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Critical Behavior at the Nematic-to-Smectic-*A* Transition in a Strong Magnetic Field

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The critical divergence of the smectic-order correlation lengths parallel and perpendicular to the director, $\xi_{\parallel,\perp}$, and the susceptibility, σ_0, near the nematic-to-smectic-*A* phase transition has been measured in a 5 T magnetic field. The high magnetic field reduced the mosaicity and improved the effective transverse resolution by almost 2 orders of magnitude and permitted measurements nearly over four decades of reduced temperature. The results provide important new insights into mosaicity correction. The values of the critical exponents of $\xi_{\parallel,\perp}$ and σ_0 were $\nu_\parallel = 0.79 \pm 0.02$, $\nu_\perp = 0.68 \pm 0.02$, $\gamma = 1.45 \pm 0.04$, respectively. They become smaller for a narrower nematic range.

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Liquid crystals provide good model systems for studying phase transitions and testing the universality concept. One of the most interesting and most extensively studied transitions is the nematic (N) to smectic-*A* (Sm*A*) (or *NA*) phase transition. Since the Sm*A* phase can be described in terms of a two component complex order parameter, Ψ, the *NA* transition was, at first, expected to be in the 3D-*xy* universality class [1]. However, experiments [2] have revealed the much more complex nature of this transition and raised two major issues: nonuniversal critical behavior and anisotropic divergence of the correlation lengths $\xi_{\parallel,\perp}$ parallel and perpendicular to the director $\hat{n}$ that is reflected in unequal values of their critical exponents $\nu_{\parallel,\perp}$, respectively. The situation is further complicated by the existence of the Landau-Peierels instability [3] in the Sm*A* phase. Several theoretical approaches have been used to understand these issues. The superconductor analogy [1,4,5] suggests that the *NA* transition should be in the inverted 3D-*xy* universality class, and the *x-ray* correlation lengths should display a crossover from isotropic ($\nu_\parallel = \nu_\perp = \nu_{xy}$) to strongly anisotropic ($\nu_\parallel = 2\nu_\perp$) divergence. The defect-mediated melting theory [6] predicts strongly anisotropic behavior, which agrees with the existence of a $\nu_\parallel = 2\nu_\perp$ fixed point in the anisotropic scaling theory [4]. Finally, self-consistent one-loop calculations [7] predict a gradual crossover from isotropic to strongly anisotropic ($\nu_\parallel = 2\nu_\perp$) behavior including a broad region of weak anisotropy ($1 \leq \nu_\parallel/\nu_\perp \leq 4/3$) consistent with experimental observations [8].

As emphasized by Garland and Nounesis [2], the complexity of the *NA* transition results mostly from two types of coupling. First, coupling of the Ψ to the nematic orientational order parameter, S, causes a crossover from critical to tricritical behavior with decreasing nematic range [9–11]. The effects of this Ψ-S coupling are minimal in materials with a wide nematic range. The second coupling is between Ψ and director fluctuations which can drive the transition weakly first order [12] and lead to anisotropic critical behavior [7]. Experimentally, it is not possible to avoid the effects of this coupling since a complete quenching of director fluctuations requires [13] an immense field $B \gtrsim 300$ T. Even in the vicinity of the tricritical point, a field $\gtrsim$33 T is needed [13] to observe this effect.

Measurements of $\xi_\parallel$ and $\xi_\perp$ in the vicinity of the transition are essential to observe a crossover to strongly anisotropic behavior. However, x-ray scattering measurements very close to the transition temperature, T_{NA}, are hindered by poor transverse resolution which is limited by the sample *mosaicity,* i.e., imperfect macroscopic alignment of $\hat{n}$. All previous x-ray measurements [2] have been done using low magnetic fields ($\sim$0.1–0.8 T), with the mosaicity width substantially larger than the instrumental transverse resolution. The data have been corrected [8,14,15] with the *unproven* assumption that the mosaicity measured at T_{NA} remains unchanged at higher temperatures. Dasgupta [5] suggested that a careful examination of the effects of mosaicity may provide important insight into the puzzling behavior of the correlation lengths at this transition.

