8-27-2012

Biaxial Nematic Order Induced by Smectic Fluctuations

C. Zhang
Kent State University - Kent Campus

S. Chakraborty
Kent State University - Kent Campus

T. Ostapenko
Kent State University - Kent Campus

Samuel N. Sprunt
Kent State University - Kent Campus

Antal Jakli
Kent State University - Kent Campus, ajakli@kent.edu

See next page for additional authors

PHYSICAL REVIEW E **86**, 020704(R) (2012)

Biaxial nematic order induced by smectic fluctuations

C. Zhang,[1] S. Chakraborty,[2] T. Ostapenko,[2] S. Sprunt,[2] A. Jákli,[1] and J. T. Gleeson[2]
[1]*Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA*
[2]*Department of Physics, Kent State University, Kent, Ohio 44242, USA*
(Received 9 April 2012; published 27 August 2012)

We report on a series of measurements on the microscopic structure and the magneto-optical properties of a calamitic liquid crystalline compound in its nematic phase. Structural studies show the existence of short-range, tilted smectic order consistent with pretransitional effects above an underlying smectic phase. Concomitantly, magneto-optical results exhibit the existence of an optic axis not collinear with the uniaxial director. This apparent biaxial nature is discussed within the context of coupling between the tensor nematic and the smectic order parameters.

DOI: 10.1103/PhysRevE.86.020704 PACS number(s): 61.30.Eb, 61.30.Gd

Introduction. Biaxial nematic orientational order [1] has long been known to be possible, but discovering thermotropic compounds and mixtures that spontaneously exhibit this symmetry has proven to be both challenging [2,3] and somewhat controversial [4–6]. It is also fully established that external fields can induce biaxial order [7], and the determination of this effect is well documented [8,9]. Furthermore, when a liquid crystalline phase possesses additional broken symmetries beyond purely orientational order, this can also promote biaxiality. Indeed, de Gennes and Prost state plainly that biaxiality is implicit in tilted, layered structures [10]. This is because the additional restriction on molecular arrangement imposed by packing into a layered structure can significantly hinder rotation about a molecule's long axis and promote biaxial order. In this Rapid Communication we show that strong fluctuations of smectic-*C* order can also induce biaxiality in a material that, based on molecular properties alone, one would not expect to form a biaxial nematic.

Experiment. We studied the material 4-*n*-octyloxyphenyl 4-*n*-hexyloxybenzoate. [11] The molecule is depicted in the inset for Fig. 1; we refer to it as 6OO8. Based upon its energy-minimized shape, this compound falls into the category of a "rod-shaped" (or calamitic) liquid crystal. It also has a relatively simple phase sequence (Cr-38 °C-Sm*C*-46 °C-*N*-87 °C-*I*), and a wide nematic range. In order to study positional order, we examined this compound using small-angle x-ray scattering (SAXS) on beamline X6B at the National Synchrotron Light Source at Brookhaven National Laboratory. Because we were also interested in how the positional order is related to orientational order, the SAXS sample chamber was equipped with two rare-earth permanent magnets that imposed a field of approximately 1.3 T in a direction perpendicular to the x-ray beam. Since the sample was held in a 1 mm diameter x-ray capillary, the applied field far exceeds the Freedericksz threshold, and, as 6OO8 has positive diamagnetic anisotropy, the nematic uniaxial director (average molecular long axis) was fully aligned along the field direction. Further details of the experimental arrangement for SAXS are found in Ref. [12].

