This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Confinement and orientational study at liquid crystal phase transitions

Germano Iannacchione[a]; Daniele Finotello[a]
[a] Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio, U.S.A.

To cite this Article Iannacchione, Germano and Finotello, Daniele(1993) 'Confinement and orientational study at liquid crystal phase transitions', Liquid Crystals, 14: 4, 1135 — 1142

To link to this Article: DOI: 10.1080/02678299308027821

URL: http://dx.doi.org/10.1080/02678299308027821

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 1135–1142

Confinement and orientational study at liquid crystal phase transitions

by GERMANO IANNACCHIONE and DANIELE FINOTELLO*

Department of Physics and Liquid Crystal Institute,
Kent State University, Kent, Ohio 44242, U.S.A.

We have studied the heat capacity of the thermotropic liquid crystal, octylcyanobiphenyl (8CB), confined to the nearly cylindrical, 0·2 μm diameter pores of Anopore membranes. Orientation of the nematic director within the pores can be controlled with surface treatment. It is known from NMR measurements that the nematic director is aligned parallel to the pore axis in the untreated membrane. A perpendicular alignment is obtained when the pore surface is treated with lecithin. The second order smectic A to nematic (S_{A-N}) and the weakly first order nematic to isotropic (N–I) phase transitions of 8CB were studied in these pores, for both director orientations, using an AC calorimetry technique. Effects on heat capacity amplitudes, transition temperature shifts, rounding and broadening of these phase transitions will be presented and contrasted with bulk measurements.

1. Introduction

In the operation of nematic liquid crystal cells, surface effects [1] play a major role, and hence have attracted considerable attention. These effects may also be probed by confining liquid crystals to submicron size pores. Quadrupole splitting measurements using deuterium nuclear magnetic resonance spectroscopy (^{2}H NMR) on 4′-pentyl-4-cyanobiphenyl (5CB) [2] confined to the pores of Nuclepore (polycarbonate) membranes showed, in the isotropic phase, an orientationally ordered molecular layer at the pore wall. This layer is governed by local molecular interactions having a temperature independent surface order parameter. Further NMR work [3] on 5CB confined to Anopore (aluminium oxide) membranes (in the isotropic phase) determined the degree of residual nematic order and the surface coupling constant for various treatments of the pore wall. This method is sensitive to the magnitude and orientation of the nematic director, and, in the nematic phase, led to the first experimental determination of the surface elastic constant K_{24} [4].

Using AC calorimetry, we studied the specific heat of the liquid crystal 8CB confined to the nearly cylindrical cavities of Anopore membranes, simultaneously probing orientational and confining effects at the weakly first order nematic to isotropic (N–I) and second order smectic A to nematic (S_{A-N}) phase transitions. A richness of effects, strongly dependent on the surface treatment and on the order of the transition, are found. More extensive work, also covering 5CB, 7CB, 10CB, and 12CB and the smectic A to isotropic phase transition, has been recently submitted for publication [5].

A brief overview of the AC calorimetric technique as well as sample preparation will be presented in section 2. Section 3 contains our major results for 8CB confined to

---

* Author for correspondence.

Anopore membranes for two different director orientations within the cavities. The results are summarized in section 4.

2. Experimental

AC calorimetry [6] has been widely used in the study of phase transitions on several liquid crystal systems [7–9]. In this technique, a sinusoidal voltage (0·055 Hz typical frequency) is applied to a 50 Ω evanohm heater in contact with a sample. The induced temperature oscillations, whose ~2 mK amplitude is inversely proportional to the sample heat capacity [6], are detected with a DC biased, 10 kΩ thermistor, previously calibrated against a platinum thermometer. A heater and thermistor are attached with a small amount of 1266 Stycast epoxy to one side of a sapphire disc, 10 mm in diameter and 0·1 mm thick, chosen for its rigidity, flatness, low heat capacity and good thermal conductivity. Bulk or confined liquid crystal samples are either rested or tied down to the other side of the sapphire disc. This assembly is enclosed and thermally anchored to a brass ring fitted with a heater and a thermometer. The brass ring, regulated to better than 0·3 mK and changed by 5–10 mK steps, is weakly anchored inside an evacuated copper chamber to a thermal reservoir. With lock-in amplification and computer averaging for 15 min at every temperature, a resolution of 0·2 per cent or better in heat capacity is achieved. The previously measured addendum heat capacity of the heater, sapphire disc, thermistor, and filter, is subtracted from measurements with liquid crystal present. Liquid crystal samples are thermally cycled on several occasions, and then, left in the isotropic phase overnight, before any measurements. Calorimeter details will be presented elsewhere [10].