In this Letter, we report the results of a high-resolution x-ray diffraction study of the *NA* transition under magnetic fields as large as 5 T. A field of 5 T allowed us to reduce the mosaicity and improve the effective transverse resolution by almost 2 orders of magnitude. Two mixtures of the sixth and seventh homologs of the 4-4'-alkylazoxybenzene (DnAOB) series and octylcyanobiphenyl (8CB) were studied. DnAOB represents a series of two-benzene-ring nonpolar compounds, which exhibit a simple isotropic-N-Sm-*A*-crystal phase sequence. We prepared mixtures with 15% and 40% D7AOB in D6AOB. These mixtures denoted as D6.15AOB and D6.4AOB have T_{NA}/T_{NI} of 0.89 and 0.91, respectively. For both mixtures, the *NA* transition is well removed from the tricritical point [16–18] and they are good candidates for critical behavior studies with minimal Ψ-S coupling. The *NA* transition in 8CB ($T_{NA}/T_{NI} = 0.98$) is believed to be very close to the tricritical point [10,11] or even weakly first order [13,19]. 8CB was studied to compare the high field measurements with previous x-ray [10,14] and light scattering [20] results.

The x-ray scattering experiments were performed using a 12-KW Rigaku rotating-anode generator and a custom designed split-coil superconducting magnet mounted on a two-circle Huber goniometer [8]. The magnet produced a horizontal field and had two orthogonal horizontal bores with an angular opening of ~14°. We used a Mo target and its $K_{\alpha_{1,2}} = 0.71$ Å line to maximize the q range. For some measurements, a Cu target and only the Cu K_{α_1} line was used to simplify the data analysis. Single crystals of Si(111) were used as the monochromator and analyzer that provided resolutions: $\Delta q_\parallel \simeq 2 \times 10^{-4}$ Å^{-1}, $\Delta q_\perp \simeq 10^{-5}$ Å^{-1}, and (out-of-plane) $\Delta q_z \simeq 4 \times 10^{-2}$ Å^{-1}. The sample, approximately 6 mm in diameter and 1 mm thick, was sealed between two ~8 μm thick Mylar films and placed inside a two-stage oven (with Be windows) mounted inside the magnet. The long (24 h) and short (1 h) term temperature stability was $\lesssim \pm 1$ mK and $\lesssim \pm 0.5$ mK, respectively. The data were corrected for the observed small drift in $T_{NA} \sim 0.5$ mK/day for D6.15AOB and D6.4AOB and 2 mK/day for 8CB.

We studied the dependence of the sample mosaicity on the magnetic field ranging from 0.25 to 5 T. Figure 1 shows the sharpest $q_\perp$ scans taken at the closest temperature to T_{NA}, as a function of B for D6.15AOB. Their widths, $\Delta q_M(B)$, represent the effective transverse resolution and are a measure of the mosaicity. At 5 T, the $q_\perp$ scan is essentially limited by the instrumental transverse resolution [$\Delta q_M(5\text{ T}) \simeq \Delta q_\perp$]. This scan has the same profile as a resolution limited $q_\parallel$ scan and could be fitted to a sum of three Lonrentians, while $q_\perp$ scans at lower fields were reasonably well fitted by a single Lorentzian. The effective $\Delta q_\perp$ at 5 T is ~60 times sharper than at 0.25 T; the latter is comparable to the magnetic fields used in most previous x-ray experiments [8,14]. Clearly, the effects of sample mosaicity in a 5 T field are minimal and almost undetectable.

X-ray scattering from smectic fluctuations in the nematic phase is described by the structure factor [14], $S(\mathbf{q}) = \sigma_0/[1 + \xi_\parallel^2(q_\parallel - q_0)^2 + \xi_\perp^2 q_\perp^2 + c\xi_\perp^4 q_\perp^4]$, where q_0 is the nearly temperature independent smectic wave vector. The mosaicity effects become dominant when the width of $q_\perp$ scans, which is roughly proportional to $\xi_\perp^{-1}$, becomes comparable to the mosaicity limited transverse resolution Δq_M. Since $\xi_\perp(t) = \xi_\perp^0 t^{-\nu_\perp}$ ($\xi_\perp^0$ is the bare correlation length), we estimate the temperature, t_M, at which the effects of mosaicity become significant from the condition $\xi_\perp(t_M) \sim (\Delta q_M)^{-1}$ and obtain $t_M \sim (\xi_\perp^0 \Delta q_M)^{1/\nu_\perp}$. Thus, the mosaicity correction is insignificant when $t \gg t_M$ but essential in the region where $t \lesssim t_M$. Typically, for $\nu_\perp \sim 0.6$, $t_M(5\text{ T})/t_M(0.25\text{ T}) = [\Delta q_M(5\text{ T})/\Delta q_M(0.25\text{ T})]^{1/\nu_\perp} \simeq (1/60)^{1/0.6} \simeq 10^{-3}$. In a 5 T field, three more decades of reduced temperature become accessible without mosaicity correction than in 0.25 T. However, there are two additional limiting "reduced temperatures" in these experiments. One of them is related to the temperature stability ΔT of the oven and gives $t_s \sim \Delta T/T_{NA} \sim 2 \times 10^{-6}$, while the second depends on $\Delta q_\parallel$ and can be defined as $t_\parallel \sim (\xi_\parallel^0 \Delta q_\parallel)^{1/\nu_\parallel}$. The largest of t_s, t_M, and $t_\parallel$ sets the lower limit of the temperature range in which data are reliable.

