Isotropic to Nematic Transition of Aerosil-Disordered Liquid Crystals

M. Caggioni,[1] A. Roshi,[2] S. Barjami,[2] F. Mantegazza,[3] G. S. Iannacchione,[2] and T. Bellini[1]

[1]*INFM, Dipartimento di Chimica, Biochimica e Biotecnologie per la Medicina, Università di Milano, Milano, Italy*

[2]*Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA*

[3]*INFM, DIMESAB, Università di Milano–Bicocca, Monza, Italy*

(Received 1 April 2004; published 14 September 2004)

We present a high-resolution study of the isotropic to nematic phase transition of a low birefringence liquid-crystal compound incorporating an aerosil gel. Calorimetry, light scattering, and microscopy data coherently combine to allow for an accurate determination of the temperature dependence of the onset of the nematic state. The nematic order develops on cooling through two distinct processes while the nematic correlation length mildly decreases. We understand the doubling of the phase transition as due to a crossover from a random-dilution regime, where the silica gel couples to the scalar part of the nematic order parameter, to a low-T random-field regime, where the coupling induces distortions in the director field.

DOI: 10.1103/PhysRevLett.93.127801 PACS numbers: 64.70.Md, 61.30.Eb

The study of ordering transitions in systems within disordered environments has provided new insights into the physics of phase transitions [1,2]. Liquid crystals (LCs) incorporating low-density gels formed by silica aerosil dispersions ($\mathrm{LC} + A$) have been shown to be good experimental models to investigate both the isotropic (I) to nematic (N) and the nematic to smectic-A (SmA) phase transitions in the presence of the static (quenched) positional and orientational randomness provided by surface coupling at the silica-LC interfaces [3–6]. While most of the observed behavior at the N-SmA phase transition in $\mathrm{LC} + A$—scaling laws, structure factors, pseudocritical exponents—have been understood on the basis of the current models treating the statistical physics of random-field systems [4–6], the I-N transition in $\mathrm{LC} + A$ is more difficult to interpret. This is in part due to the first-order nature of the bulk transition where random disorder introduces a distribution of transition temperature shifts that broadens two-phase coexistence [7], as well as to the quadrupolar nature of the nematic order parameter [8]. A particular challenge is the observed doubling of the $\mathrm{LC} + A$ calorimetric peak at the I-N transition in an intermediate range of silica concentrations [8–10]. This feature is interesting because it has no analogy in the LC bulk behavior, and thus its investigation provides a unique route to access the basic physics of discontinuous transitions in artificially disordered systems.

The three-dimensional nematic orientational order, established from the I state through a weakly first-order phase transition, is describable by a symmetric and traceless second rank tensor Q_{ij}, which for uniaxial systems may be approximated on short length scales by a scalar order parameter (S) measuring the magnitude of order and on longer length scales by the director $\hat{n}$ describing the spatial variation of the orientation axis [11]. The bulk transition exhibits significant pretransitional fluctuations and is very close to a tricritical point [12]. Both aspects are nontrivially affected by random disorder.

Previous investigations have shown that the measurement of the transmitted light intensity of highly turbid $\mathrm{LC} + A$ samples as a function of temperature (T) and optical wavelength (λ) can determine, respectively, the nematic correlation length and the shape of the nematic correlation function [3,13]. The use of turbidity (τ) measurements instead of scattered intensity ($I(q)$) was motivated by the large scattering cross section of $\mathrm{LC} + A$ samples and by the unavoidable use of samples significantly thicker than the nematic correlation length. Indeed, when cyanobiphenyl $\mathrm{LC} + A$ samples are used, transmittance larger than 10% cannot be obtained without excessive thinning of the cells.

In this Letter we present an experimental study of $\mathrm{LC} + A$ samples made with a low birefringence material, 4′-transbutyl-4-cyano-4-heptyl-bicyclohexane (CCN47), in which the biphenyls group is replaced by saturated hydrocarbon analogs, yielding a birefringence (Δn) about $1/10$ that of cyanobiphenyls. The use of such a material enables a better optical characterization both through the study of $I(q)$ in the single scattering regime—where the nematic (director) correlation length ξ_N can be extracted—and through the measurement of $\tau(T)$ in the Rayleigh-Gans regime, in which the turbidity is a simple function of the relevant properties of the local nematic, namely, $\tau(T) \propto \phi_N(T)\Delta n^2(T)\xi_N(T)$ [13], where ϕ_N is the nematic volume fraction. We have thus undertaken a combined T-dependent optical and calorimetric investigation of CCN47 $\mathrm{LC} + A$ samples through the I-N transition over a range of silica densities displaying the double I-N transition peak. This work offers compelling evidence that the I-N transition with weak quenched random disorder proceeds via a two-step process in which random dilution is followed by random-field interactions on cooling from the isotropic phase, a previously unrecognized phenomenon.

