Light-Scattering Measurements in the $\bar{7}$S5-8OCB Nematic–Smectic-A–Smectic-C Liquid-Crystal System

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We report light-scattering measurements of nematic director fluctuations near the nematic–smectic-A–smectic-C multicritical point in the $\bar{7}$S5-8OCB system. Our data analysis corrects for the effects of phase-boundary curvature and elucidates the evolution in the critical behavior as the nematic–smectic-A–smectic-C point is approached from both the N-S_A and N-S_C side of the multicritical point. The results agree closely with x-ray scattering data and the bend elastic-constant behavior differs from any current theoretical predictions.

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The nature of the nematic–smectic-A–smectic-C (NAC) multicritical point and the behavior near it is not yet understood. Theoretical models fall rather broadly into two classes. The first approach predicts that the NAC point is a Lifshitz point[1] with the smectic ordering described by a single infinite-dimensional order parameter.[2] While this is an appealing model, theory[3] predicts a phase-transition temperature of 0 K in three dimensions. A way out of this difficulty is offered by the second class of models, which involve two order parameters, one for the smectic density wave and a second for the S_C tilt angle.[4–8] These theoretical approaches yield different predictions for the behavior of the nematic elastic-constant enhancements near the N-S_C transition and at the NAC point. In order to elucidate the nature of the NAC point we have studied the light scattered by director modes and we compare our results with these various theoretical predictions. We find bend elastic-constant pretransitional behavior which is not consistent with any of the existing models.

We have studied the nematic elastic-constant enhancement of the N-S_A and the N-S_C branches of the phase diagram of mixtures of heptyloxy-p'-pentyphenylthiolbenzoate ($\bar{7}$S5) and octyloxy-cyanobiphenyl (8OCB). The phase diagram for this system has the same universal shape reported in other systems by Brisbin *et al.*,[9] and has been mapped out by Martínez-Miranda[10]; it is shown in the preceding Letter.[11] We studied samples with molar concentrations $X_{8OCB} = 0.0346$, 0.0236, 0.0219, and 0.0217, which exhibit N-S_A transitions, as well as samples with $X_{8OCB} = 0.0197$ and 0.0176, which exhibit N-S_C transitions. We used surface relief gratings[12] to align our samples with the director in the plane of the sample.

In the experiments reported here we have analyzed the depolarized light scattered from the mode-1 and mode-2 nematic director fluctuations which cause dielectric tensor fluctuations

$$\langle \delta\epsilon_{iz}^2(\mathbf{q}) \rangle = \epsilon_a^2 kT[K_i q_x^2 + K_3 q_z^2]^{-1}, \quad (1)$$

where i denotes the mode, and coordinates are chosen so that the nematic director $\hat{\mathbf{n}}_0$ is parallel to $\hat{\mathbf{z}}$ and the scattering vector $\mathbf{q}$ lies in the $\hat{\mathbf{x}}$-$\hat{\mathbf{z}}$ plane. In both modes the incident polarization is perpendicular to the scattered polarization. In mode 1 the nematic director is parallel to the incident polarization, while in mode 2 it is orthogonal to the incident polarization. The nematic elastic constants are related to the correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$ in both the hydrodynamic and the critical regimes through the Jahnig-Brochard crossover function.[13] Our data were fitted by this expression according to a procedure discussed in some detail by Sprunt, Solomon, and Litster.[14]

In order to analyze properly the data from the samples exhibiting N-S_A transitions, one must account for the effect of the curvature in the N-S_A phase boundary on the observed divergences. Griffiths and Wheeler[15] pointed out how to do this, on the basis of the fact that the only unique direction of approach to a line of critical points is the one which is tangential to that line. The critical behavior observed as the line is approached from all other directions should be the same; the correlation length, for example, should scale with distance D from the phase-boundary line as $\xi \sim D^{-\nu}$. If we use the notation of Brisbin *et al.*[9] for the N-S_A phase boundary of the NAC system, replacing their $1/\eta$ by ϕ, we find $D \sim [\Delta T + T - T_{NA}]^{\phi} - [\Delta T]^{\phi}$, where $\Delta T = T_{NA} - T_{NAC} - B(X_{NA} - X_{NAC})$, and X_{NA} is the mole fraction of 8OCB of the sample with transition T_{NA}. This implies that

