High-resolution x-ray study of a smectic-A–smectic-C phase transition

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(Received 18 July 1979)

We report measurements of the tilt angle Φ and the planar spacing d_C near the second-order SmC-SmA transition in 4-n-pentyl-phenylthiol-4′-n-octyloxybenzoate ($8\bar{S}5$). We find that the ratio $\Phi/\cos^{-1}(d_C/d_A)$ is constant (1.2 ± 0.1) through the C phase, supporting a simple molecular-tilt model for the transition. For $5\times10^{-3} > 1-T/T_c > 3\times10^{-5}$, Φ exhibits mean-field behavior. A simple Ginzburg-criterion argument indicates that the true critical region should be unobservably small for most A-C transitions.

Smectic-A and smectic-C liquid crystals may be simply described as orientationally ordered fluids with one-dimensional mass-density waves.[1] The density wave may be either along (smectic A) or at an angle to (smectic C) the unique orientational axis. As recent theory and experiments have clearly illustrated, smectic liquid crystals manifest especially interesting fluctuation effects.[2] To date, most attention has been directed towards the nematic–smectic-A (N-A) transition which should be analogous to an anisotropic superconducting transition with short-range interactions but with the additional complication of algebraic decay of the positional correlations. A number of liquid crystals exhibit second-order smectic-A–smectic-C (A-C) transitions. As we shall discuss below, this should be much less complicated than the N-A transition, and indeed the simplest model predicts a direct isomorphism with the superfluid transition in helium.[1,3] The experimental situation is quite unsatisfactory, largely because the few existing studies of the A-C transition report exponents covering the range from mean field to helium $(d=3,n=2)$-like values.[4,5] In order to elucidate this problem we have carried out a high-resolution x-ray study of the A-C transition in 4-n-pentyl-phenylthiol-4′-n-octyloxybenzoate ($8\bar{S}5$) in a large magnetic field. We show that by carrying out such experiments in a magnetic field large enough to hold the liquid-crystal director fixed, one is able to measure both the tilt angle Φ and the lattice constant d simultaneously. This, in turn, enables us to demonstrate unambiguously in $8\bar{S}5$ that, in the language of structural phase transitions, Φ functions as the primary order parameter characterizing the A-C phase transition while the change in the planar spacing, $\Delta d = d_A - d_C$, functions as a secondary order parameter, that is, Δd varies as the square of Φ.

There are a number of models for the A-C transition with varying degrees of complexity.[3] Here we shall present the simplest picture, which, in fact, is completely adequate to describe all of our results. In the smectic-A phase the density wave, which in $8\bar{S}5$ is close to an ideal sine wave, is oriented along the nematic director. Hence, with a large magnetic field holding the director fixed in space, one observes a single peak at $q_A=(0,0,q_\parallel)$ with $q_\parallel=2\pi/d_A$ (here, we consider $q_\parallel>0$). In the limit that the molecule is symmetric in the azimuthal plane, one may then take as the tilt order parameter for the C phase $\pi_C=\Phi e^{i\psi}$; here ψ gives the azimuthal direction of the molecule with respect to the normal of the smectic layers, or equivalently of the layer with respect to the molecular axis. The invariance of the free energy under rotations of the molecules about the normal to the smectic layers is the analogue of gauge invariance in superfluid helium.[1,3] In this model the C phase is characterized by an isotropic two-component order parameter; hence one should observe asymptotic critical behavior identical to that of superfluid helium. The above geometry manifests itself in a very direct fashion in reciprocal space. In the limit that the director is held fixed, the A peak at $(0,0,q_A)$ spreads out into a *ring* of scattering in the C phase at $q_C=(q_\perp\cos\psi,q_\perp\sin\psi,q_\parallel)0\le\psi\le2\pi$, with $\Phi=\sin^{-1}(q_\perp/q_C)$ and $q_C=2\pi/d_C=(q_\parallel^2+q_\perp^2)^{1/2}$. This is shown figuratively at the top of Fig. 1. By carrying out an x-ray-scattering experiment in this geometry it is possible to measure both the tilt angle Φ and the layer spacing d_C simultaneously. This can provide a definitive test both of the appropriateness of the above model and of the detailed predictions for the critical behavior of the order parameter.

