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Light Scattering above the Nematic-to-Smectic-*C* Transition

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The behavior of the bend elastic constant above the nematic–to–smectic-*C* transition in $\overline{7}$S5 is found to follow the prediction of Chen and Lubensky. The nature of the director fluctuations in $\overline{7}$S5–$\overline{8}$S5 mixtures indicates that the nematic–to–smectic-*C* transition near the nematic–smectic-*A*–smectic-*C* multicritical point exhibits both smectic layer and tilt fluctuations and is not adequately described by existing models.

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The nematic–to–smectic-*A* (NA) transition has been studied extensively.[1] The nematic–to–smectic-*C* (NC) transition, on the other hand, has received less attention. One interesting aspect of the NC transition which has remained unresolved is the critical behavior of the Frank elastic constants. Using an infinite-dimensional density wave order parameter, de Gennes suggested that all three Frank elastic constants should diverge as $\xi^{3/2}$, where ξ is the smectic correlation length.[2] Starting from a similar point of view but describing the NA and NC transitions in the same model with different free-energy parameters, Chen and Lubensky predicted a ξ^2 divergence.[3] Finally, with an additional dipolar order parameter, Chu and McMillan predicted a divergence proportional to ξ.[4] Experimentally, the only quantitative attempt has been a measurement of the cholesteric pitch near the smectic-*C* phase, which proved to be inconclusive because of the large background contribution.[5] Another phenomenon which is not well understood is the nature of the nematic–smectic-*A*–smectic-*C* (NAC) multicritical point, which occurs when a material with an NC transition is mixed with another with an NA and a smectic-*A*–to–smectic-*C* (AC) transition.[6] This has been the subject of several theoretical[3,4,7-9] and experimental[10-12] studies. None of the suggested models describes satisfactorily the observed behavior near the NAC point. We report here the results of light-scattering studies above the NC transition in 4-*n*-pentyl-phenylthiol-4′-heptyloxybenzoate ($\overline{7}$S5) and its mixtures with the octyloxy analog ($\overline{8}$S5). Our objectives are to test the validity of the various models describing the NC transition and to provide information about the nature of the director fluctuations near the NAC point.

Our samples were synthesized by M. E. Neubert of Kent State University. Pure $\overline{7}$S5 has a first-order monotropic NC transition. With the addition of $\overline{8}$S5, which exhibits second-order NA and AC transitions, the phase diagram as a function of the mole concentration x of $\overline{7}$S5 is shown in Fig. 1. The NC transition entropy decreases from $0.84R_0$ at $x = 1$ to 0 at the multicritical concentration $x_{NAC} = 0.42$.[10]

Planar samples were formed between glass slides with the director parallel to the slides.

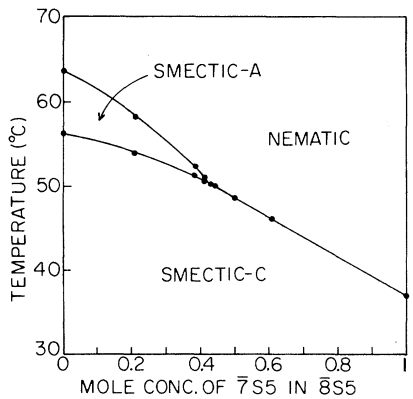

FIG. 1. Phase diagram of the $\overline{7}$S5–$\overline{8}$S5 mixtures studied.

Polarized light was incident on the sample, with the polarization direction normal to the director. The depolarized scattered-light intensity was measured at an angle chosen so that the scattering wave vector q was parallel to the director. This scattering geometry is used to probe the director bend mode. In the nematic phase, the scattering intensity I is proportional to $(K_3 q^2)^{-1}$, where K_3 is the bend elastic constant.[13] Our data for the temperature dependence of I above the NC transition in $\overline{7}$S5 ($x = 1$) are shown in Fig. 2. For comparison, the corresponding data above the NA transition in $\overline{8}$S5 ($x = 0$) are shown in Fig. 3. The sharp drop in I above the NA transition is due to the pretransitional divergence of K_3, which is proportional to the smectic correlation length $\xi_{\parallel}$ parallel to the director.[14,15] In contrast, the decrease in I above the NC transition in $\overline{7}$S5 is much more gradual. There is an abrupt change at the transition temperature T_{NC} due to the first-order nature of the transition. More significantly, I is found to be asymptotically linear with temperature in the 4-K range immediately above T_{NC}.