$$\xi = \xi'\{(\Delta T/T_{NAC})^{\phi}[(1 + tT_{NA}/\Delta T)^{\phi} - 1]\}^{-\nu}, \quad (2)$$

where $t = (T - T_{NA})/T_{NA}$, and ϕ, T_{NA}, T_{NAC}, and ΔT can be determined from the phase diagram. In the $\bar{7}$S5-8OCB system[11] ϕ is sufficiently close to 2 that we used that value for analysis of all the N-S_A transitions reported here. Equation (2) predicts that the correlation length at constant t should increase as ΔT decreases; when $\phi = 2$, it reduces to the crossover expression used in the reentrant nematic analysis.[16]

TABLE I. N-S_A results in $\overline{7}$S5-8OCB mixtures.

X_{8OCB}	$T_{NA}/\Delta T$	$\xi_{\parallel}^{0} q_0$ (with crossover)	$\nu_{\parallel}$ (with crossover)	$\xi_{\parallel}^{0} q_0$ (without crossover)	$\nu_{\parallel}$ (without crossover)	$\Delta\chi^2/\chi^2$ (%)
0.0346	23	0.87	0.89 ±0.04	0.78	0.89 ±0.05	26
0.0236	68	2.0	0.89 ±0.03	0.75	1.00 ±0.03	120
0.0219	74	2.1	0.90 ±0.03	0.68	1.04 ±0.03	94
0.0217	264	8.8	0.88 ±0.04	1.3	1.11 ±0.04	410

When $tT_{NA}/\Delta T \ll 1$, Eq. (2) reduces to a simple power law given by

$$\xi = \xi'[(\phi T_{NA}/\Delta T)(\Delta T/T_{NAC})^{\phi}]^{-\nu} t^{-\nu} \equiv \xi^0 t^{-\nu}.$$

For the samples with N-S_A transitions, light-scattering measurements at $q_\perp = 0$, where mode 1 and mode 2 are degenerate, were made. The Jahnig-Brochard function then gives a relatively simple form for the scattered intensity, $I(T)$, near the transition

$$\frac{I(T_{NA})}{I(T)} = \frac{(2/\pi)[(1+1/X^2)\tan^{-1}X - 1/X] + B_0}{1+B_0}, \tag{3}$$

where $B_0 = 16K_3^0 q_z/kTq_0^2$ is a small term from the background bend constant K_3^0, and $X = \frac{1}{2}\xi_{\parallel} q_z$. The transition temperature was chosen as the point of maximum slope in an I^{-1} vs T plot. Thus $I(T_{NA})$ and T_{NA} were not adjustable parameters in the fit. Our data were fitted by (3) with two adjustable parameters, a temperature-independent background and $X(T)$. Since q_z was known from the scattering geometry, it was a simple matter to determine $\xi_{\parallel}$ from $X(T)$. The correlation length was fitted both by the crossover equation (2) and by a simple power law $\xi_{\parallel}^{0} t^{-\nu}$. Table I tabulates the fitted coefficient and exponent for both of these fits, along with the percentage difference in the goodness of fit (χ^2) values. For meaningful comparison with the simple power law, the value of $\xi_{\parallel}' q_0$ obtained from (2) has been scaled by the dimensionless expression $[(\phi T_{NA}/\Delta T)(\Delta T/T_{NAC})^{\phi}]^{-\nu}$ to obtain $\xi_{\parallel}^{0} q_0$. The data and the fits by (2) are shown for three of the samples in Fig. 1. The smectic density wave vector q_0 was obtained from x-ray scattering.

A notable feature in these data is the increase in the correlation length as the NAC point is approached. This effect is accounted for by the geometry of the N-S_A phase boundary, and was demonstrated in the reentrant nematic system.[16] It is clear that Eq. (2) gives a consistent exponent (~ 0.90) for all samples studied, while the simple power law does not. For all samples except $X_{8OCB} = 0.0346$, the crossover form (2) clearly provides a better fit; the latter is far enough from the NAC point that there is no difference between the two expressions.