The experiments were carried out using a high-resolution x-ray spectrometer which has been described previously.[2] In these particular measurements the instrumental resolution, expressed in

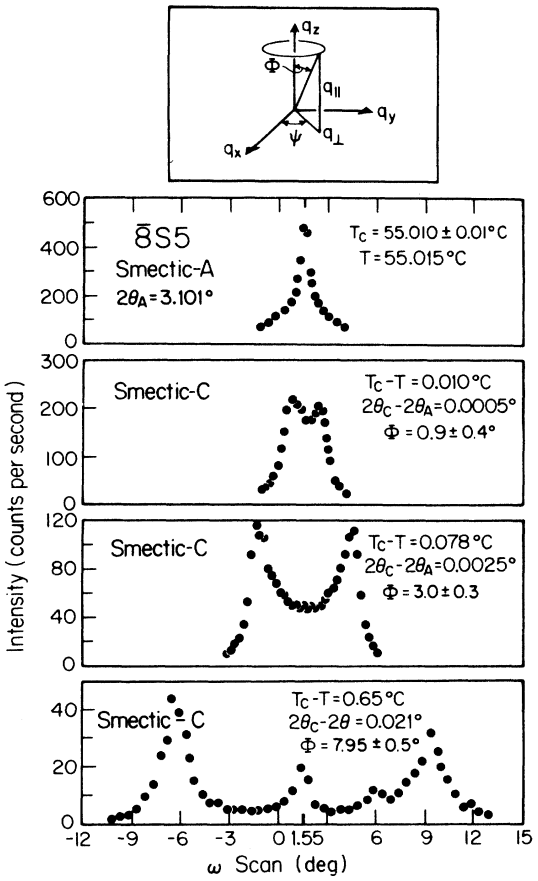

FIG. 1. Upper panel: X-ray-scattering spectrum in reciprocal space. Lower panel: Intensity profiles of scans exhibiting symmetrical splitting of the SmA peak into a ring in reciprocal space as the SmC phase of $\bar{8}S5$ is entered. In these measurements the field value was 6 kG.

terms of the half width at half maximum (HWHM) was 4.3×10^{-4} Å^{-1} in the longitudinal direction, $< 2 \times 10^{-5}$ Å^{-1} in the transverse direction and 0.5×10^{-2} Å^{-1} in the direction perpendicular to the scattering plane. The transverse resolution was limited by the sample mosaicity which for these measurements was typically 0.5° HWHM. The $\bar{8}S5$ was contained in a flat rectangular vessel $12 \times 12 \times 2$ mm^3 with 0.25-mm beryllium windows. Most of the measurements were performed in an applied magnetic field of 6 kG in order to provide alignment of the director; limited measurements were also performed in a 0.4-kG field in order to verify that the critical behavior of $d_C - d_A$ was independent of the magnitude of the applied field. In general, only the center 1×3 mm^2 of the sample was illuminated with x rays. The liquid crystal was mounted in a single-stage servo-controlled oven; typically the temperature was constant to within 3×10^{-3} °C during an x-ray scan.

The $\bar{8}S5$ was prepared by esterification of 4-*n*-octyloxybenzoyl chloride with 4-*n*-pentylbenzenethiol and recrystallized three times from absolute ethanol. Details are planned for presentation in later papers by M. E. Neubert. The sample purity was estimated to be 99.9% by differential scanning calorimetry and elemental analysis.

