample.[11] If we cool a first-order sample from Sm*A* to Sm*C*, the phase transition occurs before the sample reaches the divergence temperature T^*: For the pure C7 compound we find $T_{A\text{-}C} - T^* = 550$ mK (T^* determined by linear extrapolation). For a second-order transition the transition temperature should coincide with the divergence temperature and accordingly we observe a decrease of the values of $T_{A\text{-}C} - T^*$ if we approach the TCP by increasing the 10.O.4 portion of our sample (Fig. 1). On the other hand, our data indicate that the difference $T_{A\text{-}C} - T^*$ does not become exactly zero for the second-order transitions but retains a finite value of about 30 mK. This behavior may be interpreted as a consequence of the helical tilt orientation in the Sm*C* phase: In a strict sense, our tilt susceptibility, measured by a homogeneous field, does not correspond to the generalized susceptibility diverging at the Sm*A*-ferroelectric-Sm*C* phase transition, which can be measured only by a helicoidal field.[12,13] Thus, we cannot expect a true divergence of our homogeneous tilt susceptibility.

However, a more important result is that the behavior of the susceptibility is described by a power law with the value of the exponent γ being close to the mean-field value of 1 for all our mixtures, regardless of whether first or second order or whether close to or far from the TCP. The data shown in Fig. 1 indicate that the TCP is in the composition range of 10–11 mole% 10.O.4.

We now turn to our measurements of the spontaneous polarization P_s. The values of P_s are determined by integrating the displacement current peak which appears due to the reversal of P_s as a response to an applied triangular voltage (5 Hz, 20 $V_{p\text{-}p}$) as described in Ref. 14. As shown in the inset of Fig. 2, the values of a first-order sample clearly exhibit a jump at the phase transition where P_s drops discontinuously to zero. The magnitude of the P_s discontinuities is plotted in Fig. 2 for all our samples. In agreement with our susceptibility measurements, the polarization data indicate that the TCP is in the composition range between 10 and 11 mole% where the P_s discontinuities vanish.

For the second-order samples a difficulty arises which is inherent in all experimental methods of measuring the spontaneous polarization by reversing it by an applied electric field: The presence of the electric field destroys the phase transition by inducing a nonzero order parameter, i.e., a tilt angle, in the high-temperature phase. In a strict sense, a second-order Sm*A*-ferroelectric-Sm*C* transition can exist only in the absence of an external electric field. For the susceptibility measurements this effect may be neglected because of the very low values of the applied field; for the polarization measurements, however, where we use a field 3 orders of magnitude larger, the effect of the "smearing out" of the phase transition is to observe an S-like shape of the temperature dependence of our polarization data near the transition.[15] Thus, in the immediate vicinity (10–100 mK) of the phase transition, the integral of the polarization current peak does not exactly correspond to the true (field free) value of P_s. However, for temperatures below $T_{A\text{-}C} - 0.1$ K the peak integral can be considered to equal $2P_sA$ (A denoting the electrode area). Concerning the behavior near the TCP our polarization data show the same crossover behavior observed for the tilt angle in an earlier study:[7] For the mixture close to the TCP the polarization varies as

$$P_s \propto (T_{A\text{-}C} - T)^{\beta}, \tag{2}$$

with the value of the exponent β being close to the tricritical value of 0.25 in the whole temperature range of the SmC phase, whereas for the mixtures far from the TCP the value of β depends on the closeness to the transition temperature ($\beta \approx 0.25$ far below the transition, $\beta \approx 0.5$ near the transition, Fig. 3).

Our results reported so far are consistent with a mean-field-tricritical behavior of the tilt susceptibility and the spontaneous polarization. Recently, we have shown[9] that the SmA-SmC transition of the C7 compound in an external electric field is well described by a simple Landau model using a free energy consisting only of the series expansion in powers of the tilt angle and a bilinear coupling between tilt and polarization. Here we make some quantitative comparisons between our results and the predictions of this Landau model concerning tricritical behavior. According to the Landau model[9] the difference $T_{A\text{-}C} - T^*$ for the first-order transitions and the jump of the polarization at the first-order transitions ΔP_s are predicted to be