The critical exponent $\nu_{\parallel}$ for this system is larger than for other liquid-crystal systems. This is also observed in the x-ray scattering measurements, which are in close agreement with our results. For example, if we compare the fit results obtained with the crossover expression, x-ray scattering measurements for the $X_{8OCB} = 0.0346$, 0.0219, and 0.0217 samples give $\nu_{\parallel} = 0.91$, 0,91, and 0.88, and $\xi_{\parallel}^{0} q_0 = 0.62$, 2.13, and 10.6, respectively. Since the fit by (2) has already included the crossover effects of the N-S_A phase-boundary curvature, the explanation for the large exponents must lie elsewhere. It would be interesting to test hyperscaling in this system by measurements of the specific heat exponent α.

Measurements of mode-1 and mode-2 director fluctuations in the nematic phase as the S_C phase is approached were made for the $X_{8OCB} = 0.0197$ and 0.0176 samples. Mode-1 geometry with $q_{\parallel} = 0$ yields the behavior of K_1. In the mode-2 geometry two scattering angles were probed in order to measure both pure K_3 and a combination of K_2 and K_3. Since we do not know that the Jahnig-Brochard expression is valid above the S_C phase we cannot use it to deduce the absolute value of the correlation lengths from the light-scattering data. Therefore the data have simply been scaled to agree with the x-ray results for $T > T_{NC} + 6$ K.

The nematic phase behavior of K_3 and K_2 for the $X_{8OCB} = 0.0197$ and 0.0176 samples is shown in Fig. 2,

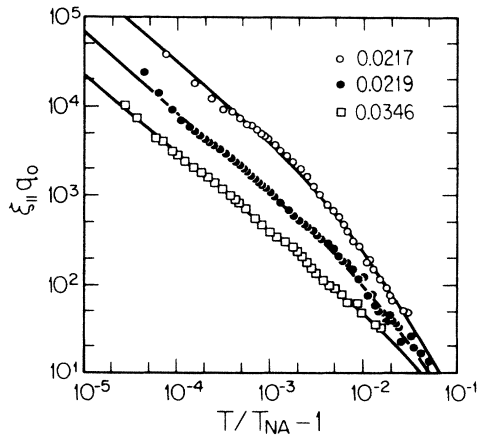

FIG. 1. $\xi_{\parallel} q_0$ in the N-S_A samples. The key gives the mole fraction of 8OCB in the mixtures.

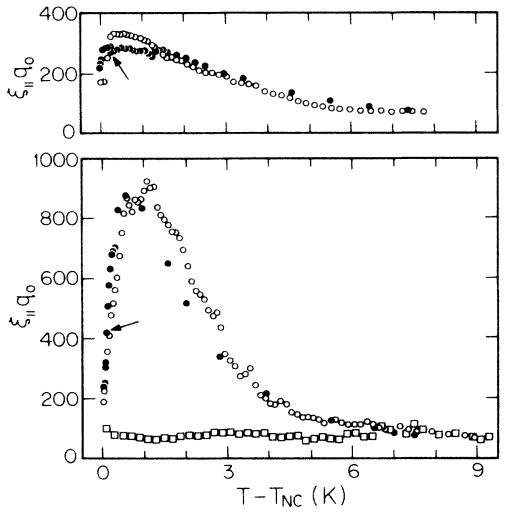

FIG. 2. Nematic phase behavior in the N-S_C samples. The open circles are the light-scattering (inverse intensity) data which have been scaled to agree with the x-ray results at $T > T_{NC}+6$ K, and the solid circles are the x-ray data measured at $q_\perp = 0$. The arrow indicates the Lifshitz line. The upper panel is the $X_{8OCB} = 0.0176$ sample, and the lower panel is the 0.0197 sample. The square symbols in the lower panel are the K_2 data points.