The experimental results are quite straightforward. We carried out five sets of measurements on three different samples in fields of 6 and 0.4 kG with identical results in each case. We discuss here explicitly only one of the measurements. With the director held fixed one observes a single peak at $(0, 0, q_A)$ in the A phase whereas in the C phase one obtains a ring of scattering given by $q_C = (q_\perp \cos\psi, q_\perp \sin\psi, q_\parallel)$, which intersects the scattering plane at $(\pm q_\perp, 0, q_\parallel)$. Hence by carrying out the usual crystallographic ω and $(\theta - 2\theta)$ scans one obtains directly Φ and $d_C = \lambda/2 \sin\theta_C$ where λ is the x-ray wavelength. We should note that special care must be taken in extracting Φ and d_C very near the phase transition where, for small Φ, the vertical extent of the scattering ring is comparable to the out-of-plane component of the instrumental resolution function.

We show in Fig. 1 a series of ω scans as a function of temperature in the A and C phases. In these scans 2θ was fixed at the peak value determined by $\theta - 2\theta$ scans through the outer peaks. The phase transition was determined to be second order within $\pm 10^{-2}$ °C with $T_c = 55.010 \pm 0.005$ °C in the sample explicitly discussed here. At $T = T_c + 0.005$ °C (upper panel) the x-ray spectrum is sharply peaked about the Sm-A position with a mosaicity of 0.12° (HWHM) while at $T = T_c - 0.010$ °C one observes the C peaks symmetrically displaced about the A position; the peak separation grows with decreasing temperature, as expected from our previous discussion. The angular separation between the two peaks is just 2Φ, where Φ is the magnitude of the smectic-C order parameter. We should note that near T_c there is still considerable scattering between the two peaks because of vertical resolution effects. Far below T_c (lower panel in Fig. 1) there is a small residual peak at the A position; this presumably originates from smectic-C crystallites with orientations controlled by wall effects.

The experimental results near T_c are summarized in Fig. 2. These are by far the most accurate data which have been obtained on the C order parameters to date; further they represent the only case in which Φ and $\Delta 2\theta$ have been obtained simultaneously. Clearly Φ and $\Delta 2\theta = 2\theta_C - 2\theta_A$ are consistent with a second-order transition with behavior at least close to that expected from mean-field theory. We have carried out a variety of power-law least-squares fits to the data. For reduced temperatures $5 \times 10^{-3} > t = 1 - T/T_c > 3 \times 10^{-5}$, Φ follows the simple power law $\Phi = \Phi_0 (1 - T/T_c)^\beta$ with $\beta = 0.47 \pm 0.04$, $T_c = 55.010 \pm 0.005$ °C, and $\Phi_0 = 139 \pm 14°$. The error

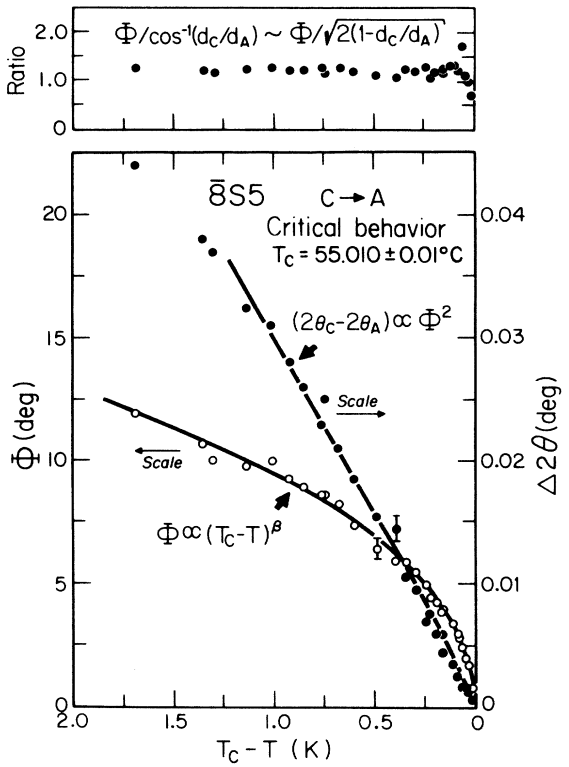

FIG. 2. Upper panel: Temperature dependence of the ratio $R = \Phi/\cos^{-1}(d_C/d_A)$. Lower panel: Temperature dependence of the tilt angle and the change in planar spacing $\Delta d = d_A - d_C \propto \Delta 2\theta$ in $\bar{8}S5$; the solid lines are the results of nonlinear least-squares fits with $\beta_\Phi = 0.47$ and $\beta_{2\theta} = 0.98$ as described in text.