Unambiguous detection of the biaxial nematic state is not trivial and to some extent remains a question that is not fully settled [13]. Examination using polarized light microscopy of a liquid crystal layer possessing "homeotropic" alignment is a useful method for characterizing orientational order in nematics. In this geometry, the uniaxial director (i.e., eigenvector corresponding to the largest eigenvalue of the order parameter tensor) is parallel to the light propagation direction. Under these circumstances, a uniformly dark texture, independent of sample rotation between crossed polarizers, is indicative of uniaxial order. On the other hand, the persistent presence of birefringence in the plane perpendicular to the uniaxial director, which will show up either as a variation in transmitted light intensity as the sample is rotated or as a splitting of isogyres in the conoscopic figure, would indicate biaxial order. However, one can only draw definite conclusions on biaxiality from simple microscopy if perfect homeotropic alignment has been obtained [14]; it is difficult to separate true biaxiality from defects in alignment or surface anchoring transitions. More germane to our study is the fact that the material 6OO8 has resisted every attempt (unrubbed homeotropic polyimide coatings, silane surface treatments, surfactants) to produce stable uniform homeotropic alignment over the nematic range.

As a result, we employed an alternative optical detection method utilizing a large external magnetic field to first orient the uniaxial director along the field and then, with increasing field, to approach a saturation of this alignment. Using standard, high-sensitivity techniques to measure the optical phase difference, [15] we probed for optical birefringence in the plane perpendicular to the uniaxial director [4,16,17]. Such birefringence would be evidence of biaxiality because it indicates an optic axis that is not parallel to the uniaxial director. Our technique is based upon an extrapolation to infinite external field of the optical phase difference (proportional to the effective birefringence in a direction perpendicular to the director) for light propagating parallel to the magnetic field; we define this extrapolated phase shift as φ_∞.

The surfaces of our sample cell were treated for strong planar anchoring of the uniaxial director. In the case of infinitely strong anchoring, it is straightforward to show [17] that for positive diamagnetic anisotropy and H much greater than the Freedericksz threshold value, $\varphi(H) \propto 1/H$, so that $\varphi_\infty = 0$. On the other hand, a uniaxial material with *finite* anchoring strength will have $\varphi_\infty < 0$, while the only explanation for $\varphi_\infty > 0$ is nonzero birefringence in the plane perpendicular to the uniaxial director, i.e., a biaxial state. In order to maximize the accuracy of determining φ_∞, we

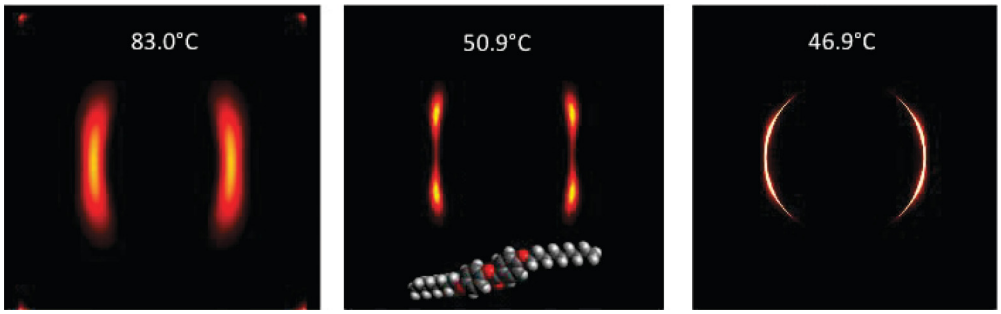

FIG. 1. (Color online) SAXS diffraction intensities at three different temperatures. The x-ray wavelength employed was 0.775 Å and there is a ∼1 T magnetic field applied horizontally. The centers of the diffuse peaks in the middle image lie at $q = 0.23$ Å^{-1} and at an angle 31° to the horizontal which corresponds to a layer periodicity of 27.3 nm. The molecular structure of 6OO8 is shown in the inset.

performed the experiments using the 31 T solenoid at the National High Magnetic Field Laboratory, Tallahassee, FL, USA. This allowed us to achieve fields exceeding 15 times the Freedericksz threshold field required to reorient the uniaxial director. It is important to note that for materials that have no order other than nematic, and that have positive uniaxial diamagnetic anisotropy, fields above the threshold tend to suppress rather than induce biaxiality [6], so that in this case a positive φ_∞ cannot simply be the result of the magnetic field coupling to the nematic order parameter. We also note here that in principle a biaxial nematic also possesses a biaxial diamagnetic susceptibility tensor. It is therefore possible that the principal axis of this tensor differs from that of the optical indicatrix, but we have no reason to expect this difference to be significant. Prior measurements [16] on standard rod-shaped and several bent-core nematics established the high sensitivity of our technique and exhibited negative values of φ_∞, consistent with a purely uniaxial state.

