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Measurement of Smectic-*A*-Phase Order-Parameter Fluctuations near a Second-Order Smectic-*A*–Nematic-Phase Transition

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The anisotropic liquid-structure factor of *p*-cyanobenzylidene-amino-*p*-*n*-octyloxybenzene has been measured in the nematic phase using Cu $K\alpha$ x rays. This material exhibits a second-order phase transition to the smectic *A* phase at $T_c = 82.8$ °C. The liquid-structure factor shows a non-Lorentzian peak at a wave number of $q_0 = 0.179$ Å^{-1} (equivalent *d* spacing 35.0 Å) of the following form: $S_q = 1 + \{3.5\epsilon^{\gamma} + 10\ [(q_{\parallel} - q_0)/q_0]^2 + 0.6(q_{\perp}/q_0)^{\eta}\}^{-1}$, where $\epsilon = (T - T_c)/T_c$, $\gamma = 1.49 \pm 0.1$, $\eta = 2.5 \pm 0.2$, and $\hbar q_{\parallel}$ ($\hbar q_{\perp}$) are the momentum transfers parallel (perpendicular) to the orienting field.

I. INTRODUCTION

The author[1] has recently published a measurement of the anisotropic-liquid-structure factor in the nematic phase of *p*-*n*-octyloxybenzylidene-*p*-toluidine (OBT), a material which has a first-order nematic-smectic-*A*-phase transition. The liquid-structure factor is peaked in field direction and at a scattering angle equal to the smectic-*A* Bragg angle. The peak shape is Lorentzian and the peak height grows as one approaches the transition to the smectic-*A* phase. This pretransition phenomenon is physically due to small regions of the nematic fluctuating into a smectic-*A*-like configuration. Mathematically one describes the phenomenon using a Landau theory of the phase transition and calculating the scattering due to order-parameter fluctuations. The Landau theory is due to the author[2] and to deGennes.[3] The theory predicts a Lorentzian peak in the liquid-structure factor with the peak height varying as $(T - T^*)^{-1}$, where T^* is a critical temperature somewhat below the first-order transition temperature. The measurements on OBT agreed well with the peak shape and temperature dependence predicted by the Landau theory. The correlation length is 84 Å, 0.3 °C above the phase transition.

In the present paper we present a measurement of the anisotropic-liquid-structure factor in the nematic phase of *p*-cyanobenzylidene-amino-*p*-*n*-octyloxybenzene (CBAOB). In this material the smectic-*A*-nematic-phase transition is second order. The peak height varies as $(T - T_c)^{-\gamma}$ with $\gamma = 1.49 \pm 0.1$ and the peak shape is no longer Lorentzian but falls off faster in the transverse direction. The longitudinal correlation length is very long, ~2500 Å, 0.2 °C above the phase transition.

The x-ray apparatus has been described previously. The present sample showed stronger scattering near the phase transition and it was, therefore, possible to work at higher resolution; collimators of 0.3×3 mm were used in addition to the 1×3-mm collimators used previously.

The sample of CBAOB obtained from Eastman (No. 923247) was relatively pure and was recrystallized once from ethanol. The transition temperatures were measured with a polarizing microscope equipped with a Mettler FP5 hot stage and the transition entropies were measured on a Perkin–Elmer DSC-1B differential scanning calorimeter; these results are reported in Table I. The smectic-*A*-nematic transition was unobservable on the calorimeter, which can detect a transition entropy of about $0.02R_0$; this transition is presumably second order.

The experimental results are presented in Sec. II and analyzed in Sec. III.

TABLE I. Transition temperatures and transition entropies of CBAOB. The smectic-*A*-nematic transition is unobservable on the scanning calorimeter.