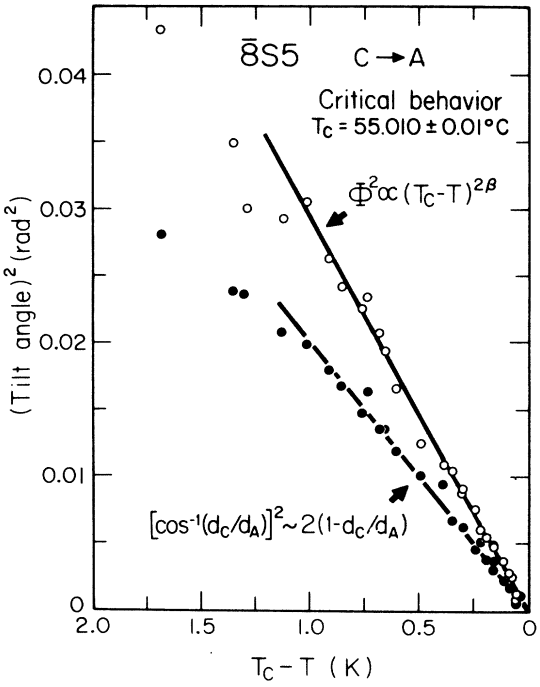

FIG. 3. Square of the tilt angle Φ and $[\cos^{-1}(d_C/d_A)^2]$ as a function of temperature. For a simple molecular tilt model $\cos\Phi = d_C/d_A$. The solid lines indicate mean-field behavior.

bars represent two-standard-deviation statistical errors. For temperatures less than $T = T_c - 3$ °C, as may be seen in Figs. 3 and 4, the data begin to fall significantly below this asymptotic power-law fit. Concomitantly, least-squares fits which include data further and further from T_c yield values for β less than 0.47. Explicit power-law fits to the $\Delta 2\theta$ data for $t < 2 \times 10^{-3}$ yield an exponent $\beta_{2\theta} = 0.98 \pm 0.12$, so that $\beta_{2\theta} = 2\beta$ within errors. This, in turn, necessitates that the tilt angle Φ is the primary order parameter of this A-C transition and that the change in the lattice constant is driven by the tilting, that is, it functions as a secondary order parameter.

In Fig. 3 we show the square of the tilt angle together with $[\cos^{-1}(d_C/d_A)]^2$. For a simple molecular-tilt model $\cos\Phi = d_C/d_A$. The straight lines through the data indicate classical mean-field behavior within one degree of the transition and an eventual crossover to saturation of the C order parameters. This rather early $(1 - T/T_c \simeq 5 \times 10^{-3})$ crossover has caused many workers to characterize