Results. SAXS intensity plots are shown in Fig. 1 for the nematic and smectic-*C* phases. In the smectic phase, four peaks, narrow in $|\mathbf{q}|$, indicate long-range positional order. In the nematic phase, rather than narrow peaks we see four broad peaks. As the temperature decreases through the nematic range, the peak position smoothly shifts from about 0.21 Å^{-1} to about 0.24 Å^{-1}, which corresponds to a periodicity shifting from 29.9 to ∼27 Å, just slightly less than the 30.3 Å molecular length [18], as is expected for a tilted structure.

The peaks in the nematic phase are caused by so-called "cybotactic groups" [19,20], i.e., pretransitional fluctuations of the smectic order parameter in the nematic phase. The fourfold symmetry of the peaks arises due to coupling between the nematic director and the Bragg wave vector of the short-range smectic layering that results in a relative tilt between the two. The width of these peaks is inversely proportional to the average length scale over which smectic fluctuations decay (the average correlation length) and is strongly dependent on $T - T_{NS}$, where T_{NS} is the nematic-smectic transition temperature. Figure 2 shows SAXS intensity versus wave vector along a line in q space from the origin through the position of maximum diffracted intensity. As T_{NS} is approached the peak narrows dramatically as the characteristic size of cybotactic groups increases. Below T_{NS} the peak width (on the detector) is comparable to the beam size, indicating long-range layering characteristic of a smectic phase.

Results of our of magneto-optic measurements of the optical phase difference φ as a function of magnetic field are shown in Fig. 3 for two temperatures in the nematic phase of 6OO8. This figure not only nicely shows the Freedericksz transition at low fields but also exhibits how φ decays as H is increased above this transition. The inset to the figure shows φ plotted versus $1/H$. While φ indeed decreases as $1/H$, the graph's finite intercept for $1/H \to 0$ indicates that φ_∞ is positive. According to our discussion in the previous section, this result indicates that for the temperatures plotted 6OO8 has biaxial nematic order.

Figure 4 shows a more comprehensive series of measurements of φ vs $1/H$ at temperatures throughout the nematic

