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

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We report measurements of the tilt angle \(\Phi\) and the planar spacing \(d_c\) near the second-order
Sm\(C\)–Sm\(A\) transition in 4-n-pentyl-phenylthiophenyl-4'-n-octyloxybenzoate (85\&). We find that the
ratio \(\Phi/\cos^{-1}(d_c/d_a)\) is constant (1.2 \pm 0.1) through the \(C\) phase, supporting a simple
molecular-tilt model for the transition. For \(5 \times 10^{-3} > 1 - T/T_c > 3 \times 10^{-5}\), \(\Phi\) 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 rec-
tent 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-\(A\) (\(N\)–\(A\)) tran-
sition which should be analogous to an anisotropic
superconducting transition with short-range interac-
tions 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 cover-
ing 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-
phenylthiophenyl-4'-n-octyloxybenzoate (85\&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 mea-
sure both the tilt angle \(\Phi\) and the lattice constant \(d\)
simultaneously. This, in turn, enables us to demon-
strate unambiguously in 85\&5 that, in the language of
structural phase transitions, \(\Phi\) functions as the pri-
mary 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 para-
meter, that is, \(\Delta d\) varies as the square of \(\Phi\).

There are a number of models for the \(A\)–\(C\) transi-
tion 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 85\&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 \(q_a = (0, 0, q_H)\) with \(q_H = 2\pi/d_a\) (here,
we consider \(q_H > 0\). 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 \(\pi_c = \Phi e^{i\theta}\);
here \(\psi\) 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 rota-
tions of the molecules about the normal to the smec-
tic layers is the analogue of gauge invariance in su-
perfluid helium.\(^1,3\) In this model the \(C\) phase is
characterized by an isotropic two-component order
parameter, hence one should observe asymptotic criti-
cal 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
\(q_c = (q_{c1} \cos \psi, q_{c2} \sin \psi, q_H)\) with
\(\Phi = \sin^{-1}(q_{c1}/q_c)\) and \(q_c = 2\pi/d_c = (q_{c1}^2 + q_{c2}^2)^{1/2}\).
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
\(\Phi\) 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 measure-
ments the instrumental resolution, expressed in
The S5S was prepared by esterification of 4-n-octyl-oxybenzoyl chloride with 4-n-pentybenzenethiol 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 \(q_C = (q_x \cos \psi, q_y \sin \psi, q_z)\), which intersects the scattering plane at \((\pm q_y, 0, q_z)\). Hence by carrying out the usual crystallographic \(\omega\) and \((\theta - 2\theta)\) scans one obtains directly \(\Phi\) and \(d_C = \lambda/2 \sin \theta_C\) where \(\lambda\) is the x-ray wavelength. We should note that special care must be taken in extracting \(\Phi\) and \(d_C\) near the phase transition where, for small \(\Phi\), 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 \(\omega\) scans as a function of temperature in the \(A\) and \(C\) phases. In these scans \(2\theta\) 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 \(2\Phi\), where \(\Phi\) 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 \(\Phi\) and \(\Delta \theta\) have been obtained simultaneously. Clearly \(\Phi\) and \(\Delta \theta = 2\theta_C - 2\theta_A\) 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 \(5 \times 10^{-3} > t = 1 - T/T_c > 3 \times 10^{-5}\), \(\Phi\) 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
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 \( \beta \) 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 \( \Phi \) 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 \( (1 - T/T_c = 5 \times 10^{-3}) \) crossover has caused many workers to characterize...
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 (Δ2θ = Δd) order parameters as functions of reduced temperature.

The relationship between d and Φ may be exhibited by plotting R = Φ/ cos³(Δc/Δd) (top of Fig. 4). The ratio R = 1.2 ± 0.1 throughout the C phase. The large fluctuations in R very near Tc are related primarily to the uncertainties in Δ2θ; we should emphasize that Δ2θ 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 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 855.