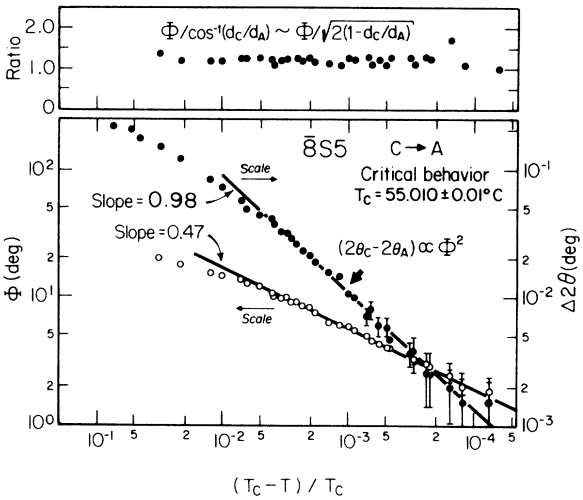

FIG. 4. Upper panel: Temperature dependence of the ratio $R = \Phi/\cos^{-1}(d_C/d_A)$. Lower panel: Primary (tilt angle Φ) and secondary ($\Delta 2\theta \propto$ change in planar spacing $d_A - d_C$) order parameters as functions of reduced temperature. The solid lines are the results of nonlinear least-squares fit with $\beta = 0.47 \pm 0.04$ and $\beta_{2\theta} = 0.98 \pm 0.12$ as discussed in the text.

erroneously the behavior of the C order parameter with superfluid helium exponents. The experimental results over the entire temperature range are summarized in Fig. 4. We show the primary tilt (Φ) and secondary ($\Delta 2\theta \propto \Delta d$) order parameters as functions of reduced temperature.

The relationship between d and Φ may be exhibited by plotting $R = \Phi/\cos^{-1}(d_C/d_A)$ (top of Fig. 4). The ratio $R = 1.2 \pm 0.1$ throughout the C phase. The large fluctuations in R very near T_c are related primarily to the uncertainties in $\Delta 2\theta$; we should emphasize that $\Delta 2\theta$ is, nevertheless, measured to an accuracy of about ± 0.0005 degrees, so that a significant improvement in the data would not be easily achieved. For the simplest model of rigid rods with a saturated nematic order parameter $R = 1$. The observed departure of R from 1 measures the extent to which this simplistic model breaks down. Any mechanism which causes a change in the effective length of the molecule in the C phase and which scales like Φ^2 will contribute to R. Possible contributors are subtle conformational changes in the molecule and changes in the nematic orientational order parameter. Such "nonideal" effects turn out to be surprisingly small in $\bar{8}S5$.

We now discuss the observed critical behavior. From the $d = 3$, $n = 2$ model one expects[6] $\beta = 0.346$ whereas in mean-field theory $\beta = 0.50$. Over the reduced temperature range $5 \times 10^{-3} > t > 3 \times 10^{-5}$ we find $\beta = 0.47 \pm 0.04$ which is consistent with mean-field theory and clearly excludes the helium value. To assess the significance of this discrepancy with the $d = 3$, $n = 2$ model we estimate the reduced temperature range in which asymptotic critical behavior should be observed. We do this on the smectic-A side of the transition. Near a second-order C-A transition the onset of order is characterized[3] by the complex number $\pi_C = \Phi e^{i\Psi} \equiv n_x + i n_y$; n_x, n_y give the projection of the molecular orientation on the plane of the smectic-C layer. In addition, for symmetry reasons, one needs to include in the free-energy phase fluctuations $\partial u/\partial x$, $\partial u/\partial y$ of the smectic-A order[1] $\psi_A = |\psi_A| e^{iq_A u}$. The free energy is

$$F = \frac{1}{2}\int d\vec{x}\,\{\mathcal{F}_0 + D[(n_x + \partial_x u)^2 + (n_y + \partial_y u)^2] + \cdots + B(\partial_z u)^2 + K_1(\partial_x n_x + \partial_y n_y)^2 + K_2(\partial_x n_y - \partial_y n_x)^2 + K_3[(\partial_z n_x)^2 + (\partial_z n_y)^2]\}\ , \tag{1}$$

where z is along the nematic director, B and D are, respectively, the restoring forces for fluctuations in layer thickness and for fluctuations of the director away from the normal to the layers, and K_1, K_2, and K_3 are the splay, twist, and bend elastic constants. The relevant critical fluctuations are contained in the tilt-tilt correlation function. For $T > T_{C\text{-}A}$ one obtains