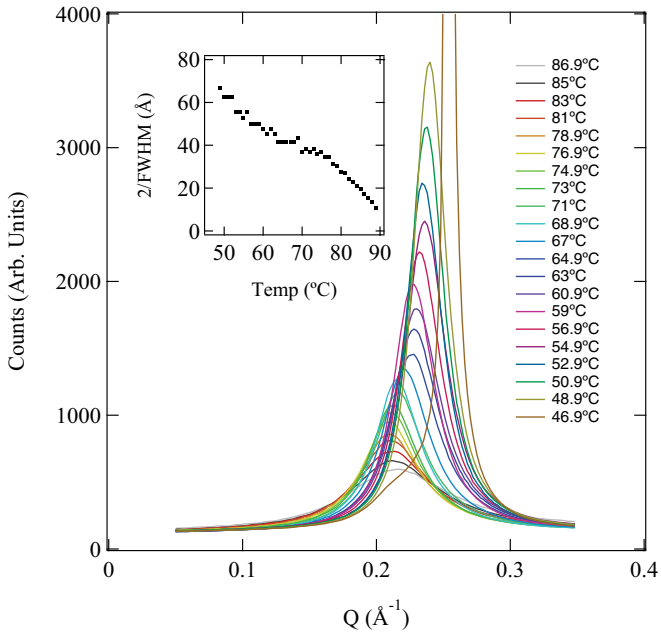

FIG. 2. (Color online) SAXS line profiles along the line of maximum intensity at various temperatures throughout the nematic range. As the temperature decreases, the linewidth decreases dramatically, and then abruptly drops as the transition to the Sm*C* phase occurs. The line at 46.9 °C is not fully shown as it is more than twice as high as the higher temperatures. Inset: Inverse linewidth (i.e., 2 × inverse of peak full width at half maximum) as a function of temperature. The width of the peak in the smectic phase is not shown as it is more than five times smaller than in the nematic phase.

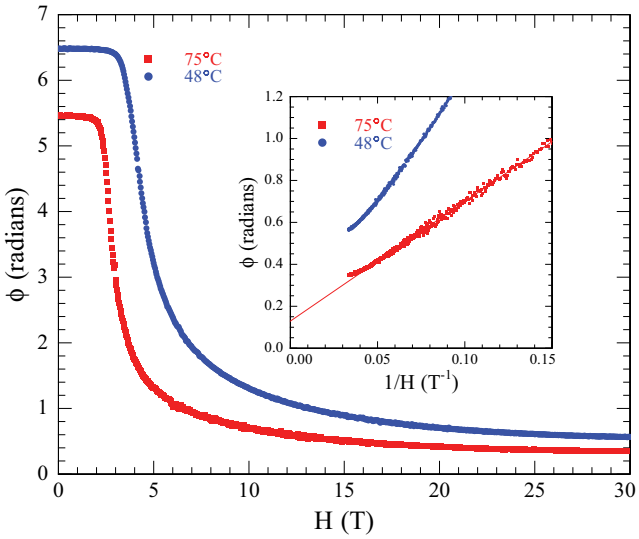

FIG. 3. (Color online) Optical phase difference (for a 5.5 μm thick sample and $\lambda = 632.8$ nm) vs magnetic field at two different temperatures. The Freedericksz transition is clearly seen below 5 T. Inset: Behavior at very large fields. In both cases the phase difference at infinite field is positive.

range. As T_{NS} is approached, the positive value of the optical phase difference at 30 T increases, and the value to which this quantity extrapolates as H becomes infinite (or $1/H \to 0$) increases as well. That is, a positive value for φ_∞, which is a proxy for biaxiality, increases as T_{NS} is approached. We note that at 75 °C, the decrease of φ with $1/H$ is essentially linear, as predicted, but, at 48 °C, φ still decreases smoothly with $1/H$, but now has significant upward curvature—possible reasons for this are discussed below. Because of this behavior, accurately extrapolating to infinite field is more difficult as the temperature decreases. Nonetheless, it remains evident that the residual optical phase difference at infinite field not only

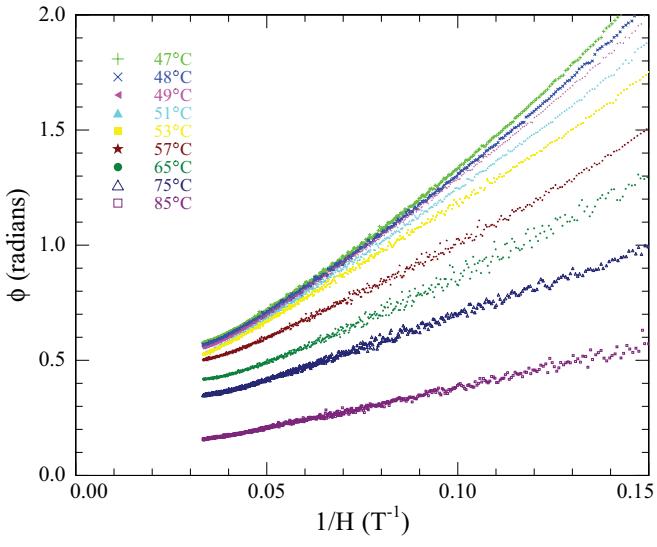

FIG. 4. (Color online) Optical phase difference vs inverse magnetic field at nine different temperatures throughout the nematic range. As the smectic phase is approached, the residual phase difference at infinite field increases.