$$T_{A\text{-}C} - T^* = 3b^2/16ac \tag{3}$$

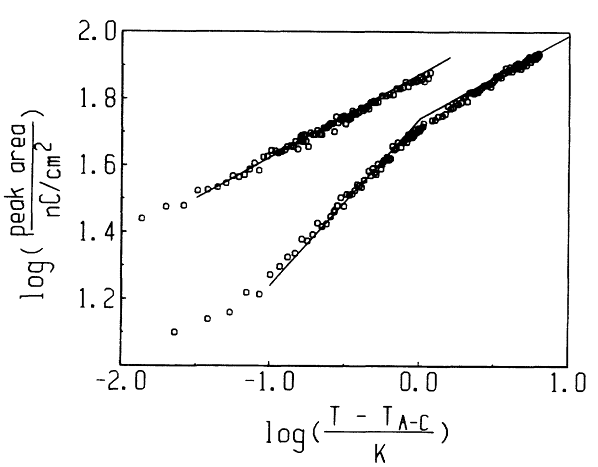

FIG. 3. Log-log plot of the temperature dependence of the spontaneous polarization. Upper curve: 10.7% mixture (close to tricritical), the slope of the solid line is 0.25. Lower curve: 19.7% mixture (second order, showing crossover behavior), the slopes of the solid lines are 0.5 and 0.25.

and

$$\Delta P_s = C\chi_0\varepsilon_0(-3b/4c)^{1/2}, \tag{4}$$

where a, b, and c are the coefficients of the θ^2, θ^4, and θ^6 term, C is the bilinear tilt-polarization-coupling constant, χ_0 is the electric susceptibility for fixed θ, and ε_0 is the vacuum permittivity. The sign of the coefficient b determines whether the model describes a first-order ($b<0$), a second-order ($b>0$), or a tricritical transition ($b=0$). In order to describe the experimental behavior by the theoretical model, we have to relate b to the composition of our mixtures in a way that b changes its sign at the tricritical composition of about 10.5%. We assume as the simplest possibility a linear relation:

$$b = b^0(0.105 - x_{10.O.4})/0.105. \tag{5}$$

Here, b^0 denotes the value of the pure C7 and $x_{10.O.4}$ the mole fraction of 10.O.4. The number 0.105 corresponds approximately to the composition of the tricritical mixture.

Furthermore, because we mix a chiral compound (ferroelectric) with a nonchiral compound (nonferroelectric, coupling constant $C=0$), we assume a linear variation of the bilinear tilt-polarization-coupling constant C from the value of the pure C7 to zero in the pure 10.O.4:

$$C = C^0(1 - x_{10.O.4}), \tag{6}$$

where C^0 is the value of the pure C7. The values of b^0 and C^0, and of a, c, and χ_0 (which are for simplicity assumed to stay constant with increasing $x_{10.O.4}$) are given in Ref. 9.

Before doing a quantitative comparison we should note a qualitative agreement between the experimental behavior and the theoretical model: If we relate the parameter b linearly with the distance to the TCP, we expect (on the first-order side of the TCP) for the $T_{A\text{-}C} - T^*$ vs $x_{10.O.4}$ curve a positive curvature, whereas the ΔP_s vs $x_{10.O.4}$ curve should show a negative curvature, as is indeed observed experimentally (Figs. 1 and 2).

The quantitative values of $T_{A\text{-}C} - T^*$ and ΔP_s calculated using Eqs. (3)–(6) are shown as the solid lines in Figs. 1 and 2, respectively. Concerning $T_{A\text{-}C} - T^*$, we have added an "offset" of 30 mK to the values calculated by Eq. (3) in order to take into account the effect of the helical tilt orientation in the SmC phase.[16] There is a reasonable agreement between the experimental data and the values predicted by our simple theoretical approach, and no obvious deviation from the mean-field behavior describable by Landau theory is to be observed.

In conclusion, we have presented the first measurements of the electroclinic tilt susceptibility and of the spontaneous polarization in the vicinity of a SmA–ferroelectric-SmC tricritical point. The reciprocal susceptibility shows a linear (Curie-Weiss-like) temperature dependence on both the second-order and the first-order side of the TCP. The discontinuity of the spontaneous polarization at the first-order transitions shrinks to zero on approaching the TCP. On the second-order side, the spontaneous polarization shows a crossover behavior similar to the behavior observed for the tilt angle.[7] Our experimental results indicate a mean-field-like behavior near the TCP.

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