The CCN47 liquid crystal features a wide range N phase between I SmA phases. According to our data, $T_{IN} = 330.21$ K and $T_{NA} = 301.63$ K, in agreement with previous investigations [14]. Measurements of the bulk birefringence Δn_B by birefringence compensation at the microscope can be described by $\Delta n_B = \Delta n^{**} + A(T^{**} - T)^{\beta}$, where $\Delta n^{**} = 0.0085$, $A = 0.0096$, $T^{**} - T_{IN} \approx 0.14$ K, and $\beta \cong 0.28$, consistent with typical values for nematics [15]. Characterization of the I-N transition by calorimetry reveals a weak first-order character, with a latent heat $\Delta H \approx 1.55\ \mathrm{J\,g^{-1}}$ and a total transition enthalpy (including the pretransitional contribution δH) $\Delta H_T = \delta H + \Delta H \approx 5.65\ \mathrm{J\,g^{-1}}$.

We performed a systematic investigation of CCN47 + aerosil samples prepared by incorporating dried hydrophilic silica nanoparticles forming a mass-fractal gel (Degussa, aerosil type 300, 7 nm diameter) at various silica densities ρ_S (0.050, 0.075, 0.100, and 0.200 g SiO_2 per cm^3 LC; hereafter we drop the units) via evaporation of an intermediate solvent mixture [9]. The same samples have been used for ac and nonadiabatic scanning (NAS) calorimetry, optical turbidity, integrated low angle light scattering (ILALS), as well as for optical microscopy observation. The ac and NAS calorimetry were performed in a multimode calorimeter on the same sample + cell arrangement [16].

Since heat capacity measures the entire spectrum of energy fluctuations ranging from short range molecular interactions to fluctuations in long-range order (S and $\hat{n}$ for nematics), direct comparisons with other experiments are sometimes difficult. In particular, optical studies naturally probe nematic order of submicron size and larger. For a quantitative comparison, the contribution to C_P related to optical length scales, i.e., in a bulklike manner, is required. Typically for studies of first-order transitions, C_P(ac) is truncated through the two-phase coexistence region, then subtracted from C_P(NAS), which is then integrated to determine the transition latent heat ΔH [6,9]. The two techniques are completely consistent outside the two-phase coexistence region. However, disorder can seriously alter the dynamics and T width of the two-phase conversion region allowing C_P(ac) to sense a significant fraction of the transition latent heat. By foregoing the usual truncation of C_P(ac), we extract $\Delta C_B = C_P(\mathrm{NAS}) - C_P(\mathrm{ac})$ that can be associated with domain conversions slower than the ac cycle. Since our ac cycle is already quite slow (15 mHz), these domains should be large. Its integration gives the enthalpy $\Delta H_B(T, \rho_S) = \int \Delta C_B dT$, which we propose to be directly proportional to the fractional conversion of I into N, ϕ_N, as optically measured through the two-phase coexistence region.

The turbidity $\tau(T)$ was measured by spatial filtering the light transmitted through the LC + A sample in the forward direction [3]. The ILALS technique consists in collecting into an integrating sphere all the depolarized light scattered within a cone limited by the scattering vector q. Selecting depolarized light suppresses the largest part of transmitted light and of the light scattered by the silica structure. This simple technique, though less precise than the direct measurement of $I(q)$, still permits a reliable measurement of the director correlation length ξ_N in the single scattering regime [17].

The $\Delta C_B(T)$ variation for $\rho_S = 0.075$ is shown in Fig. 1 as a function of the temperature shift $\Delta T = T - T_{IN}(\rho_S)$, where $T_{IN}(\rho_S)$ is the temperature of the first appearance of nematic in LC + A samples. The double calorimetric feature is thus evident here as it was for other LCs [8,9]. Figure 1 also shows, for the same sample, in a cell 48 μm thick, $\tau(T)$ (left axis) together with the bulk behavior of $\Delta n^2(T)$ (right axis). The match between $\tau(T)$ and $\Delta n^2(T)$ extends over a large T interval at lower temperature [inset Fig. 1(b)], indicating that, outside the transition region, ξ_N is constant, as previously reported [13]. An analogous matching is found, over the same T region, between the ΔC_P measured for the bulk and the LC + A CCN47 samples, which is completely consistent with data reported in Ref. [9]. This confirms that below the transition region, the T dependence of LC + A systems is entirely expressed by the variation of a bulk-like local order parameter S, with no director or silica re-

