plot the density from the pressure measurement versus the sum of the $|a\rangle \rightarrow |d\rangle$ and $|b\rangle \rightarrow |c\rangle$ ESR signals, p/kT vs n_{ESR}, for $T = 310$ mK in Fig. 3. Deviations from equilibrium which would be expressed by deviations from a straight-line behavior are random and at most 14.5 mK. A systematic deviation at higher densities due to increasing heating, which is proportional to n^2, is absent. We thus establish that the Kapitza resistance is not yet a problem for the conditions studied.

We thank P. Wyder for suggesting the multiplier technique of generating the high-frequency microwave power, and H. A. Dijkerman for the loan of a klystron and stabilizer when ours malfunctioned. The technical help of O. Höpfner is acknowledged as well as financial support from the Stichting voor Fundamenteel Orderzoek der Materie.

[a]Current address: Lyman Laboratory of Physics, Harvard University, Cambridge, Mass. 02138.

[1]For a review, see I. F. Silvera, Physica (Utrecht) 109&110B+C, 1499 (1981).

[2]I. F. Silvera and J. T. M. Walraven, Phys. Rev. Lett. 44, 164 (1980).

[3]R. W. Cline, T. J. Greytak, and D. Kleppner, Phys. Rev. Lett. 47, 1195 (1981).

[4]R. Sprik, J. T. M. Walraven, G. H. van Yperen, and I. F. Silvera, Phys. Rev. Lett. 49, 153 (1982).

[5]B. W. Statt and W. N. Hardy, private communication, have reported preliminary high-field ESR results.

[6]J. T. M. Walraven and I. F. Silvera, Phys. Rev. Lett. 44, 168 (1980).

[7]T. Niinikoski and L. Dick, private communication.

[8]N. S. Nishioka, P. L. Richards, and D. P. Woody, Appl. Opt. 17, 1562 (1978).

[9]B. W. Statt and A. J. Berlinsky, Phys. Rev. Lett. 45, 2105 (1980).

[10]A. J. Berlinsky and R. W. Cline, private communication.

High-Resolution X-Ray Scattering Study of the Nematic-to-Smectic-*C* Transitions in $\overline{8}$S5-$\overline{7}$S5 Mixtures

C. R. Safinya

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

and

L. J. Martínez-Miranda, M. Kaplan,[a] J. D. Litster, and R. J. Birgeneau

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 8 March 1982)

Measurements of the mass-density fluctuations associated with the first-order nematic–to–smectic-*C* transitions in $\overline{8}S5_{1-x}$-$\overline{7}S5_x$ mixtures are reported. This binary system exhibits nematic, smectic-*A*, and smectic-*C* phases, and a multicritical point x_{NAC}. As a function of decreasing temperature for $x > x_{NAC}$, the scattering in the nematic phase evolves from smectic-*A* to pretransitional smectic-*C* fluctuations described by a Lifshitz model of Chen and Lubensky. Important discrepancies remain with the predictions of the model near x_{NAC}.

PACS numbers: 61.30.Eb, 64.70.Ew

The nematic–to–smectic-*A* (NA) transition has been studied in considerable detail.[1] On the other hand, very little accurate information is available on the NC transition, and indeed the global nature of the entire multicritical NAC region where the NA and NC lines meet is not understood. To elucidate the problem, we have carried out a high-resolution x-ray scattering study of the critical mass-density fluctuations associated with the nematic–to–smectic-*C* transition in mixtures of octyl and heptyl oxy-*p*′-pentyphenylthiolbenzoate ($\overline{8}S5_{1-x}$-$\overline{7}S5_x$). By approaching x_{NAC}, one is able to study the transition as the tilt angle and latent heat are continuously decreased along the NC line; this line terminates at a second-order multicritical point at concentration x_{NAC}, and branches off into second-order nematic–smectic-*A* and smectic-*A*–smectic-*C* lines (Fig. 1). The NAC problem has two features which make it a prototype for problems of broad interest. First, in the de Gennes[2] description of an infinite-dimensional density order parameter, the NC system

