Interferometric measurements at a smectic-A–smectic-C-phase transition

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We report measurements of the tilt angle ψ near the second-order SmA-SmC transition in azoxy-4,4′-di-undecyl-α-methylcinnamate. Data analysis shows that this transition, which belongs to the same universality class as ^{4}He, has, in the absence of a constraining field, a critical exponent $\beta = 0.36 \pm 0.005$.

The smectic-A–to–smectic-C (A-C) phase transition in liquid crystals[1] is characterized by the continuous emergence of an angle between the director $\vec{n}$ and the normal to the layers $\vec{z}$ [Fig. 1(a)]. This tilt angle ψ may be identified with the amplitude of the order parameter of the transition; and the azimuthal angle ϕ giving the tilt direction may be associated to its phase. That means that this transition belongs to the helium category ($d=3$, $n=2$), with which some similarities should exist.[2] In reality, the experimental situation is confused. The few existing studies of the A-C transition report critical exponents from mean-field[3,4] to nonclassical values.[5] The reason for this discrepancy is probably that, as for all phase-transition measurements, the experimentalist has to overcome two major difficulties inherent in the second-order phase transitions:

(a) At the transition temperature T_c, the susceptibility of the order parameter diverges; therefore, any small additional field makes large perturbations in the critical region, and particularly an apparent shift of T_c.

(b) Owing to stabilization time and to the difficulties of the ψ measurement process, each T correction needs time; therefore, T_c cannot be approached conveniently, nor directly measured.

In this Communication, we report measurements of the tilt angle ψ (i.e., the amplitude of the order parameter) versus the temperature T in order to determine, in particular, the critical exponent β at the A-C transition in pure azoxy-4,4′-di-undecyl-α-methylcinnamate (AMC-11). The experiments were carried out using an interferometric method which allows a high resolution of the tilt angle, provided that the alignment of the sample is homogeneous. Thus we have to be careful about the orientation of the sample and check it constantly.

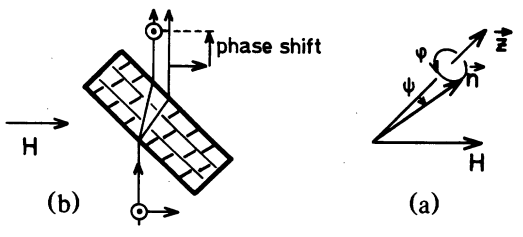

FIG. 1. (a) ψ is the angle defined by the normal to the layers $\vec{z}$ and the director $\vec{n}$. The azimuthal angle ϕ measured from the zH plane specifies the direction of the director. (b) The laser light splits into two rays of orthogonal polarizations inside the sample. The phase shift between them is measured and yields the tilt angle ψ.

The sample is homeotropically aligned in the A phase using a silane coating of the glass plates.[6] In the C phase, in order to suppress the director tilt degeneracy, we apply a weak magnetic field H (which forces $\phi=0$). The angle (Fig. 1) between the normal to the layers $\vec{z}$ and H is chosen to be equal to 45° in order to maximize the orienting torque. In this way we can perfectly orient the smectic-C samples with the layers parallel to the plates. The uniformity of the alignment and the absence of defects make the sample as transparent as in the A phase. Probably because of the small thickness of our samples (<1 mm), and because of the strong surface anchoring imposed by the silane, the layers do not tilt, in spite of magnetic field action. This is demonstrated by the absence of remanent tilt when returning to the A phase.

In order to avoid excessive chemical degradation, the sample is sealed and is then left to stabilize for a week. During this time, the gradients of T_c (probably due to unavoidable oxidation when preparing the sample) are reduced under the action of molecular diffusion to an unestimable value; i.e., the sample gives the same ψ value over its whole width (4 mm). In spite of sealing, a drift of T_c persists which is less than 10^{-3} K/h. Although this drift is small, we have to organize the measurements in various series of short duration (a few hours) and make a small correction of T_c on each point, taking time into account. The sample is placed inside a two-stage servo-controlled oven, the temperature being measured by means of a platinum resistor. This oven has to be small to fit inside the electromagnet; it has also to be fast and precise. Its time response is a few seconds, and its accuracy is better than 10^{-3} K. Note that we have to take into account the small magne-

toresistance of the platinum probe.