The D6.15AOB sample was studied at $B = 5$, 0.5, and 0.25 T over ~3.5 decades of t. The data were first analyzed without mosaicity correction by simultaneously fitting both $q_\parallel$ and $q_\perp$ scans to the convolution of the structure factor with the instrumental resolution function to yield $\xi_{\parallel,\perp}$ and σ_0. Figure 2 shows log-log plots of

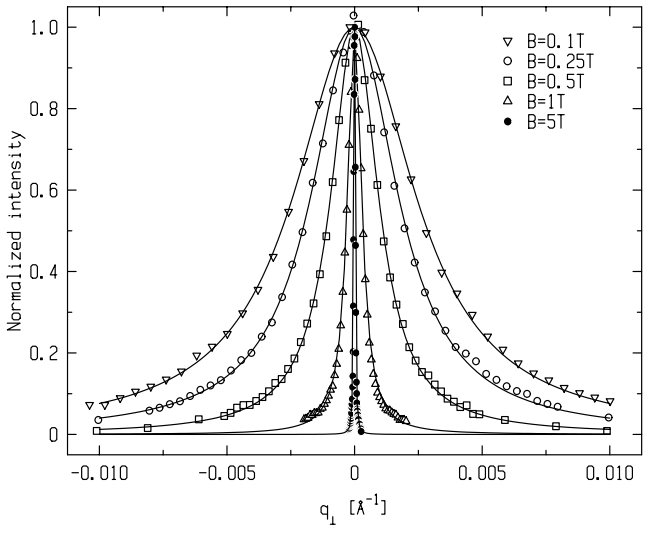

FIG. 1. The sharpest normalized $q_\perp$ scans for D6.15AOB obtained at the temperature closest to T_{NA} represent the effective transverse resolution at different fields. The solid lines are fits to a sum of three Lorentzians for 5 T and a single Lorentzian for other fields.

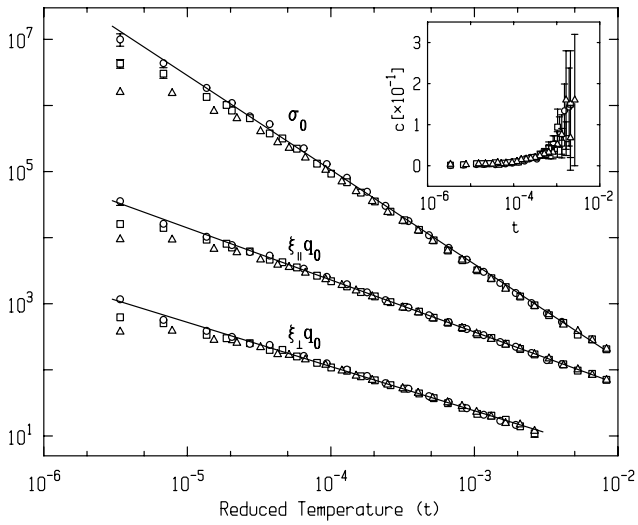

FIG. 2. Temperature dependence of (dimensionless) $\xi_{\parallel,\perp} q_0$ and σ_0 for D6.15AOB without mosaicity correction at different fields ($q_0 = 0.237$ Å^{-1}). The bend at small fields and t is due to sample mosaicity. The (○), (□), and (△) represent the data at 5, 0.5, and 0.25 T, respectively. The solid lines are the fits to 5 T data discussed in the text. The inset shows temperature dependence of c for different fields.

