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Magnetic-birefringence determination of the tilt susceptibility of the smectic-A–smectic-C phase transition in butoxybenzylidene heptylaniline

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We have used magnetically induced birefringence to determine the divergence of the susceptibility for the smectic-C order parameter in butoxybenzylidene heptylaniline (40.7). The critical exponent γ was 0.98 ± 0.04, consistent with a mean-field model and the Ginzburg criterion.

Both the smectic-A and -C phases of liquid crystals exhibit a one-dimensional density wave in a three-dimensional (3D) liquid with long-range nematic (molecular-orientational) order. In the A phase the density wave vector is parallel to the nematic director, while there is a finite tilt angle between them in the C phase. The A-C transition may be described by an order parameter[1] $\Psi_C = \Phi e^{i\psi}$ where Φ is the magnitude of the tilt angle and ψ is the azimuthal direction. If one ignores the Landau-Peierls instability of the density wave, then the A-C transition belongs in the universality class of the 3D XY model and superfluid helium. Some controversy has arisen, however, with both heliumlike and mean-field critical behavior being reported.[2–8] While it is widely accepted that the asymptotic critical behavior of the A-C transition should be heliumlike, this will only be observed within a critical temperature range ΔT_c of the transition temperature T_c. From the Ginzburg criterion[9] one estimates

$$\frac{\Delta T_c}{T_c} = \frac{k_B^2}{32\pi^2 (\Delta C)^2 (\xi_\parallel^0)^2 (\xi_\perp^0)^4} , \quad (1)$$

where ΔC is the mean-field heat-capacity jump, $\xi_\parallel^0$ and $\xi_\perp^0$ are the bare correlation lengths along and transverse to the director, and k_B is Boltzmann's constant. In order to clarify the situation, careful measurements of a number of properties on the same material is required. Preliminary results of such a series of measurements for butoxybenzylidene heptylaniline (40.7) have recently been reported.[10] The tilt angle measurements can be consistent with either critical behavior or with mean-field behavior with a large sixth-order invariant in the Landau free-energy expansion[11]; the specific-heat data strongly suggest mean-field behavior. A definitive answer can be provided by measurements of the exponent γ characterizing the divergence of the tilt susceptibility above the transition: for helium, $\gamma = 1.32$ and for mean field, $\gamma = 1.0$. We report the detailed results of such measurements in this Communication.

Samples of 40.7 were obtained from CPAC Organix and purified by recrystallization from ethanol. The material was placed between two microscope slides separated by 125 ± 5-μm Mylar spacers. The glass was coated with the surfactant hexadecyltrimethyl ammonium bromide (HTAB) to induce perpendicular (homeotropic) alignment. The sandwich was then inserted in a 5-cm-diameter brass cylinder which served as the oven. Light portholes, which were 3 mm in diameter, were covered by glass windows. Temperature was controlled by means of a Yellow Springs Instrument Model 72 proportional controller with a pair of Fenwal UUA33J4 thermistors (3000 Ω at 25 °C), which exhibit an extremely small magnetoresistance.[12] One thermistor was used for feedback to the controller circuit and one for temperature measurement. Long-term stability was about 2 mK in a constant field.

The birefringence apparatus is described in detail elsewhere.[13] Briefly, it consisted of a pair of Glan-Thomson polarizers with an extinction ratio of better than 10^{-6}; the sample and a Pockels cell (Lasermetrics LMA-4) were placed between the two crossed polarizers. An ac voltage at $\nu_0 = 280$ Hz was then applied to the Pockels cell to modulate its birefringence. For sufficiently small total birefringence the signal V from the detector had three frequency components, at $\nu = 0$, ν_0, and $2\nu_0$, such that $V_{\nu_0} \propto (\delta - \delta_p)$. δ and δ_p were the dc phase shifts due to the sample and Pockels cell birefringences, respectively, and $\delta = k(d_e n_e - d_o n_o)$. Here, d is the pathlength of the particular polarization component, n the index of refraction for that component, and e and o refer to extraordinary and ordinary polarizations, respectively. The wave vector of light k in our experiment was 9.93×10^4 cm^{-1}. To measure δ, a dc voltage proportional to δ_p was applied to the Pockels cell to cancel δ and thereby cancel out V_{ν_0}, as measured on a lock-in amplifier. Sensitivity in δ was estimated to be 2×10^{-3}.

The experimental geometry is shown in Fig. 1. The incident polarization is given by $(\hat{y} + \hat{z})/\sqrt{2}$ and the director orientation in zero field by $(\hat{x} + \hat{z})/\sqrt{2}$, i.e., 45° with respect to the incoming beam. In this configuration a magnetic field H applied along $\hat{z}$ exerts a torque on the molecular director, inducing a small tilt Φ of the director[14] [Fig. 1(b)]. For sufficiently small Φ (a few tenths of a degree), $\Phi \propto H^2$. Moreover, as the director tilts, a phase change $\Delta\delta \{ \equiv [\delta(H) - \delta(0)]\}$ between ordinary (parallel to $\hat{y}$) and extraordinary (parallel to $\hat{z}$) polarization components occurs, where $\Delta\delta = k\Delta(d_e n_e - d_o n_o) \propto \Phi$. Thus the $q = 0$ tilt susceptibility $\chi \equiv d\Phi/dH^2|_{H=0}$ is proportional to $d(\Delta\delta)/dH^2|_{H=0}$.