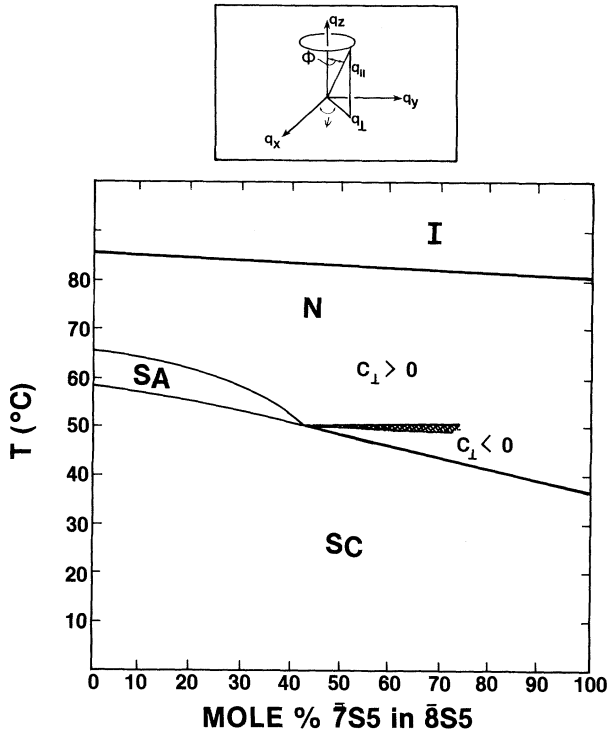

FIG. 1. Upper panel: smectic-C scattering spectrum in reciprocal space. Lower panel: NAC phase diagram reproduced from Johnson *et al.* (Ref. 6). Hatched section refers to the crossover regime which separates regions of smectic-A like ($C_\perp > 0$) and smectic-C like ($C_\perp < 0$) critical fluctuations as discussed in text.

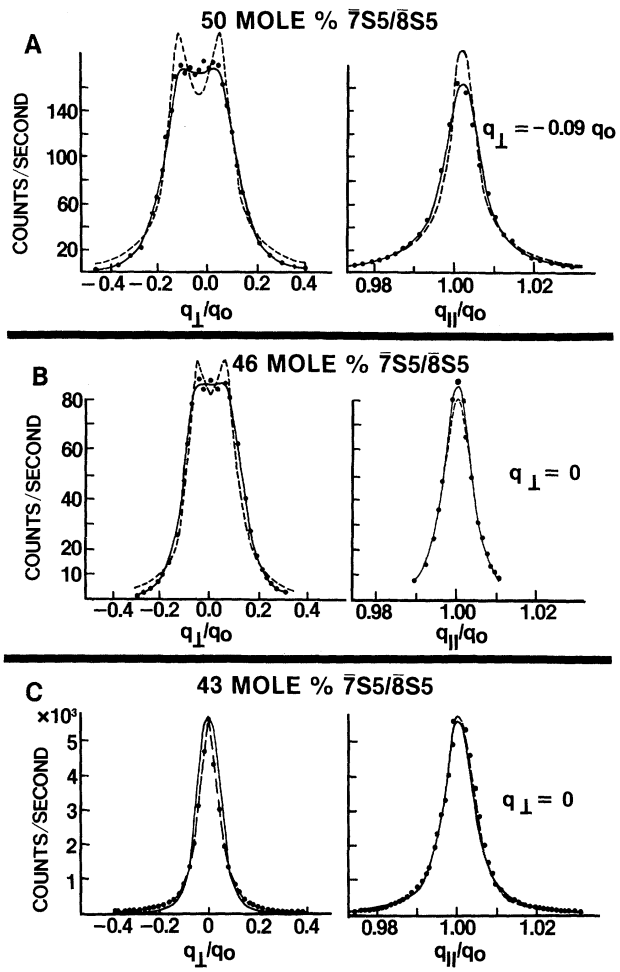

FIG. 2. Scattering profiles in the nematic phase for three mixtures, $x = 0.50$, 0.46, and 0.43, within 0.01 deg of the NC boundary. Solid lines are the result of fits by the Chen-Lubensky (CL) model for the NC transition for $x = 0.50$ (tilt = 4.9°; $\xi_\parallel = 257/q_0$, $\xi_\perp = 8.5/q_0$; $q_0 = 0.2270$ Å^{-1}) and $x = 0.46$ (tilt = 2.9°, $\xi_\parallel = 446/q_0$, $\xi_\perp = 8.4/q_0$; $q_0 = 0.2265$ Å^{-1}). The dashed lines are fits by an alternative model of Chu and McMillan [Eq. (2)]. The broken line shown in (c) is a fit by the CL model [Eq. (1) with $C_\perp > 0$] which describes NA fluctuations. All error bars are within the extent of the data points shown.

would be an example of a Brazovskii[3] type fluctuation-induced first-order transition, and second, the NAC system is among the few predicted[4] Lifshitz systems where the nature of the critical fluctuations, which provides a strong signature for such behavior, may be directly accessed by a scattering probe. A variety of models have been proposed for the NAC system which describe the phases either by two, essentially independent, two-component order parameters[5] for the density wave and the tilt angle, or alternatively by an infinite-dimensional density order parameter proposed by de Gennes[2] and Chen and Lubensky.[4] Current experimental information[5] has been claimed to support the former approach, whereas our experiments definitively establish that the latter approach is more appropriate.