We now discuss the observed critical behavior. From the d = 3, n = 2 model one expects6 β = 0.346 whereas in mean-field theory β = 0.50. Over the reduced temperature range 5 × 10⁻³ < r < 3 × 10⁻² we find β = 0.47 ± 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 characterized7 by the complex number πₖ = Φ e⁻ⁱₙπ = n₁ + i n₂/ n₁, n₂ 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 δu/δx, δu/δy of the smectic-A order parameter ψ₄ = |ψ₄| e⁻ⁱₙψ₄. The free energy is

\[
F = \frac{1}{2} \int d \vec{x} \left[ \mathcal{F}_0 + D_\perp (n_x + \partial_x u)^2 + (n_y + \partial_y u)^2 \right] + \cdots \\
+ B (\partial_x u)^2 + K_1 (\partial_x n_y + \partial_y n_y)^2 + K_2 (\partial_x n_y - \partial_y n_x)^2 + K_3 [(\partial_x n_x)^2 + (\partial_y n_y)^2] 
\]

(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 \(K_1, K_2, K_3\) are the splay, twist, and bend elastic constants. The relevant critical fluctuations are contained in the tilt-tilt correlation function. For \(T > T_{c-A}\) one obtains

\[
G(q) = \left[ (n_x(q) + i \partial_x u(q))^2 + (n_y(q) + i \partial_y u(q))^2 \right] \\
= k_B T \left[ \frac{1}{D + K_2 q_x^2 + K_3 q_y^2} + \frac{1}{D + K_4 q_x^2 + K_5 q_y^2} \right] \\
= k_B T \left[ \frac{1}{D + K_2 q_x^2 + K_3 q_y^2} + \frac{1}{D + K_4 q_x^2 + K_5 q_y^2} \right] + O(q^4) 
\]

(2)

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

\[
\xi_0 = (K_3/D)^{1/2} \quad \text{and} \quad \xi_1 = \left[ (K_1 + K_2)/2D \right]^{1/2} . \quad (3)
\]

The phase transition is, of course, driven by D going to zero. From the Ginzburg criterion7 we expect that the width of the critical region may be estimated from

\[
\frac{\Delta T_c}{T_c} = \frac{k_B^2}{32 \pi^2 (\Delta C)^2 (\xi_0a)^2 (\xi_0b)^4} . \quad (4)
\]

Using the measured value of \(\Delta C\) in 855 we estimate from Eq. (4) that the critical region will be narrower than 10⁻³; that is, inside of the region probed by all experiments to date, provided that \(\xi_0 \xi_0 > 13\) Å. Here \(\xi_0a, \xi_0b\) are the bare lengths far from \(T_c\). Unfortunately we do not yet have enough information to estimate \(\xi_0a\) and \(\xi_0b\) from Eq. (3) for 855. However, for a variety of other smectic-A materials7 we find that typically \(\xi_0 = 70\) Å. With this value of \(\xi_0\) 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 \(\xi_0\) is probably conservative. We should note that a similar explanation has been proposed for the observed mean-field behavior in spin-reorientation transitions in magnetism9; 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.\footnote{Present address: Research Establishment Risø, Roskilde, Denmark.}

The one exception is the light-scattering study of $(1/D)$ by Delaye\footnote{Present address: Dept. of Physics, Hebrew University, Jerusalem, Israel.} in $\rho$-nonyloxybenzoate-$\rho$-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 $\xi_0 \approx 6.8 \text{ Å}$; 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 $T_c$.

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\textsuperscript{5}C. A. Schantz and D. L. Johnson, Phys. Rev. A \textbf{17}, 1504 (1978). These authors interpret the specific-heat anomaly at the $A$-$C$ transition in 8.55 as a cusp with exponent $\alpha' = -0.54$; however, the data inside of $|r| = 5 \times 10^{-4}$ are also consistent with a mean-field jump $\Delta C = 10^6$ erg/cm\textsuperscript{3} K.