The implication of our result in $\overline{7}$S5 can be seen by examining the predictions of the various models. Since the NC transition is highly first order, one expects ξ to have the mean-field temperature dependence of $\xi = \xi_0 t^{-1/2}$, where $t = (T - T^*)/T^*$, and T^* is the apparent critical temperature. The pretransitional increase of K_3 above its intrinsic value K_{30} is then predicted to have the form

$$K_3 = K_{30} + \delta K_0 t^{-\zeta}, \tag{1}$$

where the exponent $\zeta = 0.75$, 1, and 0.5 according to the de Gennes,[2] Chen-Lubensky,[3] and Chu-McMillan[4] models, respectively. The light-scattering intensity I is given by

$$I = A/(K_{30} + \delta K_0 t^{-\zeta}). \tag{2}$$

The asymptotic behavior, as t approaches 0, is expected to be

$$I = (A/\delta K_0) t^{\zeta}. \tag{3}$$

It can be seen from Eq. (3) that only the Chen-Lubensky model predicts a linear asymptotic behavior, while the other two models predict quite different nonlinear temperature dependence. To further illustrate the agreement between the data in $\overline{7}$S5 and the Chen-Lubensky prediction, Fig. 4

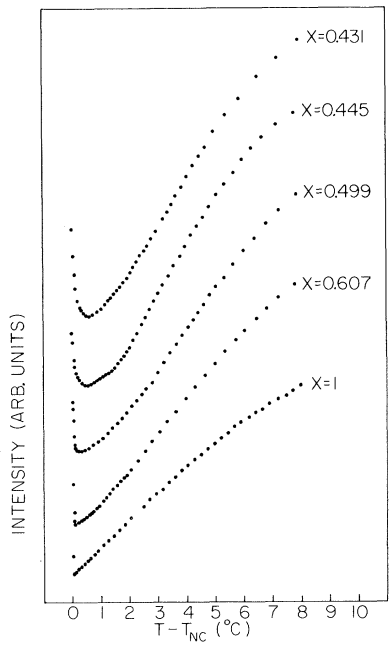

FIG. 2. Temperature dependence of light-scattering intensity above the NC transition in $\overline{7}$S5-$\overline{8}$S5 mixtures of various mole concentration x of $\overline{7}$S5. The ordinate for each x has been arbitrarily shifted.

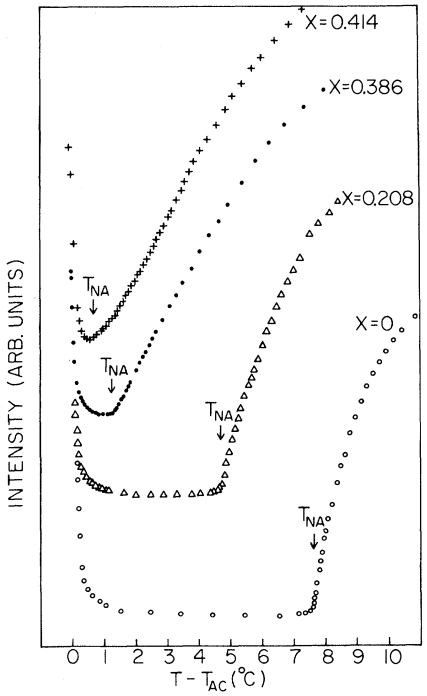

FIG. 3. Temperature dependence of light-scattering intensity near the NA and AC transitions in $\overline{7}$S5-$\overline{8}$S5 mixtures of various mole concentration x of $\overline{7}$S5. The ordinate for each x has been arbitrarily shifted and some points near T_{AC} have been deleted because of overlapping.

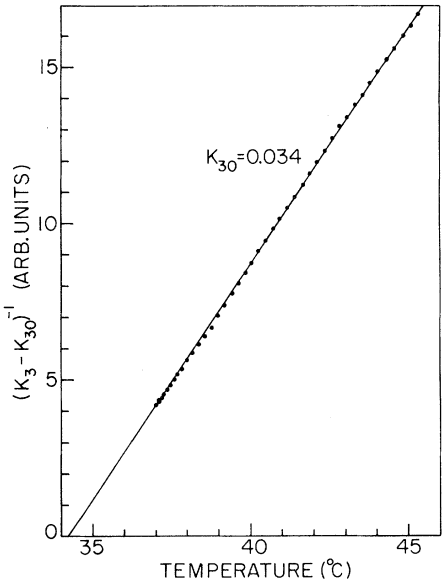

FIG. 4. Temperature dependence of $(K_3 - K_{30})^{-1}$ in $\overline{7}$S5.

shows the temperature dependence of $(K_3 - K_{30})^{-1}$, where K_{30} is chosen to be 0.034 in arbitrary units. The value of $(K_3 - K_{30})^{-1}$ varies linearly with temperature in accordance with Eq. (1) with $\zeta = 1$ over a wide range, and extrapolates to 0 at a temperature T^* which is 2.7 K below T_{NC}. This represents the first quantitative test of the validity of the Chen-Lubensky model in describing the behavior of K_3 above the NC transition.