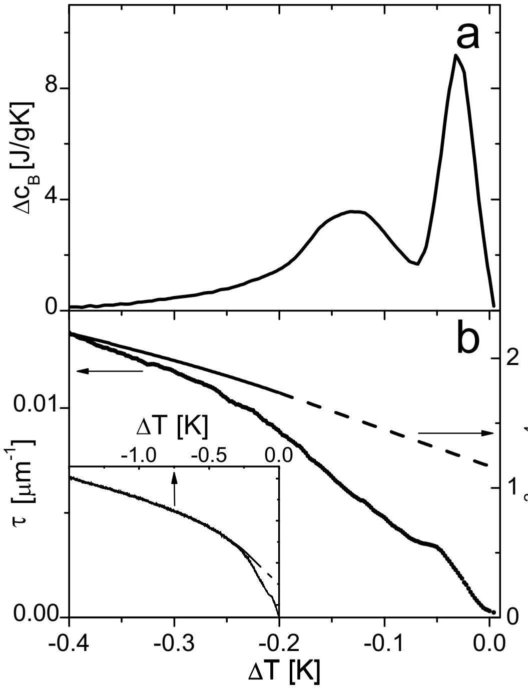

FIG. 1. Excess specific heat ΔC_B (a) and turbidity τ [(b) left axis] measured as a function of the temperature shift ΔT within the two-phase coexistence region for the LC + A $\rho_S = 0.075$ sample. Also shown, the bulk birefringence squared Δn^2 [(b) right axis]: measured values (solid line) and linear extrapolation (dashed line). Inset: τ and Δn^2 over a wide ΔT range.

structuring. In the $I + N$ coexistence region, because of the distributed local transition temperatures, the determination of the Δn^2 for the N fraction, with which to interpret τ, is more difficult. In what follows, we have adopted the simplest view and assume that the value of Δn^2 for the nematic fraction in the two-phase coexistence region is given by a linear extrapolation of the bulk Δn^2 [dashed line in Fig. 1(b)]. This is supported by NMR data on LC + A indicating that in the coexistence region the local S has a weaker T dependence than bulk [18]. The $\xi_N(T)$ extracted from ILALS data following Ref. [13] is shown in Fig. 2. The data have been obtained in a 48 μm thick sample in which the fraction of the collected light resulting from a single scattering process is, in the plotted range, always larger than 71%. As shown in the figure, first-order correction (double scattering—open dots) has a negligible effect on ξ_N. From the optically measured τ, Δn^2, and ξ_N we extract $\phi_N(T)$, shown in Fig. 3.

As Fig. 3 demonstrates, both calorimetric and optical measurements indicate that the double peak must be entirely due to a two-step transformation of the LC from the isotropic to the nematic state. The results from the calorimetric and optical techniques display remarkable agreement. The relative size of the two processes is plotted for samples having different ρ_S in the inset of Fig. 3. Apart from the 0.050 sample, which may suffer from the separation of bulk LC from the LC + A during the thin cell preparation, the agreement is very good. To interpret the double transition process, a key observation is the smoothness and the limited decrement of ξ_N data, which unambiguously demonstrate that the transition doubling *cannot* be attributed to a bimodal distributed porosity in the silica gel. However, the decrease of ξ_N as T decreases, which has been confirmed by direct optical microscopy observations shown in Fig. 2, offers an important clue for interpreting the observed behavior. Figures 2(a)–2(c) show a sample in cross-polarized microscopy at three different temperatures corresponding to the first appearance of the N phase, to a point in between the C_P peaks, and to a point near the low T end of the two-phase coexistence region that remains unchanged to lower T (see the lower right panel of Fig. 2). The nematic first appears as isolated regions with approximately uniform director alignment. As T decreases through the region of the higher-T C_P peak, the domains grow in number, distort, and exhibit recognizable defect lines, an indication of an increased coupling of the director with the silica surfaces. As this distortion proceeds, the transition slows and, for a narrow interval between the C_P peaks, no new nematic domains appear. As T decreases further, the nematic growth manifests itself in a different way. New volumes undergo the I-N transition, but no changes in the director are observed: domains appear with their "final" low T distorted structure. This is consistent with an essentially constant correlation length thereafter. Thus, the combination of microscope observations and the ξ_N data suggest that the two processes differ in the *strength* of the coupling with the silica matrix.