Transition	Temperature (°C)	Entropy
Crystal → smectic *A*	73.2	$9.1R_0$
Smectic *A* → nematic	82.8	$<0.02R_0$
Nematic-isotropic	107.5	$0.26R_0$

II. EXPERIMENTAL RESULTS

The nematic phase is uniaxial and the liquid-structure factor is a function of momentum transfer parallel to the external field $\hbar q_{\parallel}$ and transverse to the external field $\hbar q_{\perp}$. The sample is aligned in a field of 10 kG. In the nematic phase the liquid structure exhibits a peak in the field direction ($q_{\perp}=0$) for $q_{\parallel}=0.179$ Å^{-1}; the equivalent d spacing is 35.0 Å which is equal to the interplanar spacing in the smectic-A phase. The intensities measured at three temperatures are presented in Fig. 1 for the longitudinal section (I vs $q_{\parallel}$ for $q_{\perp}=0$) and in Fig. 2 for the transverse section (I vs $q_{\perp}$ for $q_{\parallel}=0.179$ Å^{-1}). The peak intensity (for $q_{\parallel}=0.179$ Å^{-1}, $q_{\perp}=0$) versus temperature was also measured from 83 to 91 °C. The data close to the peak were taken with the high-resolution 0.3×3-mm collimators and the data in the wings (open circles) were taken with 1×3-mm collimators which gave a factor of 43 greater intensity. The vertical scale in these figures is the number of counts per 4-min counting period for the 0.3×3-mm collimators. The 1×3-mm data approach a constant 70 counts/counting period (after subtracting a background of 30 counts)

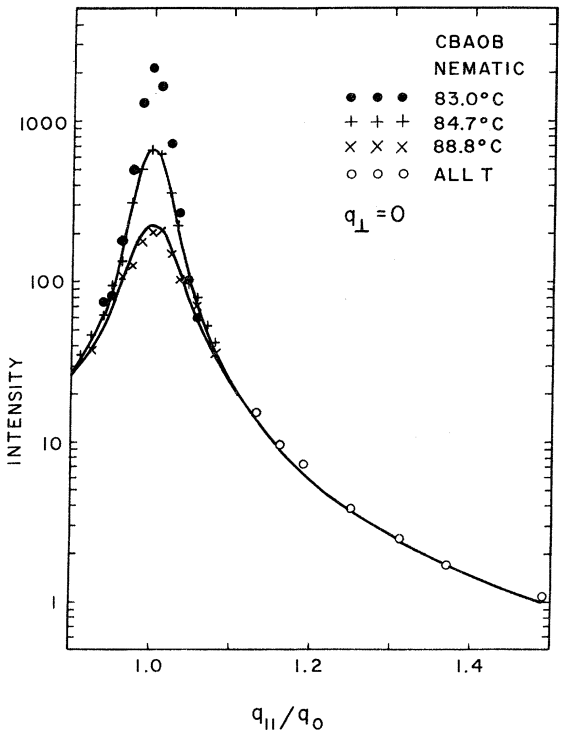

FIG. 1. Intensity versus $q_{\parallel}$ for $q_{\perp}=0$ for CBAOB in the nematic phase. The open circles are data taken with 1×3-mm collimators at all three temperatures; these data are independent of temperature. The solid lines are from Eq. (3) convoluted with the instrumental resolution function.

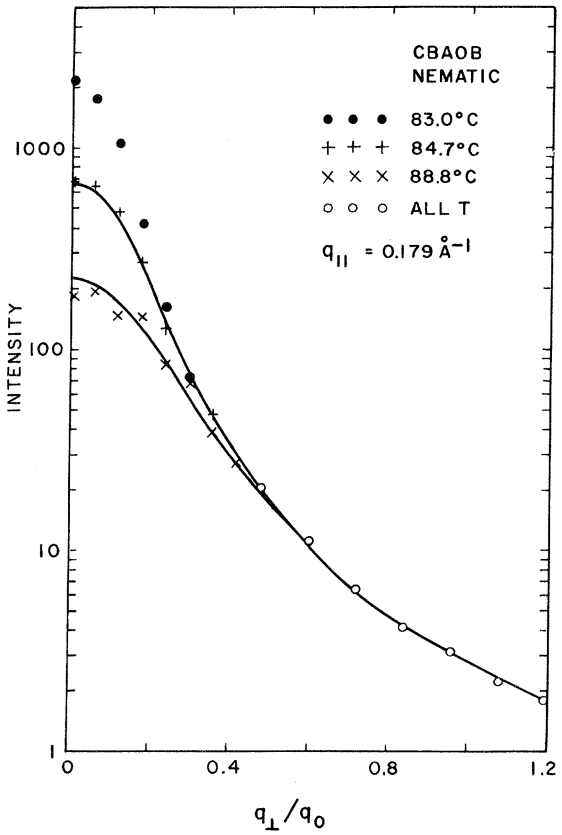

FIG. 2. Intensity versus $q_{\perp}$ for $q_{\parallel}=q_0=0.179$ Å^{-1} for CBAOB in the nematic phase. The data are labeled as in Fig. 1.

for large q in both the longitudinal and transverse directions. This is the random-gas contribution to the liquid-structure factor and permits one to determine an absolute normalization for the data. This constant term has been subtracted from the data in Figs. 1 and 2.