The temperature dependence of I above the NC transition in $\overline{7}$S5-$\overline{8}$S5 mixtures with decreasing x is shown in Fig. 2. The most striking result is the dramatic qualitative difference between the data for $x = 1$ and those for $x = 0.431$, which is just above x_{NAC}. Compared to the gradual and asymptotically linear drop in I for $x = 1$, the $x = 0.431$ plot has a steeper initial drop in I, followed by a rounding to a minimum value, and finally a pronounced increase in the 0.5-K range immediately above T_{NC}. The plots with $1 > x > 0.431$ show a gradual evolution from the former to the latter behavior. The increasing steepness of the initial drop in I as x decreases can be understood in terms of the decreasing NC transition entropy. As the transition changes from highly first order for $x = 1$ to second order at x_{NAC},[10] the critical exponent of ξ changes from the mean-field value of 0.5 to a higher non-mean-field value. The value of K_3 then increases more rapidly, and I decreases more steeply. Likewise, the rounding of I near a minimum can be explained. As the transition becomes closer to being second order with decreasing x, ξ may be able to increase to a large enough value so that $q\xi$ is comparable to 1. In this nonhydrodynamic region, K_3 appears to stop growing, resulting in a rounding of I.[16] The eventual rapid increase of I immediately above T_{NC} for mixtures with x approaching x_{NAC}, however, is anomalous, since it is not explainable by any expected behavior of K_3. It should be mentioned that this increase of I appears to be intrinsic and not related to any phase coexistence, since it occurs in a temperature range considerably larger than that of any two-phase region that is observable in these mixtures.[17]

Some hint of the significance of our findings can be obtained by examining the data for mixtures with $x < x_{NAC}$, which are shown in Fig. 3. The data for $\overline{8}$S5 ($x = 0$) is well understood. In the nematic phase, I is proportional to $(K_3 q^2)^{-1}$, and the decrease near the NA transition is due to the divergence of K_3. In the smectic-A phase, I is proportional to $(D + K_3 q^2)^{-1}$, where D is the elastic constant for the director to deviate from the layer normal.[18] The scattering intensity remains relatively constant in the smectic-A phase, but increases again near the AC transition as D approaches 0, signifying the pretransitional increase of tilt fluctuations.[2] This general behavior of I near the NA and AC transitions persists in the other mixtures with $0 < x < x_{NAC}$, except for some gradual qualitative changes. With increasing x, there is a progressive rounding of I near the NA transition. This is a manifestation of nonhydrodynamic behavior due to the increase in the bare correlation length ξ_0 in these mixtures.[11] As x approaches x_{NAC} and the smectic-A range diminishes, the NA and AC critical effects interfere with one another. At $x = 0.414$, I simply reaches a minimum before rising again. It is difficult to determine x_{NAC} exactly. However, there is little doubt from independent birefringence measurement that $x = 0.414$ in Fig. 3 is below x_{NAC}, while $x = 0.431$ in Fig. 2 is above x_{NAC}. The significant observation to be made is that the light-scattering behavior in these two mixtures on opposite sides of x_{NAC} is almost identical. We have also studied several mixtures with $0.414 < x < 0.431$ and obtained similar results. One is faced with the conclusion that *the nature of the director fluctuations in the immediate vicinity of the NAC point is independent of whether x is greater or less than* x_{NAC}.

The result for the $x = 0.414$ mixture, which undergoes NA and AC transitions in close proximity,

is understood to be due to increasing smectic layer fluctuations with decreasing temperature, followed by increasing tilt fluctuations. The similarity of the data for the $x = 0.431$ mixture, which undergoes an almost second-order NC transition, suggests the presence of both smectic layer and tilt fluctuations. The tilt fluctuations are observable by light scattering even in the absence of long-range smectic order because the large value of ξ_0 near x_{NAC} (Ref. 11) and the wave vector used ($q \simeq 6\times 10^{-4}$ Å^{-1}) are such that $q\xi \simeq 1$ about 0.5 K above T_{NC}. In the nematic phase close to the NC transition, one might envisage the occurrence of fluctuating short-range layered regions, which are smectic-A-like,[12] as well as large fluctuations in the orientations of the director relative to the layer normal in these regions. Near $x = 1$, the cybotactic groups are smectic-C-like,[12] but tilt fluctuations are unimportant because the tilt angle is large and well defined. Our data in $\bar{7}$S5 are therefore well described by the Chen-Lubensky model. It is clear, however, that none of the existing models can adequately account for the behavior over the entire NAC phase diagram.

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