Now, let us come to the principle of the ψ measurements. A He-Ne laser beam polarized at 45° irradiates the sample at an incident angle of 45° (Fig. 1). Inside the liquid crystal, it splits into two rays of ordinary and extraordinary polarizations. Outside the sample there is a phase shift between these two rays. By use of a Soleil compensator, this phase shift can be compensated for, restoring the initial polarization which is extinguished by a crossed polarizer. If now some tilt angle ψ occurs, the phase shift increases linearly with ψ. The measurement of this phase-shift increase, when one knows the three optical indices with their temperature dependence,[7] allows us to calculate ψ exactly. This direct and first-order measurement of ψ is very accurate ($\sim 3\times10^{-4}$ rad, depending on sample thickness and alignment quality).

The magnetic field couples to the phase ϕ of the order parameter, giving a definite alignment; it also couples to its amplitude ψ, according to the weak-field approximation

$$\frac{\chi_a H^2}{2} = a(T)\psi + b(T)\psi^3 \ , \qquad (1)$$

where χ_a is the anisotropic part of the magnetic susceptibility, and a and b are the usual Landau coefficients.[2] For each temperature, we measure ψ for a set of H values from 0 to 16 kG, and we make a least-squares fit of these measurements to Eq. (1). In the A phase, we thus obtain $a(T)$, which gives the critical exponent[8] $\gamma = 1.3$; in the C phase, we find the extrapolated value of the tilt in zero magnetic field $\psi(T,H=0)$ (simply denoted as ψ) which should obey the power law $\psi = \psi_0(T_c - T)^{\beta}$.

Now, let us compare our results to this power law. Since the transition could be weakly first order, it is not convenient to use in this equation the value of T_c extrapolated from the measurements in the A phase; it is more correct to consider T_c as unknown and to make a least-squares fit with the three independent parameters: β, ψ_0, and T_c. In Fig. 2(a) is presented such a fit of a series of measurements for a sample of 340-μm thickness: ψ vs $\Delta T = T_c - T$ (where $T_c \simeq 352$ K). The fit determines T_c, which is found to coincide, within 5×10^{-4} K, our temperature resolution, with the transition temperature deduced from the A-phase study. Consequently we can consider the A-C transition as second order down to 10^{-3} K.

In order to avoid the saturation effect of ψ far from T_c, the fitting is done excluding the points away from a cutoff temperature T_l. The accuracy of the experimental data and the quality of the fit can be appreciated from the arrows which magnify 100 times the errors is ψ. This shows that the statistical error in ψ is about 2×10^{-4} rad. Such precision is at least an order of magnitude better than any other measurement of the C order parameter to date. For the first three points of the fit, the error is rather an error on the temperature than on ψ, and calculating it, we find that it is less than 5×10^{-4} K. Such a negligeable error means in reality that these first points are under the control of the fitting. Their role is just to define T_c; consequently, it is useless to get measurements closer to T_c within our present accuracy. Now, let us come back to the higher limit: We fit the data with different cutoff temperatures T_l and plot in Fig. 2(b) the resulting values of β with the calculated standard deviation as a function of $T_c - T_l$. This cutoff analysis shows the decrease of β due to ψ saturation far from the transition. On the other hand, when decreasing $T_c - T_l$, i.e., when keeping fewer and fewer points in the fit, β stabilizes with diverging error bars. The saturation introduces a variation: $\delta\beta \simeq \delta\log\psi = \delta\psi/\psi$, where $\delta\psi \propto \psi^3$ is the saturation effect on the last fitted point; we deduce $\delta\beta \propto \psi^2 \propto T_c - T_l$. Therefore, to first order, the saturation of ψ deviates β by an exponential in the scales of Fig. 2(b). A least-squares fit correctly weighted by the error bars gives the best exponential (full line). We find that saturation begins when ψ reaches 0.1 rad, which is an exceptionally low limit in comparison with the literature. We deduce also the asymptotic behavior of the order parameter ψ and the value of β with its calculated standard deviation:

$$\psi = 0{:}18\,\Delta T^{\beta} \text{ rad} \ , \qquad (2)$$

and $\beta = 0.359 \pm 0.0015$. Such precision has been obtained on our best sample, but looking now at our