The sample was first heated into the nematic phase to achieve uniform alignment. It was then cooled into the smectic-A phase to a temperature just above T_c and the dc voltage applied to the Pockels cell was adjusted to cancel out V_{ν_0}, i.e., the $H = 0$ birefringence. Several different values of magnetic field H were then applied to achieve values of $\Delta\delta$ varying between 0.04 and 0.3, corresponding to a few tenths of a degree of tilt in Φ. For temperatures within 100 mK of T_c, the fields were typically between 2 and 15 kOe, increasing to fields between 40 and 75 kOe for temperatures more than 1 K above T_c. At each temperature, then, $d(\Delta\delta)/dH^2$ was obtained from the linear plots of $\Delta\delta$ vs H^2. Since the same approximate values of Φ were induced at each temperature point, the error bar in $d(\Delta\delta)/dH^2$ remained a constant fraction of the value of $d(\Delta\delta)/dH^2$, about $\pm 4\%$.

We note that, upon application of a field H, a small upward shift in temperature was observed, due to magnet heating and magnetoresistive effects in both the feedback and measuring thermistors. Very near T_c the shifts were under 0.5 mK, well within the temperature error bar. More than 1 K above T_c,

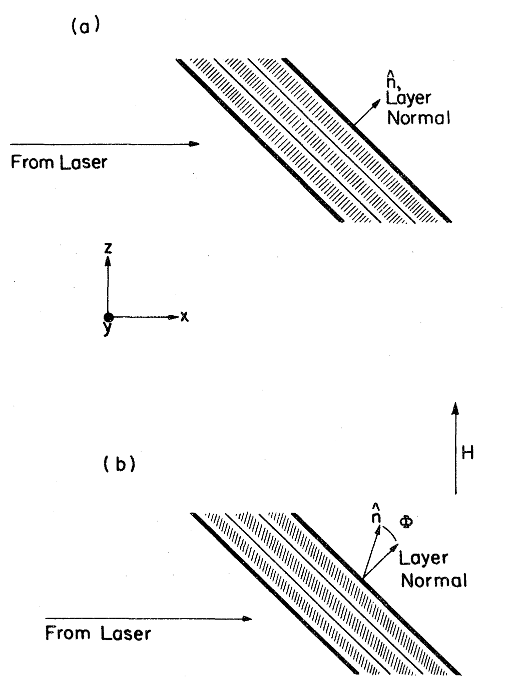

FIG. 1. Experimental geometry. The sample is oriented at 45° with respect to both the incoming laser and the magnetic field. (a) $H = 0$; (b) $H \neq 0$. Molecules tilt by angle Φ with respect to layer normal.

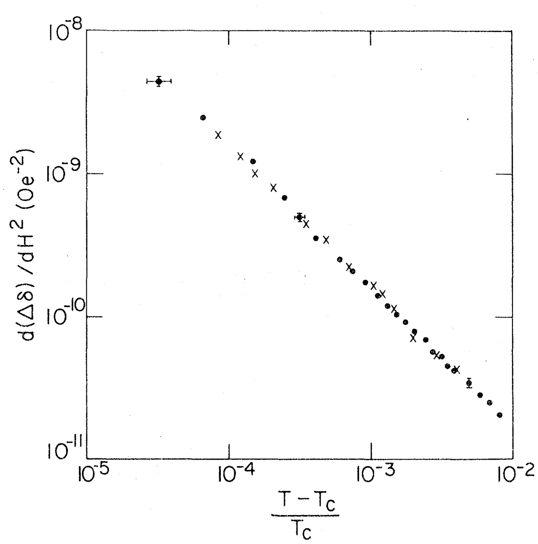

FIG. 2. Log-log plot of $d(\Delta\delta)/dH^2$, which is proportional to the susceptibility, vs reduced temperature, indicating a slope $\gamma = 0.98 \pm 0.04$ or two sets of data. Error bars in the ordinate are $\pm 4\%$, whereas the fractional error bar in the abscissa decreases for increasing reduced temperature. Typical error bars are shown in each decade of reduced temperature.

where higher fields were used, shifts of 10 to 30 mK were noted. These thermal effects were of little importance for two reasons: (1) the temperature shifts represented only a tiny fraction of the reduced temperature and (2) the quantity of interest (the field-induced phase change $\Delta\delta$) was at least two orders of magnitude larger than the corresponding signal associated with a small temperature change at zero field.

A three-parameter least-squares fit to the function $d(\Delta\delta)/dH^2 = a(T-T_c)^{-\gamma}$ was performed for each of two sets of data, shown in Fig. 2. Since the fractional error in $d(\Delta\delta)/dH^2$ remained constant over more than two decades of reduced temperature, a logarithmic weighting procedure was used. For the × and ● data, respectively, the fitted parameters were $a = (1.93 \pm 0.02) \times 10^{-13}$ and $(1.75 \pm 0.02) \times 10^{-13}$ Oe^{-2}, $T_c = 50.170 \pm 0.004$ and 50.308 ± 0.004 °C, and $\gamma = 0.98 \pm 0.04$ and 0.99 ± 0.04. (A nonweighted fit yields values of γ in the neighborhood of 0.96 to 0.97.) It should be noted that the temperature corrections discussed earlier have an insignificant effect on these results.

Comparing these values of γ to theoretical mean-field ($\gamma = 1$) and helium ($\gamma = 1.32$) values, it it clear that in the reduced temperature range reported, mean-field behavior was observed. This is consistent with the extremely small critical region $\Delta T_c/T_c \sim 1.5 \times 10^{-5}$ predicted by Eq. (1) using the bare correlation lengths and heat-capacity jump for 40.7 reported in Ref. 10. Our conclusion is that the A-C transition in 40.7 is unambiguously mean field over the observable reduced temperature range. This is likely true for most A-C transitions, including undecylazoxymethyl-cinnamate.[5,8] There is, however, one material in which heliumlike critical behavior combined with smaller bare correlation lengths has been reported[6]; this is an interesting candidate for further investigations.

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