Produced from an electrochemical anodizing process [11], Anopore membranes are composed of a high purity alumina matrix and are compatible with a variety of surface treatments. Characterized by SEM and nitrogen adsorption isotherms [12], they are found to have a 40 per cent porosity. This allows the confinement of a relatively large amount of liquid crystal within a single membrane. Anopore membranes have 0·2 μm diameter, with nearly cylindrical pores extending through its 60 μm thickness. They are extremely flat which ensures good thermal contact to the sapphire disc. In fact, to within experimental resolution, identical specific heats were measured whether the filter was tied down with dental floss or merely rested on the sapphire disc.

The membranes, cut and shaped into 8–9 mm diameter discs, were cleaned in an ultrasonic acetone bath, then thoroughly dried. They were dipped in 8CB and heated deep into the isotropic phase to insure complete filling of the pores. The excess liquid crystal was removed by pressing the discs between Whathan filtration paper. Similarly, the pore surface was treated with lecithin, known to produce homeotropic alignment [13]. From NMR work on 5CB, the nematic director within the untreated pore was aligned parallel to the pore axis (axial) [3]. A radial-type director configuration was found after lecithin treatment [3]. Hereafter, we assume that the orientation was the same for 8CB. Bulk 8CB measurements consist of a drop, less than 5 mg, 9 mm in diameter and approximately 0·3 mm thick. The purity of our liquid crystal material was found by high pressure liquid chromatography to be better than 99·9 per cent.

3. Results and discussion

Specific heat as a function of temperature summarizing our results for bulk, axially and radially aligned 8CB are presented in figure 1. Both the S_{A-N} and N–I phase transitions are found to shift in temperature, and suppress and broaden considerably upon confinement. They are dependent on different director orientation and on the

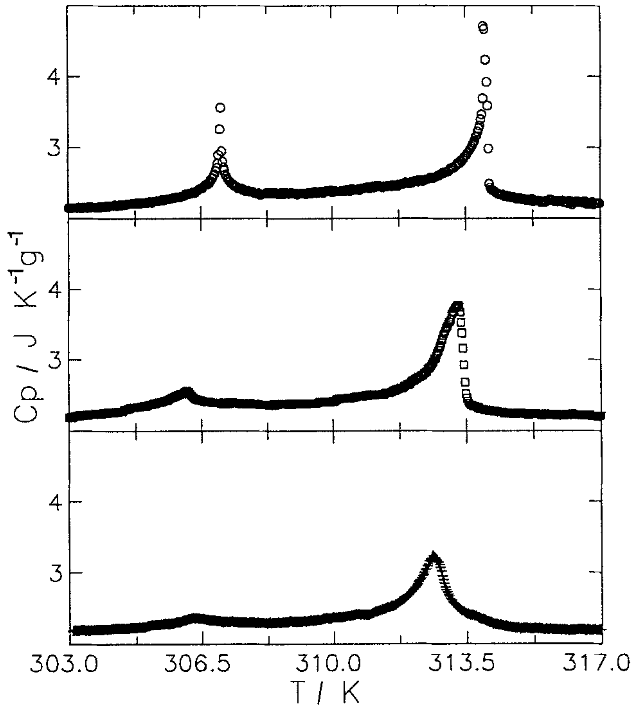

Figure 1. Specific heat as a function of temperature for bulk (○), axially (□), and radially (+) aligned liquid crystal 8CB over a wide temperature range covering the smectic A, nematic, and isotropic regions. Note the drastic changes upon confinement and depending on orientation.

order of the phase transition. The amounts of the liquid crystal material used were 4·55, 2·75 and 2·11 mg for bulk, axial, and radial alignment, respectively.