dimensionless numbers $q_0 \times \xi_{\parallel,\perp}(t)$ and $\sigma_0(t)$, where t was corrected for the T_{NA} drift. The 5 T data lie on straight lines indicating single power-law divergences, i.e., $\sigma_0 = \sigma_0^0 t^{-\gamma}$, $\xi_\parallel = \xi_\parallel^0 t^{-\nu_\parallel}$, and $\xi_\perp = \xi_\perp^0 t^{-\nu_\perp}$, where σ_0^0 and $\xi_{\parallel,\perp}^0$ are the bare values. As expected, no mosaicity effects can be seen in the 5 T results, which are in the $t \gg t_M \sim 10^{-8}$ regime. In contrast, the data at 0.5 and 0.25 T clearly show the signature of mosaicity. Far from the transition, in the $t > t_M$ $[t_M(0.5\text{ T}) \simeq 1 \times 10^{-5}, t_M(0.25\text{ T}) \simeq 3 \times 10^{-5}]$ region, the mosaicity effects are insignificant. However, in the $t \lesssim t_M$ regime (at $t \sim 10^{-5}$), the effects of mosaicity cause bending of the $\xi_{\parallel,\perp}(t)$ and $\sigma_0(t)$ curves away from the 5 T data and single power law fits. This bending is a pure artifact of mosaicity, has nothing to do with any type of crossover behavior, and is distinct from that previously reported [10] for weakly first-order transitions.

Clearly, the mosaicity correction is essential for the low field data to obtain the *true* values of $\xi_{\parallel,\perp}(t)$ and $\sigma_0(t)$. We should caution here that fits to single power laws treating T_{NA} as a fitting parameter, T_{NA}^f, yield a value far below the experimental value of T_{NA}. We measured T_{NA} with 1 mK precision by monitoring the $q_\perp$ scans. For the 5 T data, $|T_{NA} - T_{NA}^f| < 0.5$ mK, well within experimental uncertainty. However, for the 0.25 T, $|T_{NA} - T_{NA}^f| \simeq 3$ mK. Thus, the use of T_{NA} as a fit parameter produces artificially lower transition temperatures. This is evident in some previous x-ray studies, where the data were shown only for $t > 10^{-5}$ even with a temperature stability of 1 mK [8,10,14,15].

To correct the D6.15AOB data for the effects of mosaicity, the smectic structure factor $S(\mathbf{q})$ was convoluted with the instrumental resolution function and a Gaussian mosaicity, and simultaneously fitted to $q_{\parallel,\perp}$ scans. The correction for the 5 T data was found to be negligible, in full agreement with our expectations. The Gaussian mosaicity width σ_M was initially fixed to the width of the sharpest $q_\perp$ scans ($\sigma_M = \Delta q_M$) [8,14,16]. This resulted in unexpectedly large changes [15] in $\xi_{\parallel,\perp}$ and σ_0 suggesting that it is not a proper way to correct for mosaicity.

The 5 T data were essentially free from mosaicity effects. Thus, we selected a data point near the transition and varied σ_M until the values of $\xi_{\parallel,\perp}$ and σ_0 became close to the corresponding 5 T values. This value of σ_M was then used as the sample mosaicity for correcting the remaining data. With this procedure, the corrected low field data were in excellent agreement with the 5 T data (see Fig. 3) with $|T_{NA} - T_{NA}^f| < 0.5$ mK. But, σ_M used in this analysis was ~3.5 times smaller than Δq_M for both the 0.5 and 0.25 T data. Thus, while the previously used assumption that mosaicity is temperature independent holds true, the actual mosaicity is significantly smaller than the width of the sharpest $q_\perp$ scan. We estimate that this "correct" mosaicity would be measured at a temperature <0.2 mK above T_{NA} which has never been accessed in x-ray studies.

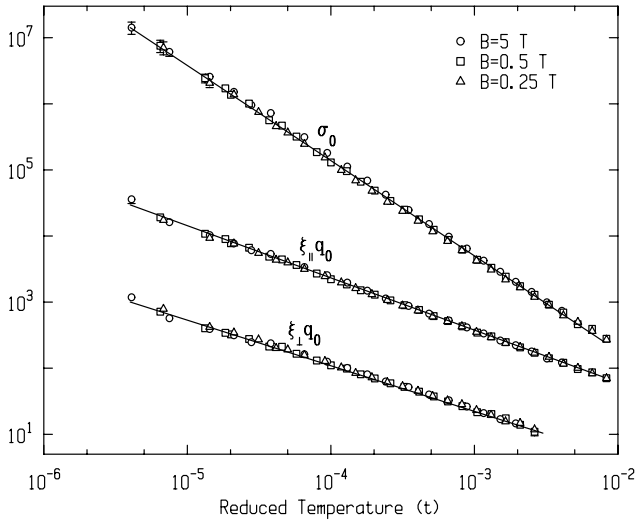

FIG. 3. Temperature dependence of mosaicity corrected $\xi_{\parallel,\perp}$ and σ_0 for D6.15AOB for different fields. The solid lines represent single power-law fits.