is positive but also increases as $T \to T_{NS}$. It is instructive to compare this with the inverse SAXS linewidth, or average smectic correlation length (roughly the size of the cybotactic groups), as plotted in the inset to Fig. 2. A comparison between Figs. 2 and 4 shows that both effects (biaxiality and size of cybotactic group) increase as $T \to T_{NS}$.

Discussion. As noted above, the manner in which φ decreases with increasing H deviates from the prediction of Frank-Oseen elasticity as the temperature decreases. This renders it difficult to unambiguously extrapolate to infinite field and obtain an accurate value for φ_∞ at every temperature. At 75 °C, φ_∞ is approximately 0.12, which implies a residual optical birefringence (i.e., birefringence perpendicular to the uniaxial director) of ∼0.002. At lower temperatures, even though it is evident that φ_∞ is positive for all temperatures below 85 °C, it is more difficult to determine φ_∞. Furthermore, while the magnetic field can completely align the uniaxial director, we have little knowledge of the alignment of the biaxial director. While it may be possible that the surface treatment on the plates can lend a direction to this axis, it may also be that it is degenerate in the plane perpendicular to the uniaxial director and the residual birefringence measured reflects an average over multiple directions. The deviation from linear dependence of φ on $1/H$ could potentially be explained by higher order terms in the uniaxial elastic free energy that become important at lower T, although this is arguably improbable. A more promising mechanism arises when one notes that the trend in the deviation from linearity at high fields is always upwards. Because of this we submit that the likeliest explanation for this is that the intense magnetic field can further enhance tilted smectic order and thus further enhance biaxial order. This might be through magnetic-field suppression of thermal fluctuations of the uniaxial director, which would make it easier for cybotactic groups to grow. Unfortunately, as intriguing as this mechanism is, the technical capability to test for it—SAXS in the presence of high magnetic fields—is lacking at present. We further note that our present optical measurements cannot provide information on the spatial localization of biaxiality, except to point out that this effect must be correlated over at least the micrometer scale in order for the effect to be measurable.

To account for the clear correspondence between the characteristic size of smectic fluctuations and the biaxial order observed through the positive value of φ_∞, we consider the lowest order terms in the Landau–de Gennes free-energy coupling the tensor nematic order parameter (Q) to gradients in the smectic density wave ($\psi = \rho e^{iq\cdot r}$), where ρ is the amplitude of density fluctuations and $\boldsymbol{q}$ is the Bragg wave vector of the layering, as described in Ref. [21]. We focus specifically on the term having the lowest order in both Q and ψ, $eQ_{\alpha\beta}\partial_\alpha\psi\partial_\beta\psi^*$, where e is a coupling coefficient. Note that this term has an identical form to the standard coupling term between nematic order and external fields, such as $-\Delta\varepsilon_s Q_{\alpha\beta}E_\alpha E_\beta$, where E is the electric field and $\Delta\varepsilon_s$ is the saturated dielectric anisotropy. This latter coupling, as is well established, induces biaxial order when the coupling constant (for this case, the anisotropy in the dielectric constant) is negative and the field sufficiently large [7]. On the other hand, while the coefficient e above is not known, it can certainly be positive, so that smectic order may induce biaxiality.

This also consistent with the assertion in Ref. [10] that biaxiality is a necessary consequence of tilted smectic order. An alternative context would be to analyze this situation within the context of the formalism presented in Ref. [22], which also includes coupling between uniaxial nematic and smectic order; however, this theory would need to be augmented to account for both biaxial order and external magnetic field. An additional framework that is particularly intriguing is the conjecture [23,24] that, in the vicinity of the triple point where the nematic, smectic-*A*, and smectic-*C* transitions meet, there intervenes a biaxial phase between the nematic and smectic-*C* phases possessing long-range bond-orientational order, but short-range translational order.