The weakly first order N–I phase transition for the three samples are presented in an expanded view in figure 2. For the axial alignment, as compared with bulk, the transition temperature shifts down by 0·75 K, while the specific heat peak is suppressed by 43 per cent and broadened by a factor of 3·5. We refer to broadening as the full width at half maximum. The specific heat peak retains the bulk-like sharp decrease on the isotropic side of T_{NI}. These effects are enhanced for the radial alignment where a more symmetric peak, reminiscent of a continuous phase transition, is observed. The transition shifts down by 1·4 K, the peak is suppressed by 65 per cent and broadened by a factor of 4. The charactieristic area under the peak, amplitude multiplied by the width at half maximum, increases by 158 per cent and 76 per cent for the axial and radial cases, respectively. See the table for per cent changes from bulk values. The specific heat, for example 0·2 K above T_{NI}, is higher for the radial than the axial alignment, both above bulk (see inset of figure 2). This is suggestive of the residual nematic order at the pore wall in the isotropic phase determined by NMR [3].

The suppression of the specific heat peak may be understood for the radial alignment by considering that only a fraction of the liquid crystal within the pores participates in the ordering [5, 15]. This becomes possible if pinning at the pore surface is occurring; a stronger pinning would lead to a smaller peak as less material undergoes the transition. From NMR, the surface coupling constant is an order of magnitude larger for the lecithin treated than for the untreated pores [3]. This is consistent with

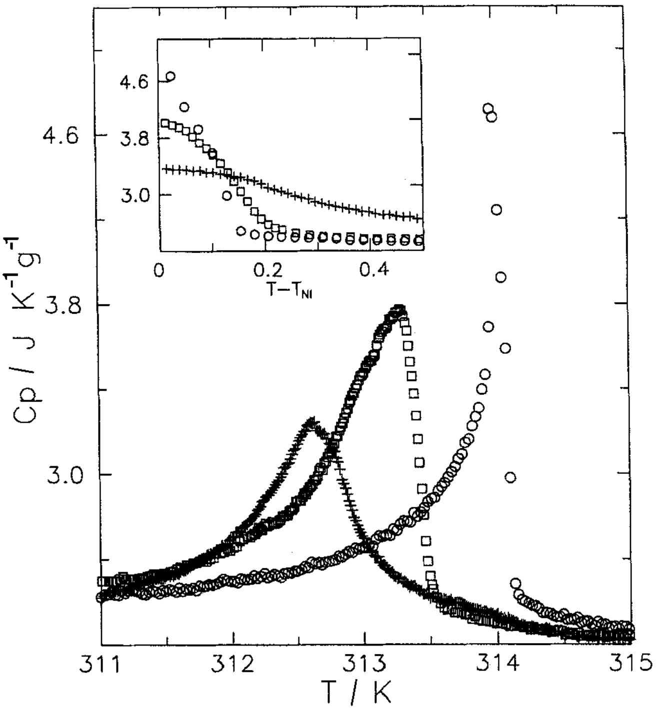

Figure 2. Expanded view of the weakly first order nematic to isotropic (N–I) phase transition. Note the symmetric peak for the radially aligned case. Inset: isotropic side of the transition indicating the excess specific heat for the radial and axial alignments. Peak temperatures: (+) radial 312·63 K, (□) axial 313·28 K, (○) bulk 313·97 K.

Characteristics of the N–I and S_{A-N} phase transitions for bulk, axial and radial samples of 8CB. Widths are at half peak maximum and the area under the peak has either a constant (for N–I) or a linear (for S_{A-N}) background subtracted over 10^{-2} in reduced temperature.

	8CB	T_c/K	Amplitude/J K^{-1} g^{-1}	Width/K	Area/J g^{-1}
N–I	Bulk	313·97	2·52	0·15	1·86
	Axial	313·28	1·55	0·77	1·99
	Radial	312·63	1·03	0·93	1·65
S_{A-N}	Bulk	307·02	1·27	0·08	0·28
	Axial	306·12	0·27	0·96	0·41
	Radial	306·31	0·11	1·28	0·11

the radially aligned case having a smaller peak and larger specific heat value at the same reduced temperature on the isotropic side. This argument does not appear to be equally suitable for the axial alignment because of the much weaker surface coupling constant [3]. A weaker pinning would translate into a larger peak than in the radial case. Indeed, the peak height for the axial alignment that we measured is a factor of 1·6 larger than for the radial alignment. Yet, it might be too suppressed, when compared to bulk, for pinning to be the only mechanism.