The phase diagram of the binary mixture ($\overline{8}S5_{1-x}$-$\overline{7}S5_x$) has been mapped out by Johnson *et al.*[6] For $x > x_{NAC}$ they find a first-order NC transition line with a continuously decreasing latent heat as x_{NAC} is approached (Fig. 1). We have carried out x-ray diffuse scattering studies for five concentrations, $x = 0.70$, 0.60, 0.50, 0.46, and 0.43; $x_{NAC} = 0.422$. The experimental configuration was identical to that discussed previously.[7]

In the nematic phase, the critical scattering near the NA transition is centered at $(0, 0, \pm q_\parallel^0)$. In the vicinity of an NC transition, the peaks spread out into two rings at $\vec{q}_c = (q_\perp^0 \cos\psi, q_\perp^0 \sin\psi, \pm q_\parallel^0)$, $0 \le \psi \le 2\pi$, and the density order parameter ρ exhibits large fluctuations for an infinite number of Fourier components $\rho(\vec{q}_c)$ near T_{NC}.

The scattering is shown figuratively at the top of Fig. 1, where the tilt angle $\Phi = \tan^{-1}(q_\perp^0/q_\parallel^0)$. The rings intersect the scattering plane at $(\pm q_\perp^0, 0, q_\parallel^0)$. In all mixtures, we carried out transverse ($q_\perp$ varied, $q_\parallel = q_\parallel^0$) and several longitudinal ($q_\parallel$ varied) scans through the edge ($q_\perp = \pm q_\perp^0$) and center $q_\perp = 0$ of one ring, for each temperature.

We first discuss the critical behavior at the NC boundary for a series of concentrations approaching x_{NAC}. We show in Fig. 2 scattering profiles for scans in the nematic phase in three mixtures, $x = 0.50$, 0.46, and 0.43, along the NC boundary. The tilt angles are $4.9° \pm 0.5°$ and $2.9° \pm 0.5°$ for $x = 0.50$ and 0.46, respectively, and for the mixture $x = 0.43$ [Fig. 2(c)] closest to x_{NAC} the data allow a tilt value of zero within the experimental uncertainties. In each mixture the transition is weakly first order with a concomitant jump of about 2° in the tilt angle across the phase boundary. We see in Fig. 3(a) (bottom) that for the large tilt angle (11.2°) when $x = 0.70$, a transverse cut through the ring yields a double-peaked profile, while in mixtures with smaller tilts for $x = 0.50$ and 0.46, the overlap of the peaks results in a flat-top profile.

The data have been analyzed quantitatively with the predictions of various models. The solid lines through the data are the results of least-squares fits of the predicted cross section for the NC transition of a NAC Lifshitz model of Chen and Lubensky (CL),[4]

$$S(\vec{q}) = \frac{A\xi_\parallel^2}{\tilde{a} + \xi_\parallel^2(q_\parallel - q_\parallel^0)^2 + (C_\perp/a)q_\perp^2 + (D_\perp/a)q_\perp^4}, \quad (1)$$

convoluted with the instrumental resolution function, to the experimental data. Here, the square of the transverse correlation length is $\xi_\perp^2 = 2|C_\perp|/a$, $a = a_0(T - T_{NC})$, $\tilde{a} = 1 + C_\perp^2/4aD_\perp$, and $C_\perp < 0$ is the coefficient of the transverse-gradient-squared term in the Hamiltonian model of CL. When $C_\perp$ is negative $S(\vec{q})$ peaks on the ring at $\vec{q}_c = (q_\perp^0 \cos\psi, q_\perp^0 \sin\psi, q_\parallel^0)$, $0 \le \psi \le 2\pi$, with $q_\perp^{02} = (|C_\perp|/2D_\perp)$ which is characteristic of the NC transition. For symmetry reasons, we only consider $q_\parallel > 0$. In this model, which is based on the infinite-dimensional density order parameter,[2] the tilt angle $\Phi = \tan^{-1}(q_\perp^0/q_\parallel^0)$, with $q_\perp^{02} = (|C_\perp|/2D)$, is determined by the competition between the second- and fourth-order transverse-gradient terms and does not enter as an independent order parameter. Clearly, Eq. (1) (solid lines) describes the data very well for $x \ge 0.46$ along the NC boundary as shown in Figs. 2(a), 2(b), 3(a) (bottom), and 3(b) (bottom). When $C_\perp$ is positive, Eq. (1) peaks for $q_\perp = 0$ and is characteristic of smectic-A fluctuations.[1,4] Therefore, in the nematic phase, a crossover line $C_\perp(x, T) = 0$ separates regions with A-like ($C_\perp > 0$) from those with C-like ($C_\perp < 0$) critical behavior. Along this line which terminates at x_{NAC}, $S(\vec{q})$ is predicted to exhibit Lifshitz $q_\perp^{-4}$ fluctuations.[4] An alternative model by Chu and McMillan[5] which describes the NC transition through two order parameters gives for the scattering