With the 0.3×3-mm collimators the instrumental resolution in both longitudinal and transverse directions is adequate at the two higher temperatures; however at the lowest temperature the peak height is resolution limited. An attempt to fit these data with a two-dimensional Lorentzian failed; the data in the longitudinal direction are accurately Lorentzian but in the transverse direction the intensity falls off more rapidly than $q_{\perp}^{-2}$. In order to probe this behavior, the collimators were rotated 90° (3×0.3 mm) to provide high resolution in the transverse direction, and the final collimator was opened up to 8×0.3 mm. In this configuration one is measuring the integral of the liquid-structure factor over $q_{\parallel}$ but with high resolution in the transverse direction. These data are shown at the lowest temperature in Fig. 3. The peak intensity versus temperature was also measured.

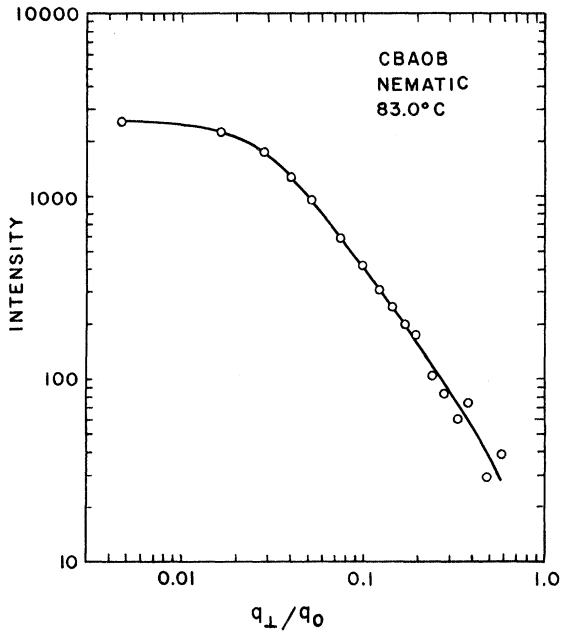

FIG. 3. Intensity versus $q_\perp$ for the 3×0.3-mm collimators for CBAOB in the nematic phase. The solid line is from Eq. (3) integrated over $q_\parallel$. Finite slit-height corrections are included here.

III. DATA ANALYSIS

The Landau theory of the smectic-A phase predicts a Lorentzian peak in the liquid-structure factor:

$$S_q = 1 + \left[\beta(T) + \alpha_\parallel\left(\frac{q_\parallel - q_0}{q_0}\right)^2 + \alpha_\perp\left(\frac{q_\perp}{q_0}\right)^2\right]^{-1}, \quad (1)$$

with β varying linearly with temperature,

$$\beta = \beta_0(T - T_c)\ . \quad (2)$$

In order to fit the data on CBAOB we must modify this expression in two ways. The exponent of $q_\perp$ must be increased and the exponent of $T - T_c$ must be increased. The data of Figs. 1–3 are fitted nicely by choosing the exponent of $q_\perp$ to be 2.5 rather than 2. The solid lines in these figures show the fit obtained with the parameters given in Eq. (3); the instrumental resolution has been folded in. Once the other parameters have been fixed one can determine β at any temperature from a measurement of peak height at that temperature. Values of $\beta/\alpha_\parallel$ determined from the peak height versus temperature for both the 0.3×3-mm and 3×0.3-mm collimator runs are shown in Fig. 4. The straight line is drawn with an exponent of 1.49. Thus, we find experimentally that the liquid-structure factor of CBAOB is given by

$$S_q = 1 + \left[\beta_0\epsilon^\gamma + \alpha_\parallel\left(\frac{q_\parallel - q_0}{q_0}\right)^2 + \alpha_\perp\left(\frac{q_\perp}{q_0}\right)^\eta\right]^{-1},$$

with $\epsilon \equiv (T - T_c)/T_c$, $\gamma = 1.49 \pm 0.1$, $\eta = 2.5 \pm 0.2$, $\beta_0 = 3.5$, $\alpha_\parallel = 10$, and $\alpha_\perp = 0.6$. The absolute normalization is accurate only within ± 20% and $\alpha_\parallel$ and $\alpha_\perp$ are independent of temperature within ± 5%. The solid lines in Figs. 1–3 were computed from this expression with instrumental resolution folded in.