Impurities and elastic strains induce downward shifts in the transition temperature, while surface induced nematic order should cause an upward shift [16]. As previously stated, the purity of our 8CB liquid crystal was better than 99·9 per cent and, our bulk transition temperatures are as high as reported in the literature. To investigate whether some of these effects might be attributed to the lecithin if it detaches from the pore wall and contaminates the 8CB within the pore, we performed parallel studies with mixtures of 5CB and lecithin [14]. For 20 per cent and 50 per cent mixtures, an almost perfect matching of the specific heats was found on the nematic and isotropic side of the transition, including the bulk-like sharp drop at the isotropic side. From this study, we calculate that a 3–5 per cent mixture (our estimate for the maximum contamination if all the lecithin detached from the pore wall) would show a 0·01 K downward shift and less than a 5 per cent peak suppression. These effects are far too small to explain the present observations.

More likely, downward temperature shifts for the radial alignment are due to surface aligned nematic material at the pore wall acting as an imposed deformation [19]. The nematic director far from the pore wall must arrange itself to minimize the elastic energy as established by this existing distortion. Expressing the free energy in terms of only quadratic terms in the order parameter (see [17]), a crude estimate of the temperature shift due to elastic distortion is given by $\Delta T = (\kappa_0/2a_{20})(2\pi/R)$ [2]. Here, the Frank elastic constant is assumed to behave as $\Psi \sim \kappa_0 S^2$, where S is the nematic order parameter and a_{20} is the constant of the temperature dependent coefficient for the quadratic term in the free energy. Using typical values for alkylcyanobiphenyls and the radius of the pore, the transition temperature shifts down by 1·2 K, or 0·4 per cent, in good agreement with our observation for the radial case. Also, the shifts observed here are consistent with recent calculations by Lin *et al.* [19] and are of the same order as in other confined systems [15] and in our own work with 5CB and 7CB [5]. For the axial configuration, the transition shift seems to be related to the weaker surface coupling constant. Indeed, as seen in NMR, when the pore surface of Anopore membranes was treated with PIBMA, the alignment for the 5CB nematic director remained axial [3]. However, both the surface coupling constant and surface order parameter decreased as compared to the same axial alignment in the untreated pores. The N–I transition temperature for 5CB decreased from the value obtained in the untreated Anopore membranes by 1·21 K.

Results for the second order $S_{A\text{–}N}$ phase transition for all samples are presented in figure 3. These show further suppression and broadening when compared to the N–I transition. For the axial alignment, the transition temperature shifts down by 0·9 K while the specific heat peak is suppressed by 84 per cent and broadened by a factor of 9. The radial case is altered more, being suppressed by 93 per cent and broadened by a factor of 14. However, its transition temperature shifts down only by 0·64 K. This is less than the axial case and opposite to the shifts at the N–I transition. We believe that this is a further indication that impurities are not playing a major role in these measurements. Since impurities would have to be introduced by the membranes (hardly any shift can be attributed to the lecithin), transition shifts should be nearly the same for both alignments, if driven by impurities. Instead, the axial and radial alignments shift differently according to the order of the phase transition. Also, experimental runs using Anopore membranes from different batches find transition temperatures different by at most 0·1 K, or, 7 times less than the smallest shift with respect to the bulk transition. The nematic width $(T_{NI} - T_{S_AN})$ is 6·95, 7·16, and 6·32 K, or McMillan ratios of 0·978, 0·977, and 0·980 for bulk, axial, and radial respectively. The