along with the parallel correlation length extracted from the x-ray linewidth for momentum transfer along the director, i.e., $\xi_\parallel q_0$ for $q_\perp = 0$. A minimum of the bend light-scattering intensity above the N-S_C transition is clearly evident. This behavior was first observed by Witanachchi, Huang, and Ho,[17] although their interpretation was impeded by the lack of x-ray data on the same samples. In the $X_{8OCB} = 0.0197$ sample (lower panel) the K_3 scattering intensity changes by a factor ~ 9, with a maximum occurring $\sim 1°$ above the Lifshitz line ($C_\perp = 0$), and in the $X_{8OCB} = 0.0176$ sample (upper panel) the K_3 scattering intensity changes by a factor ~ 4.5. This behavior is clearly paralleled in the x-ray measurements of the quantity we call $\xi_\parallel q_0(q_\perp = 0)$. When the nematic fluctuations are S_A-like, the maximum x-ray scattering intensity occurs at $q_\perp = 0$, and $\xi_\parallel q_0(q_\perp = 0) \equiv \xi_\parallel q_0$. Below the Lifshitz line, when the nematic fluctuations have changed from S_A- to S_C-like, the maximum x-ray scattering intensity occurs at a nonzero value of $q_\perp$, called $q_\perp^0$. In this region, which includes only the four lowest-temperature data points of the lower panel of Fig. 2, $\xi_\parallel q_0(q_\perp = 0)$ is smaller than $\xi_\parallel q_0(q_\perp = q_\perp^0)$ and is a quantity whose precise interpretation depends on the specific model used for the x-ray line shape; it is apparently this quantity which is proportional to K_3 when the short-range order becomes S_C-like. Neither of these N-S_C samples shows a significant observable enhancement in K_1 or K_2.

We now discuss what our results imply about the validity of the various models which predict elastic-constant behavior near the NAC point. The Chen-Lubensky (CL) model predicts that near the N-S_C transition the nematic elastic-constant K_3 should scale as $\xi_\parallel \xi_\perp$; at the Lifshitz point (LP) and along the N-S_A line K_3 should scale as $\xi_\parallel$, and K_1 and K_2 should have a weak divergence ($\sim \ln\xi$) at the LP. The Chu-McMillan[4] model predicts that K_3 scales as $\xi_\parallel$ everywhere and de Gennes[2] predicts $K_3 \sim \xi^{3/2}$ above the N-S_C line. While the models make differing predictions about the behavior of K_1 and K_2 at the LP and along the N-S_C line, they all predict divergent contributions which will be strongly reduced by the anisotropy in the correlation lengths. For example, the Chu-McMillan model[4] predicts $K_2/K_3 = (\xi_\perp/\xi_\parallel)^2 + \beta_0^2/2$, where $\theta = \tan^{-1}\beta_0$ is the most probable tilt angle, and $K_1/K_3 = \beta_0^2/2$. This effect will be particularly pronounced in this system because the correlation-length anisotropy[11] is the largest observed to date. These ratios are very small and therefore the fact that we do not observe significant enhancement of K_1 or K_2 does not test the models.

Clearly the CL predictions for the LP and N-S_A line are consistent with our data. To the extent that we place any importance on the small departure of the four lowest-temperature points for the X_{8OCB} sample from $\xi_\parallel q_0(q_\perp = q_\perp^0)$, it could be the beginning of a crossover to the $K_3 \sim \xi_\parallel \xi_\perp$ prediction of the CL model. In the context of the CL model, this suggests that the LP predictions dominate along the Lifshitz line ($C_\perp = 0$). X-ray measurements demonstrate that the $C_\perp = 0$ line is a function of both concentration and temperature, and in the vicinity of the NAC point is very near the N-S_C boundary. As one moves away from the LP the N-S_C transition becomes more strongly first order, and thus our experiments probably never explore the asymptotic N-S_C critical region. However, the Chu-McMillan prediction $K_3 \sim \xi_\parallel$ is also consistent with our measurements, with the possible exception of the four lowest-temperature points for the $X_{8OCB} = 0.0197$ sample. We do not find any evidence for the existence of a biaxial nematic phase predicted by the most recent NAC model.[7]

The most striking result of our studies is the increase of the elastic constant K_3 to a maximum value at a temperature above that of the N-S_C transition, and then a decrease as the transition is approched. This behavior is also clearly observed in the x-ray measurements of $\xi_\parallel q_0$. Both K_3 and $\xi_\parallel$ peak at the same temperature and the decorrelation of the smectic short-range order begins on the S_A side of the Lifshitz line. Comparison with x-ray scattering measurements on the same sample show that the minimum in the light-scattering intensity found above the N-S_C line near the Lifshitz point is caused by a decorrelation of the smectic short-range order. This pronounced effect is not

anticipated by any of the existing models and needs to be addressed.

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