IV. CONCLUSIONS

We have found a material with a second-order smectic-A-nematic-phase transition and have measured the liquid-structure factor in the nematic phase. The order-parameter fluctuations are in a critical regime with peak height $\alpha\epsilon^{-1.49}$ and longitudinal and transverse coherence length proportional to $\epsilon^{-0.75}$ and $\epsilon^{-0.6}$, respectively. The value of $\gamma = 1.49$ is somewhat larger than that found for other phase transitions and the anisotropy of the exponents for the coherence lengths was unexpected. The hot stage used here was not designed for critical-point work, and it was not possible to work closer than 0.2 °C to the phase transition. The longitudinal coherence length is 2500 Å, 0.2 °C above the transition and the longitudinal resolution is ~ 300 Å. It is desirable to have this experiment repeated with an improved hot stage and with the

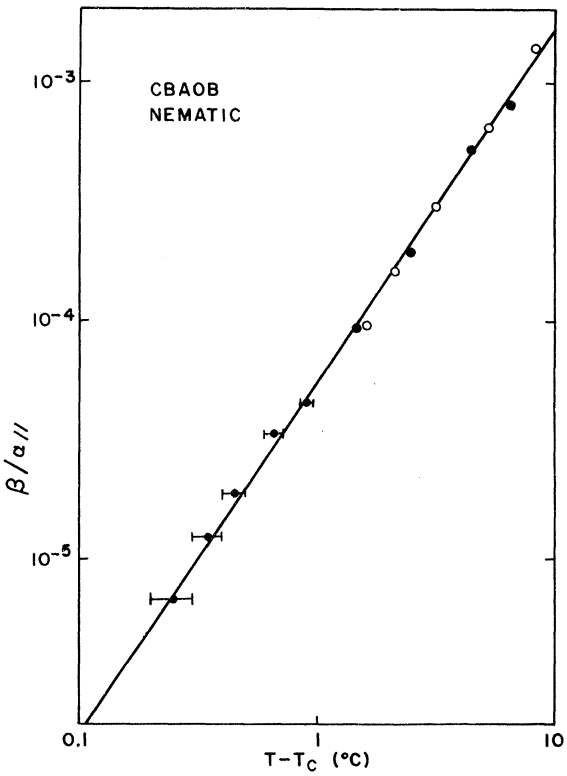

FIG. 4. Inverse peak height versus temperature from the 0.3×3-mm collimator data (open circles) and the 3×0.3-mm collimator data (filled circles). The data have been corrected for instrumental resolution. The solid line is drawn with a slope of 1.49.

full resolution of single-crystal techniques. Because of the resolution problem it was not possible to separate the fluctuation and Bragg-scattering contributions in the smectic-A phase. It is desirable to have measurements on this material of other properties (e.g., heat capacity and elastic constants) which are expected to exhibit critical behavior.

Some feeling for the domain of validity of the "classical" Landau[2,3] and microscopic[4,5] theories is beginning to emerge from this series of measurements. The phase diagram predicted by the microscopic theory appears to be qualitatively correct. In a given homologous series the shorter members exhibit a wide-temperature range of the nematic phase and a second-order smectic-A-nematic-phase transition. With increasing molecular length the width of the nematic phase decreases and at some point the smectic-A-nematic-phase transition becomes first order; the entropy of this transition then increases with increasing molecular length. Finally the smectic-A-nematic and nematic-isotropic transitions coalesce. In the region where the smectic-A-nematic transition entropy is moderately large ($>0.5R_0$), both the microscopic theory (tested on cholesteryl myristate[2]) and the Landau theory (tested on octyloxybenzylidene-toluidene[1]) work quite well. For very small transition entropy (cholesteryl nonanoate[2]) the microscopic theory does not work, and we have shown that the Landau theory fails for a second-order transition.

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