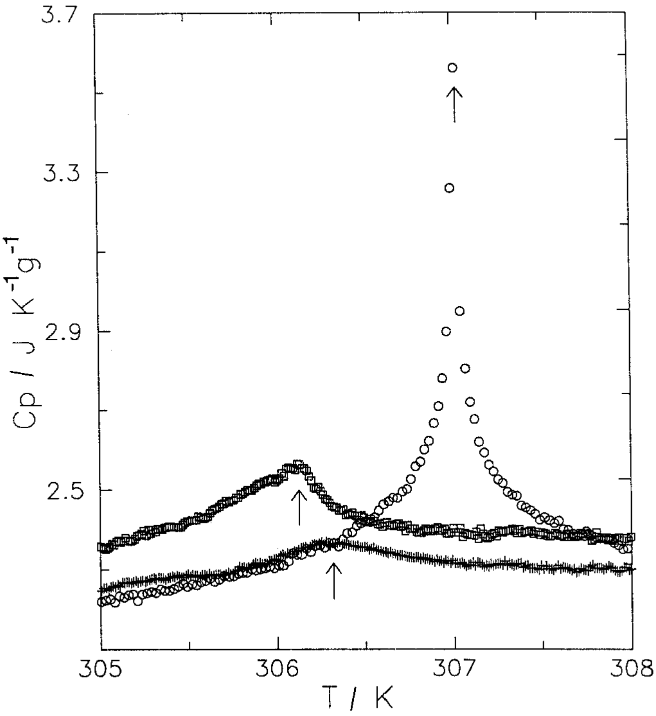

Figure 3. Expanded view of the second order smectic bulk A to nematic (S_{A-N}) phase transition. Note the extreme suppression and broadening for both orientations and the higher peak temperature of the radial case, indicated by arrows and given for all three samples. (+) Radial 306·31 K, (□) axial 306·12 K, (○) bulk 307·02 K.

characteristic area increases by 61 per cent for the axial and 13 per cent for the radial case, much smaller than the corresponding areas at the N–I transition (see the table). The specific heat peak appears to retain the symmetric nature of the bulk peak for both alignments.

Because of the lecithin coating and stronger anchoring at the surface, the effective pore radius is presumably smaller for the radial than the axial case. In addition, the smectic phase is less tolerant of elastic distortion so as smectic layering progresses towards the centre of the pore, elastic distortions prevent further layering. As a consequence, only a cylindrical shell of material undergoes the S_{A-N} transition, leaving a core of nematic material. Indeed, X-ray studies on larger pore sizes, 25 μm in diameter, found that smectic layers (likely distorted and of varying thickness and separation) form only near the pore wall as the energy cost to bend the director increases as the pore centre is approached becoming prohibitive near the centre [20]. Our pore size is a factor of 100 smaller and this effect should be enhanced. This may explain the extreme suppression of the S_{A-N} transition for the radial alignment. With decreasing pore size and as seen in [15], we expect that the S_{A-N} peak will disappear while the N–I peak will remain prominent. The S_{A-N} peak will disappear at a different pore size depending on orientation.

The axially aligned configuration is affected by the weak surface anchoring at diametrically opposing surfaces, hence, the difficulty in establishing smectic A layers that span the entire diameter of the pore. As the sample is cooled, the smectic phase first forms near the centre of the pore. It will attempt to grow towards the pore wall, but, is unable to form a single, undistorted layer covering the entire diameter of the pore. A shell of nematic material is left near the pore wall. This material does not participate in the S_{A-N} transition, and hence a suppressed specific heat peak.

Finite size effects play a role at a second order phase transition, and, for example [17], at a reduced temperature of 10^{-3} (or about 0·3 K from the transition), the correlation length parallel to the director, $\xi_{\parallel}$, is 380 Å, while the correlation length perpendicular to the director, $\xi_{\perp}$, is 70 Å. This suggest that $\xi_{\parallel}$ dominates as it becomes comparable to the pore size. Indeed, as discussed previously, the region over which the S_{A-N} transition occurs may be much smaller than the pore size as previously discussed. Hence, we expect finite size effects to be important for the S_{A-N} transition. The rounding of the specific heat peak, observed for both alignments, is the typical signature of finite size behaviour. The further peak suppression and broadening as compared to the N–I transition is thus attributed to finite size effects.

4. Conclusions

Specific heat measurements on 8CB liquid crystal confined to Anopore membranes show departures from bulk behaviour strongly dependent on confinement and director orientation. The second order S_{A-N} transition is affected more than the weakly first order N–I transition.

At the N–I phase transition specific heat peak suppression and broadening are found for the axial case. The radial alignment enhances these effects, and exhibits a more symmetric specific heat peak. Due to confinement, elastic deformation and strong anchoring play a major role at the N–I transition. Studies as a function of pore size, using Nuclepore membranes, are underway to determine whether other possible mechanisms that may lower the transition temperature such as a temperature dependent anchoring energy, are present, and to separate orientational from confining effects [21].