$$\begin{aligned} G(\vec{q}) &\equiv \langle |n_x(\vec{q}) + iq_x u(\vec{q})|^2 + |n_y(\vec{q}) + iq_y u(\vec{q})|^2 \rangle \\ &= k_B T\left[\frac{1}{D + K_2 q_\perp^2 + K_3 q_z^2} + \frac{1}{D + K_1 q_\perp^2 + K_3 q_z^2}\left(1 + \frac{q_\perp^2 (K_1 q_\perp^2 + K_3 q_z^2)^2}{DBq_z^2 + (D_{q_\perp}^2 + Bq_z^2)(K_1 q_\perp^2 + K_3 q_z^2)}\right)\right] \\ &= k_B T\left[\frac{1}{D + K_2 q_\perp^2 + K_3 q_z^2} + \frac{1}{D + K_1 q_\perp^2 + K_3 q_z^2}\right] + O(q^4)\ . \end{aligned} \tag{2}$$

The correlation lengths associated with the fluctuations into the smectic-C phase thence are

$$\xi_\parallel = (K_3/D)^{1/2} \quad \text{and} \quad \xi_\perp \simeq [(K_1 + K_2)/2D]^{1/2}\ . \tag{3}$$

The phase transition is, of course, driven by D going to zero. From the Ginzburg criterion[7] we expect that the width of the critical region may be estimated from

$$\frac{\Delta T_c}{T_c} \simeq \frac{k_B^2}{32\pi^2 (\Delta C)^2 (\xi_{0\parallel})^2 (\xi_{0\perp})^4}\ . \tag{4}$$

Using the measured value[6] of ΔC in $\bar{8}S5$ we estimate from Eq. (4) that the critical region will be narrower than 10^{-5}; that is, inside of the region probed by all experiments to date, provided that $\bar{\xi}_0 = \xi_{0\parallel}^{1/3} \xi_{0\perp}^{2/3} > 13$ Å. Here $\xi_{0\parallel}$, $\xi_{0\perp}$ are the bare lengths far from T_c.

Unfortunately we do not yet have enough information to estimate $\xi_{0\parallel}$ and $\xi_{0\perp}$ from Eq. (3) for $\bar{8}S5$. However, for a variety of other smectic-A materials[2] we find that typically $\bar{\xi}_0 \simeq 70$ Å. With this value of $\bar{\xi}_0$ one would, for practical purposes, never leave the mean-field region. We might also mention that in materials undergoing an A-C transition one might anticipate on the basis of microscopic considerations that D would be small even far from T_c so that the above estimate of $\bar{\xi}_0$ is probably conservative. We should note that a similar explanation has been proposed for the observed mean-field behavior in spin-reorientation transitions in magnetism[8]; in that case the bare length is the spin-wave coherence length.

We believe that all existing A-C data can be understood within the above picture. Firstly, some of the

earlier measurements claiming to see helium exponents were in fact carried out sufficiently far from T_c that the data were strongly influenced by saturation effects; hence the exponents so obtained are not reliable. All but one of the more recent high-precision experiments obtain mean-field exponents, consistent with our Ginzburg-criterion argument.[4] The one exception is the light-scattering study of $(1/D)$ by Delaye[9] in *p*-nonyloxybenzoate-*p*-butyloxyphenol; in the reduced temperature above T_c of $\sim 10^{-2}$ to $\sim 10^{-5}$ she deduces $\gamma = 1.25 \pm 0.05$ and $\nu = 0.66 \pm 0.06$, in good agreement with the helium model. However, in this material she also estimates $\bar{\xi}_0 = 6.8$ Å; for this bare length the true critical region from Eq. (4) should begin at $\sim 5 \times 10^{-4}$ consistent with her results. This situation is, we believe, very much the exception and as stated above we anticipate that in most materials one will observe mean-field behavior over the experimentally accessible temperature range close to T_c.

The work at MIT was supported by the NSF-MRL under Contract No. DMR 76-80895-A02 and by the Joint Services Electronics Program under Contract No. DAAG-29-78-C-0020.

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