Analysis of the D6.15AOB data yields $\gamma = 1.46 \pm 0.04$, $\nu_\parallel = 0.79 \pm 0.02$, and $\nu_\perp = 0.69 \pm 0.02$. Far above T_{NA}, the $q_\perp$ scans were truncated by the magnet bore. Although the truncated $q_\perp$ scans, fitted simultaneously with $q_\parallel$ scans, produced larger uncertainties in the values of $\xi_\perp$, they still were very useful. The errors in the exponents were estimated by temperature range shrinking.

The results for the D6.4AOB sample are shown in Fig. 4 without mosaicity correction. For this sample, $|T_{NA} - T_{NA}^f| < 0.4$ mK. A Mo target allowed a larger q range and the values of $\xi_\perp$ were not truncated at large t. Results were not noticeably affected by the mosaicity at the fields used. This is consistent with the fact that $\Delta q_M \simeq 6.0 \times 10^{-4}$ Å^{-1} at 0.5 T was almost half of its value (1.1×10^{-3} Å^{-1}) for D6.15AOB. Because the value of t_M $[\propto (\Delta q_M)^{1/\nu_\perp}]$ is smaller, the mosaicity dominated regime $t \lesssim t_M$ was not accessed for D6.4AOB. The divergences of $\xi_{\parallel,\perp}$ and σ_0 obtained over almost four decades of t, the widest range covered in any x-ray experiment to date, are described very well by single power laws and exhibit no crossover behavior. The fact that critical exponents have the same value for high (5 T) and low (0.5 T) fields shows that there is no quenching of critical fluctuations. Finally, the values of the critical exponents $\nu_\parallel = 0.79 \pm 0.02$, $\nu_\perp = 0.67 \pm 0.02$, and $\gamma = 1.44 \pm 0.04$ for D6.4AOB are essentially the same as for D6.15AOB. This suggests that the values of critical exponents away from the tricritical point are the same and *material independent*. Figure 4 shows the correlation lengths and susceptibility in a 5 T field for 8CB which has a much narrower nematic range and measurements are made much closer to the tricritical point. We obtain $\nu_\parallel = 0.70 \pm 0.02$, $\nu_\perp = 0.52 \pm 0.02$, and $\gamma = 1.24 \pm 0.04$, in good agreement with the previous [10,14,20] results.

The fourth-order term in the structure factor was previously empirically found [14] necessary to fit the data,

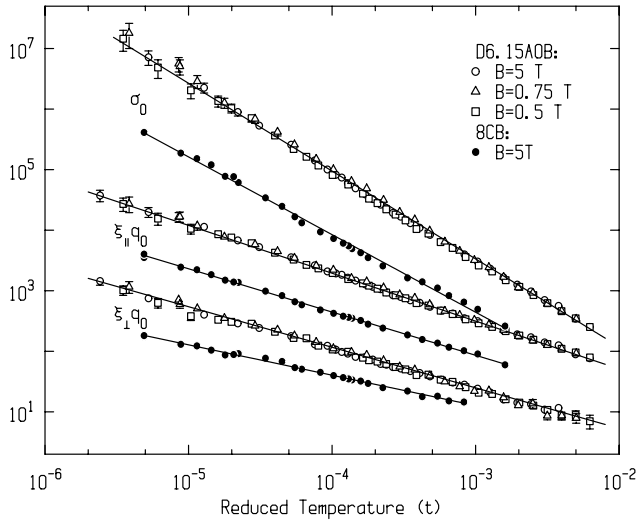

FIG. 4. Temperature dependence of $\xi_{\parallel,\perp}$ and σ_0 for D6.4AOB ($q_0 = 0.232$ Å^{-1}) and 8CB without mosaicity correction at different fields.

especially in the wings of the $q_\perp$ scans. It has been argued [5] that the non-Lorentzian behavior of $S(q_\perp)$ in the nematic phase is related to the sample mosaicity. If so, the value of c should become negligible at high fields. However, the use of this fourth-order term was found necessary to fit the data taken at 5 T. Moreover, it is evident from the inset in Fig. 2 that $c(t)$ is essentially field independent, ruling out mosaicity as the culprit.

In conclusion, the critical exponents $\nu_{\parallel,\perp}$ and γ at the *NA* transition in three compounds were measured under a 5 T field. The transverse resolution was rendered to be essentially the same as the instrumental resolution. The effects of mosaicity at low fields in D6.15AOB were clearly observed. The mosaicity correction necessary to restore the true values of critical exponents was found to be temperature independent but $\sim$3.5 times smaller than the width of the sharpest $q_\perp$ scan. Finally, the fourth-order coefficient in the structure factor is mosaicity independent.

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