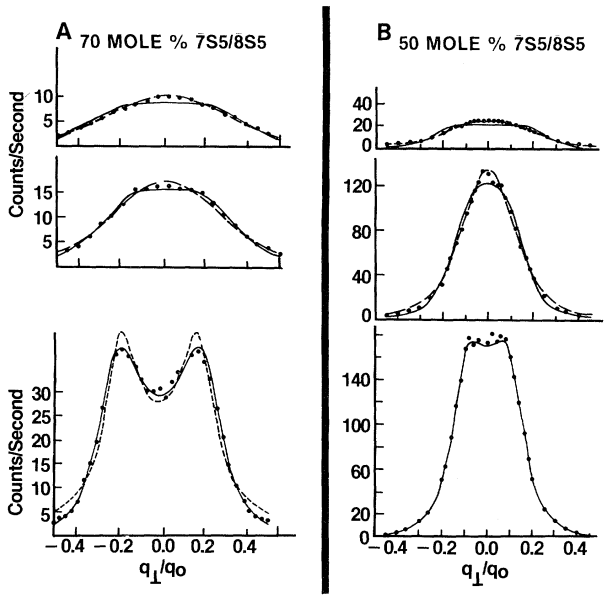

FIG. 3. Transverse profiles for (a) $x = 0.70$ (top, center, bottom are for $T - T_{NC} = 7.12$, 4.62, and 0.015 °C), and (b) $x = 0.50$ (top, center, bottom are for $T - T_{NC} = 4.78$, 1.17, and 0.005 °C), as a function of decreasing temperature in the nematic phase. The solid (broken) lines are fits by the Chen-Lubensky model with $C_\perp < 0$ ($C_\perp > 0$) and the dashed lines are fits by the Chu-McMillan model as discussed in the text. All error bars are within the extent of the data point.

$$S(\vec{q}) = \frac{A'\xi_\parallel^2}{[1 + \xi_\parallel^2(q_\parallel - q_\parallel^0)^2 + \xi_\perp^2(q_\perp - q_\perp^0)^2]^{1/2}[1 + \xi_\parallel^2(q_\parallel - q_\parallel^0)^2 + \xi_\perp^2(q_\perp + q_\perp^0)^2]^{1/2}}. \quad (2)$$

This form for the critical scattering yields $1/(q_\perp - q_\perp^0)^2$ tails while a related model by de Gennes[2] gives $1/|q_\perp - q_\perp^0|$ tails. For comparison, the dashed lines shown in Figs. 2(a), 2(b), and 3(a) (bottom) are the best fits of Eq. (2) to the data. Quite clearly, models with $1/q_\perp$ or $1/q_\perp^2$ tails do not describe the

transverse fluctuations. In fact, quantitative chi-squared (χ^2) tests show that while typically χ^2 are of order 15 for fits by Eq. (2), they decrease to about 1.5 for fits by the CL model Eq. (1). *An essential feature of the pretransitional smectic-C scattering is the highly non-Lorentzian transverse density fluctuations quantitatively accounted for by the CL Lifshitz model for the transition.* In addition, Eq. (1) describes the longitudinal scans quite well, while Eq. (2) is unable to fit the scans.

There remain, however, important discrepancies with the predictions of the CL model in the immediate NAC region. We reported earlier[8] that the density fluctuations in a mixture $x = 0.420$, close but to the left of x_{NAC}, are Lorentzian. Furthermore, we see in Fig. 2(c) that the model (solid lines) for $C_\perp < 0$ fails to describe the critical scattering for $x = 0.43$ ($x_{NAC} = 0.422$), although the transition is into the C phase with a small but measurable tilt. The broken line through the scan is a fit with the normally observed[1] pretransitional smectic-A scattering given by Eq. (1) for $C_\perp > 0$ and a small transverse $q_\perp^4$ term ($c \sim 0.05$); here $D_\perp = c\xi_\perp^4$.