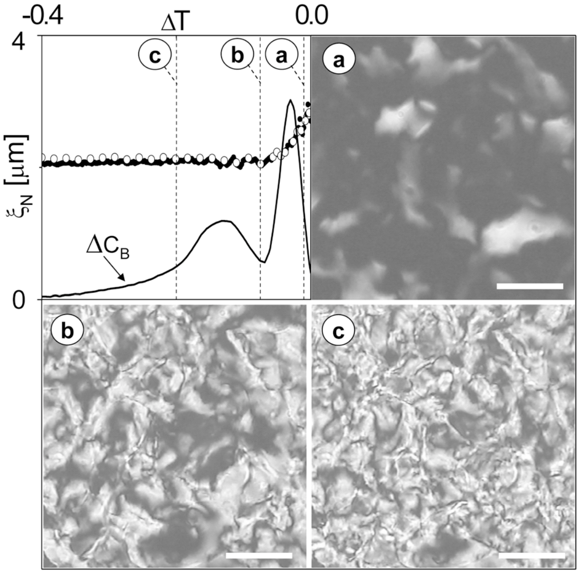

FIG. 2. Upper left panel: nematic correlation length ξ_N raw data (solid dot) and double scattering corrected (open dot) and ΔC_B (arbitrary scale) for the $\rho_S = 0.075$ sample measured as a function of ΔT. Panels (a)–(c): optical cross-polarized microscope pictures taken at a ΔT of -0.033 (a), -0.07 (b), and -0.2 K (c) indicated by the vertical dotted lines in the upper left panel. The bar corresponds to 10 μm.

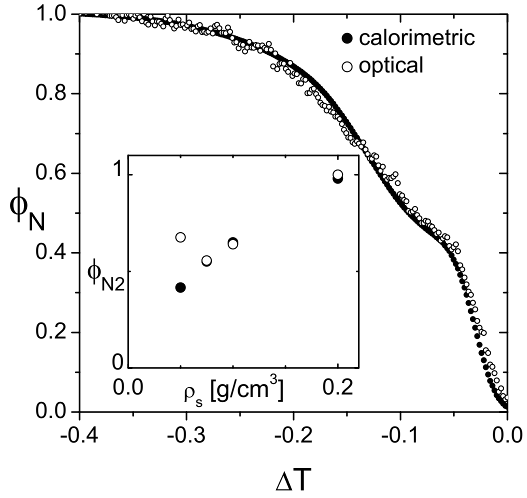

FIG. 3. Nematic volume fraction ϕ_N obtained from the integral of $\Delta C_B(0.075)$ (solid dots) and deduced from optical measurements $\phi_N \propto \tau/(\Delta n^2 \xi_N)$ (open dots) as a function of ΔT through the two-phase coexistence region. Inset: N volume fraction ϕ_{N2} converted through the low temperature C_P peak, as a function of ρ_S.

We argue that this observation leads to an explanation of the nature of the double C_P peak. Incorporation of solids in a spontaneously ordering media has different

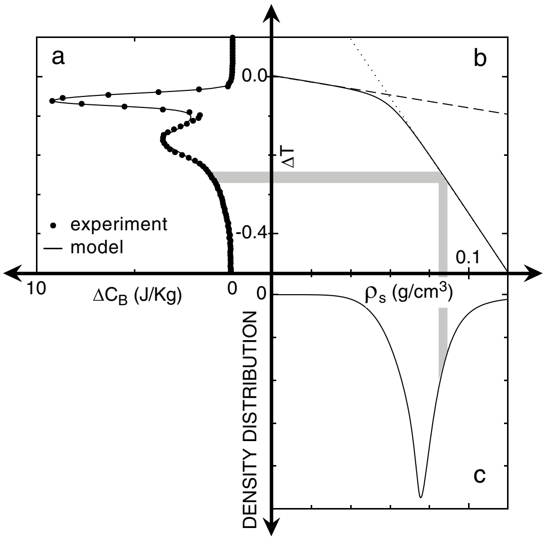

FIG. 4. Proposed interpretation. (a) Model (continuous line) and ΔC_B (full dots) versus ΔT for the $\rho_S = 0.075$ sample. (b) Distribution of transition temperatures ΔT within the two-phase coexistence region (solid line) versus disorder density (ρ_S) crossing over from random-dilution effects (dashed line) to random-field effects (dotted line). (c) Local density distribution versus disorder density which successfully reconstructs ΔC_B.