The S_{A-N} phase transition shows greater suppression and broadening than the N–I case, nearly disappearing for the radial alignment. The transition temperature for the radial case is higher than the axial case, in contrast to the N–I transition. Requirements for the formation of the semectic A phase within these pores are more strict than the nematic phase, becoming unobtainable near the pore centre. At this second order phase transition, finite size effects become important. X-ray studies to determine the smectic layer orientation in these systems would be important. Effects found for the axial alignment, although not as pronounced as in the radial alignment, are stronger than we would have anticipated. We have discussed possible mechanisms to explain some of the observed features, although we feel that they mostly apply to the radial alignment. Further experimental and theoretical work is needed in order to obtain a better understanding of these results.

We acknowledge useful discussions with D. Allender, G. Crawford, P. Palffy-Muhoray, and A. Strigazzi. We are grateful to S. Keast for performing purity checks on the 8CB samples. This research was supported by NSF Science and Technology Center ALCOM Grant No. DMR 89-20147.

References

[1] Jerome, B., 1991, *Rep. Prog. Phys.*, **54**, 391.

[2] Crawford, G. P., Yang, D. K., Zumer, S., Finotello, D., and Doane, J. W., 1991, *Phys. Rev. Lett.*, **66**, 723.

[3] Crawford, G. P., Stannarius, R., and Doane, J. W., 1991, *Phys. Rev.* A, **44,** 2558.
[4] Allender, D. W., Crawford, G. P., and Doane, J. W., 1991, *Phys. Rev. Lett.*, **67,** 1442.
[5] Iannacchione, G., and Finotello, D., 1992, *Phys. Rev. Lett.*, **69,** 2094.
[6] Sullivan, P., and Seidel, G., 1969, *Phys. Rev.*, **173,** 679.
[7] Geer, R., Huang, C. C., Pindak, R., and Goodby, J. W., 1989, *Phys. Rev. Lett.*, **63,** 540.
[8] Wen, X., Garland, C. W., and Wand, M. D., 1990, *Phys. Rev.* A, **42,** 6087. See also Garland, C. W., 1985, *Thermochim. Acta*, **88,** 127.
[9] Johnson, D. L., Hayes, C. F., de Hoff, R. J., and Schantz, C. A., 1978, *Phys. Rev.* B, **18,** 4902.
[10] Steele, L. M., Ianancchione, G. S., and Finotello, D., 1992, *Rev. Mex. Fis.* (submitted).
[11] Furneaux, R. C., Rigby, W. R., and Davidson, A. P., 1989, *Nature, Lond.*, **337,** 147.
[12] Crawford, G. P., Steele, L. M., Ondris-Crawford, R., Iannacchione, G. S., Yeager, C. J., Doane, J. W., and Finotello, D., 1992, *J. chem. Phys.*, **96,** 7788.
[13] Cognard, J., 1982, *Molec. Crystals liq. Crystals Suppl.*, **1,** 1.
[14] Iannacchione, G. S., Crawford, G. P., Doane, J. W., and Finotello, D., 1992, *Proceedings of OLC 91*, Cocoa Beach, Florida, *Molec. Crystals liq. Crystals*, **222,** 205.
[15] Bellini, T., Clark, N. A., Muzny, C. D., Wu, L., Garland, C. W., and Schaefer, D. W., 1992, *Phys. Rev. Lett.*, **69,** 788.
[16] Sheng, P., 1976, *Phys. Rev. Lett.*, **37,** 1059. Sheng, P., 1982, *Phys. Rev.* A, **26,** 1610.
[17] Litster, J. D., Als-Nelson, J., Birgenau, R. J., Dana, S. S., Davidov, D., Garcia-Golding, F., Kaplan, M., Safinya, C. R., and Schaetzing, R., 1979, *J. Phys., Paris*, **C3,** 339.
[18] Kuzma, M., and Labes, M. M., 1983, *Molec. Crystals liq. Crystals*, **100,** 103.
[19] Lin, H., Palffy-Muhoray, P., and Lee, M. A., 1991, *Molec. Crystals liq. Crystals*, **204,** 189.
[20] Mang, J. T., Sakamoto, K., and Kumar, S., 1992, *Molec. Crystals liq. Crystals*, **223,** 133.
[21] Strigazzi, A. (private communication).