Our results thus lead to the following proposition: The presence of cybotactic groups, i.e., short-range, locally smectic-*C*-like structures in certain nematics, is sufficient to induce a detectable long-range biaxial order, and this order increases as the average size of the cybotactic groups increases on approach to the nematic–smectic-*C* phase transition

Acknowledgments. The work was supported by the NSF under Grant No. DMR-0964765. The material 6OO8 was synthesized by K. Fodor-Csorba. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. Work at the National High Magnetic Field Laboratory is supported by NSF cooperative agreement No. DMR-0084173, the State of Florida, and the US Department of Energy. We acknowledge invaluable assistance and discussions with D. W. Allender, with R. Pindak and E. DiMasi at BNL, and with S. McGill at NHFML.

[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
[3] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
[4] K. Van Le, M. Mathews, M. Chambers, J. Harden, Q. Li, H. Takezoe, and A. Jákli, Phys. Rev. E **79**, 030701 (2009).
[5] B. Senyuk, H. Wonderly, M. Mathews, Q. Li, S. Shiyanovskii, and O. D. Lavrentovich, Phys. Rev. E **82**, 041711 (2010).
[6] N. Vaupotič, J. Szydlowska, M. Salamonczyk, A. Kovarova, J. Svoboda, M. Osipov, D. Pociecha, and E. Gorecka, Phys. Rev. E **80**, 030701(R) (2009).
[7] E. F. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986).
[8] R. Stannarius, A. Eremin, M.-G. Tamba, G. Pelzl, and W. Weissflog, Phys. Rev. E **76**, 061704 (2007).
[9] M. Nagaraj, Y. P. Panarin, U. Manna, J. K. Vij, C. Keith, and C. Tschierske, Appl. Phys. Lett. **96**, 011106 (2010).
[10] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, UK, 1993), p. 616.
[11] J. P. Van Meter and B. H. Klanderman, Mol. Cryst. Liq. Cryst. **22**, 271 (1973).
[12] S. H. Hong, R. Verduzco, J. C. Williams, R. J. Twieg, E. DiMasi, R. Pindak, A. Jákli, J. T. Gleeson, and S. Sprunt, Soft Matter **6**, 4819 (2010).
[13] C. Chiccoli, I. Feruli, O. D. Lavrentovich, P. Pasini, S. V. Shiyanovskii, and C. Zannoni, Phys. Rev. E **66**, 030701(R) (2002).
[14] F. Hessel and H. Finkelmann, Polym. Bull. **15**, 349 (1986).
[15] J. C. Kemp, J. Opt. Soc. Am. **59**, 950 (1969).
[16] T. Ostapenko, C. Zhang, S. N. Sprunt, A. Jákli, and J. T. Gleeson, Phys. Rev. E **84**, 021705 (2011).
[17] T. Ostapenko, Ph.D. dissertation, Kent State University, 2011.
[18] S. H. Hong, R. Verduzco, J. T. Gleeson, S. Sprunt, and A. Jákli, Phys. Rev. E **83**, 061702 (2011).
[19] A. D. Vries, Mol. Cryst. Liq. Cryst. **10**, 219 (1970).
[20] W. McMillan, Phys. Rev. A **8**, 328 (1973).
[21] P. Biscari, M. C. Calderer, and E. M. Terentjev, Phys. Rev. E **75**, 051707 (2007).
[22] T. Chen and J. Lubensky, Phys. Rev. A **14**, 1202 (1976).
[23] G. Grinstein and J. Toner, Phys. Rev. Lett. **51**, 2386 (1983).
[24] T. C. Lubensky, Mol. Cryst. Liq. Cryst. **146**, 55 (1987).