effects on the phase behavior and, in particular, on the shift and distribution of transition temperatures. The simplest expected—and, in some cases, observed [19]—effect comes from dilution, weakening of the mean molecular field. At the mean field level, this effect downshifts T_{IN} by the total reduction of the molecular coordination, provided by the contact with the solid-LC interface area. The disorder broadening of the transition can be most simply modeled by a distribution in ΔT_{IN} within the two-phase coexistence region linear in the local disorder (silica) density [dashed line in Fig. 4(b)]. If this was the only mechanism, the amount of material undergoing the I-N transformation in a given interval within the two-phase range would simply be an image of the disorder density distribution function, possibly averaged by a suitable nucleation length, in analogy to that described in other phase transitions [20]. However, as the data indicate, the disorder distribution is not bimodal and there appears at lower T a stronger coupling, resulting in stronger distortions and the appearance of topological defects, a situation of random orientational pinning not accounted for by random dilution. We suggest that this crossover is the result of the progressive thinning of a sheath of disordered LC, which screens—for a penetration length—the silica surface. As the temperature is lowered further, the disordered LC surface layer converts to a defected nematic and the random dilution turns into a random-field coupling, described by some other, certainly steeper, distribution of $\Delta T_{IN}(\rho_S)$ behavior (dotted line in Fig. 4(b)]. This crossover is proposed here to be the origin of the observed double peak. A simple disorder density distribution shown in Fig. 4(c) transforms, by virtue of the transfer function in Fig. 4(b), into a double peaked $d[\phi_N(T)]/dT$ given by the line in Fig. 4(a).

In this approach, a rather featureless disorder distribution and a simple transfer function were chosen so as to yield an overlap with the $\Delta C_B(0.075)$ data, demonstrating that these few ingredients can reproduce the observed doubled transition. This model does not address the observed [9] complex $T_{IN}(\rho_S)$ shifts, which requires a more detailed study. However, no liquid-crystal specific properties were invoked in this interpretation and, so, we speculate that this effect may be generic for first-order phase transitions with weak quenched random disorder.

We wish to thank C.W. Garland and M. Buscaglia for many discussions. This work was supported at WPI by the NSF under CAREER Grant No. DMR-0092786.

[1] M. Chan, N. Mulders, and J. Reppy, Phys. Today **49**, No. 8, 30 (1996), and references therein.
[2] T. Bellini, L. Radzihovsky, J. Toner, and N. A. Clark, Science **294**, 1074 (2001), and references therein.
[3] T. Bellini *et al.*, Phys. Rev. Lett. **85**, 1008 (2000); **88**, 245506 (2002).
[4] R. L. Leheny *et al.*, Phys. Rev. E **67**, 011708 (2003).
[5] G. S. Iannacchione *et al.*, Phys. Rev. E **67**, 011709 (2003).
[6] P. S. Clegg *et al.*, Phys. Rev. E **67**, 021703 (2003).
[7] Y. Imry and M. Wortis, Phys. Rev. B **19**, 3580 (1979).
[8] A. Roshi *et al.*, Phys. Rev. E **69**, 031703 (2004).
[9] G. S. Iannacchione *et al.*, Phys. Rev. E **58**, 5966 (1998).
[10] P. Jamee, G. Pitsi, and J. Thoen, Phys. Rev. E **66**, 021707 (2002).
[11] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, U.K., 1993), 2nd ed.
[12] A. Zywociński, J. Phys. Chem. B **107**, 9491 (2003).
[13] T. Bellini *et al.*, Phys. Rev. E **57**, 2996 (1998).
[14] Z. Li and O. D. Lavrentovich, Phys. Rev. Lett. **73**, 280 (1994).
[15] I. Chirtoc, M. Chirtoc, C. Glorieux, and J. Thoen, Liq. Cryst. **31**, 229 (2004).
[16] H. Yao and C.W. Garland, Rev. Sci. Instrum. **69**, 172 (1998).
[17] M. Caggioni, T. Bellini, S. Barjami, F. Mantegazza, A. Roshi, and G. Iannacchione (to be published).
[18] T. Jin and D. Finotello, Phys. Rev. Lett. **86**, 818 (2001).
[19] T. Bellini *et al.*, Phys. Rev. Lett. **91**, 085704 (2003).
[20] T. Bellini, N. A. Clark, and D. R. Link, J. Phys. Condens. Matter **15**, S175 (2003).