We now consider data at fixed concentrations x as a function of temperature. Shown in Figs. 3(a) and 3(b) are transverse scans in the nematic phase as a function of temperature for $x = 0.70$ and 0.50, respectively. The solid and broken lines are fits by Eq. (1) for $C_\perp < 0$ and $C_\perp > 0$, respectively. Evidently, while at high temperatures the critical scattering is characteristic of smectic-A fluctuations, at lower temperatures in mixtures $x > x_{NAC}$ away from the immediate NAC region, the fluctuations crossover into a regime with pretransitional smectic-C fluctuations predicted by the CL model for the transition. In this latter regime, the pretransitional tilt angle increases as the NC boundary is approached by decreasing the temperature; this is most evident for $x = 0.70$ where we see the tilt angle increase from 3.8° for $T - T_{NC} = 4.62$°C [Fig. 3(a), center] to 11.2° for $T - T_{NC} = 0.15$ °C [Fig. 3(a), bottom]. For $x = 0.43$ [Fig. 2(c)], the scattering exhibits smectic-A fluctuations for all temperatures in the nematic phase. The crossover region shown in Fig. 1 occurs for $49.50 \pm 0.5 \leq T \leq 51.0 \pm 0.5$ for $x \geq 0.46$, and appears to be hidden inside the first-order NC line for the $x = 0.43$ mixture. Although scans in this region [Fig. 3(b), center] can be fitted by Eq. (1) for $C_\perp > 0$ with a relatively large $q_\perp^4$ term ($c > 1$, $D_\perp = c\xi_\perp^4$), nevertheless, contrary to the predictions of the CL model, the data never show a region where the $(\xi_\perp q_\perp)^2$ term vanishes.

We now discuss the significance of these results for understanding both the NC transition and the global NAC problem. Firstly, we emphasize that the CL Lifshitz model for $C_\perp < 0$ gives a quantitative description of the critical scattering associated with the nematic–smectic-C transition along the NC boundary in mixtures away from the immediate NAC region, whereas, the Chu-McMillan model is quite unsuccessful. Therefore, the tilt order parameter is properly described as the gradient of the density wave and cannot be treated as an independent order parameter. On the other hand, the CL model as presently constructed does not predict the proper location of the crossover line, the nature of the mass-density fluctuations in the crossover region, or the nature of the fluctuations in the immediate neighborhood of the NAC point. However, since the essential physical ingredients seem to be correct, a more complete CL theory which goes beyond a mean-field approximation and includes especially the divergent phase fluctuations may possibly be more successful.

We would like to thank G. Grinstein, B. I. Halperin, P. M. Horn, D. L. Johnson, and T. C. Lubensky for stimulating conversations. This work was supported by the National Science Foundation–Materials Research Laboratory under Contract No. DMR 78-24185 and by the Joint Services Electronics Program under Contract No. DAAG-29-80-C-0104.

[a]Present address: Brookhaven National Laboratory, Upton, N.Y. 11973.

[1]R. J. Birgeneau, C. W. Garland, G. B. Kasting, and R. M. Ocko, Phys. Rev. A 24, 2624 (1981), and references therein.

[2]P. G. de Gennes, Mol. Cryst. Liq. Cryst. 21, 49 (1973).

[3]S. A. Brazovskii, Zh. Eksp. Teor. Fiz. 68, 175 (1975) [Sov. Phys. JETP 41, 85 (1975)].

[4]J. L. Chen and T. C. Lubensky, Phys. Rev. A 14, 1202 (1976).

[5]K. C. Chu and W. L. McMillan, Phys. Rev. A 15, 1181 (1977); L. Benguigi, J. Phys. (Paris), Colloq. 40, C3-419 (1979).

[6]D. L. Johnson, P. Allender, R. DeHoff, C. Maze, E. Oppenheim, and R. C. Reynolds, Phys. Rev. B 16, 470 (1977).

[7]C. R. Safinya, M. Kaplan, J. Als-Nielsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson, and M. Neubert, Phys. Rev. B 21, 4149 (1980).

[8]C. R. Safinya, R. J. Birgeneau, J. D. Litster, and M. E. Neubert, Phys. Rev. Lett. 47, 668 (1981).