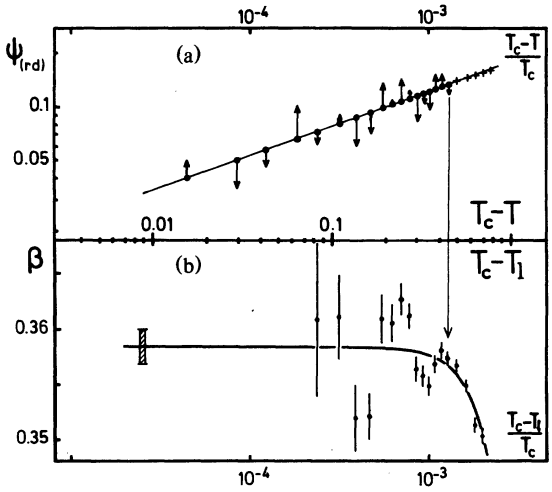

FIG. 2. (a) Log-log plot of the experimental data: ψ vs $\Delta T = T_c - T$ in kelvin (with $T_c \simeq 352$ K). The points such that $T < T_l$ (crosses) are not taken into account in this least-squares fit. The arrows display the errors $\delta\log\psi$ on each point (dots), magnified by 100. (b) Fitted β values with their associated error bars as a function of $T_c - T_l$. [The arrow shows the one corresponding to the fit displayed in (a).] Calculated β correction (full line) with its error bar. The asymptote yields $\beta = 0.359 \pm 0.0015$.

results on samples of almost the same alignment quality, we get independently $\beta = 0.36 \pm 0.005$. Although perfectly confident of the result of Fig. 2, we prefer to retain that last result, which is supported by several independent measurements.

In all the remaining samples which look more turbid, and thus which are of poorer alignment quality, with more numerous defects, we observe some hysteresis. It appears in two ways: first at a fixed temperature, a slight hysteresis of $\psi(H)$ when varying the magnetic field; second, a larger hysteresis effect of $\psi(H=0)$ when varying the temperature. Clearly the tilt angle lags slightly compared to the expected value given by (2) when T is increased or decreased. This can be understood the following way: Since the layer thickness changes with temperature,[9] the sample has to adjust the number of its layers; however, if too many defects (dislocations) are present, it will be difficult to form or to suppress a layer and this results in a constraining field which acts on the tilt ψ. If we take it into account,[8] all our measurements on samples of thickness varying from 48 to 690 μm are in perfect agreement with the asymptotic law (2). This anchoring of the layers is a general problem of defects. It should also exist in the unoriented samples of all the A-C transition measurements. It could then perturb the measurements of all the critical exponents at the transition, thus explaining the wide discrepancy mentioned above.[3-5]

We do the same analysis on the A phase,[8] with $a(T)$ being the inverse of the tilt susceptibility, and we find the nonclassical exponent $\gamma = 1.3$. Assuming the mean elastic constant $K \simeq 5 \times 10^{-7}$ (cgs) and $\chi_a \simeq 10^{-7}$ (cgs), we estimate the coherence length ξ in the C phase:

$$\xi = \left(\frac{K}{2a}\right)^{0.5} \sim 100 \Delta T^{-0.66} \text{ Å} \quad . \tag{3}$$

Now we can discuss the validity of the weak-field assumption in Eq. (1), which supposes that the magnetic energy per coherent volume is much smaller than kT. From (3) we deduce that it is true down to $\Delta T \simeq 10^{-2}$ K. In fact, the fits to Eq. (1) denote no anomaly when $\Delta T > 10^{-3}$ K.

In conclusion, we find nonclassical behavior, $\beta = 0.36$. This result can be discussed in terms of the Ginzburg criterion[10]

$$\frac{\Delta T_c}{T_c} = \frac{k^2}{32\pi^2 (\Delta C)^2 \xi_0^6} \quad , \tag{4}$$

where $\Delta C (= 10^6$ erg/cm^3 K) is the specific-heat anomaly[11] and $\xi_0 \sim 2$ Å is the correlation length at 0 K given by (3). Thus the limit of the classical region is around $\Delta T_c \sim 300$ K, which explains why we do not find a classical exponent for β. Note that Safinya *et al.*,[4] using the same Ginzburg argument, conclude the opposite: that it always has a mean-field value. This discrepancy arises because they have chosen $\xi_0 = 70$ Å from measurements taken at the nematic–smectic-A transition[12]; this transition concerns another order parameter. (Moreover and surprisingly, from their own data[12] we recalculate $\xi_0 \sim 3$ Å.) Nevertheless, their results[4] $\psi(T)$ coincide very well with ours for $\Delta T > 1$ K which reinforces the likelihood of similar behavior in A-C transitions.

Our result $\beta = 0.36$ is slightly different from that of the ^{4}He model, for which one expects[13] $\beta = 0.346$. The explanation could lie in the coupling between ψ and the smectic layers.[2] However, if the fluctuations of the layers are hindered by the plates,[14] we should revert to the helium model.[15] In our samples this would happen for ΔT smaller than 10^{-4} K.

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