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C. Rosenblatt, J.T. Ho. Magnetic birefringence determination of the tilt susceptibility above a smectic A-smectic F phase transition in nonyloxybenzylidene butylaniline. *Journal de Physique*, 1983, 44 (3), pp.383-386. 10.1051/jphys:01983004403038300 . jpa-00209608

**HAL Id: jpa-00209608**

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Submitted on 4 Feb 2008

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Classification  
 Physics Abstracts  
 64.70E — 61.30G

## Magnetic birefringence determination of the tilt susceptibility above a smectic A-smectic F phase transition in nonyloxybenzylidene butylaniline

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(Reçu le 30 août 1982, accepté le 22 novembre 1982)

**Résumé.** — Nous avons mesuré la biréfringence induite magnétiquement dans le nonyloxybenzylidene butylaniline (90.4) pour étudier la susceptibilité du paramètre d'ordre de l'angle d'inclinaison des molécules. On pense que ce matériau présente une transition de phase smectique A-smectique F. Nous avons observé que la transition était du premier ordre avec  $T_c - T^* \simeq 0,5$  K et que l'exposant critique,  $\gamma$ , était en accord avec l'exposant type champ moyen de la susceptibilité de l'angle d'inclinaison qui est caractéristique de transitions smectique A-smectique C.

**Abstract.** — We have used magnetically induced birefringence to study the susceptibility for the tilt order parameter in nonyloxybenzylidene butylaniline (90.4). This material is thought to undergo a smectic A-smectic F phase transition. The transition was observed to be first order, with  $T_c - T^* \simeq 0.5$  K, and the critical exponent  $\gamma$  was consistent with the mean-field-like tilt susceptibility exponent characteristic of a smectic A-smectic C transition.

In recent years much progress has been made in elucidating the structure of the smectic F (F) phase. In particular, X-ray studies [1-4] indicate that, like the smectic C (C) phase, the molecular director in the F phase is tilted with respect to the layer normal. Moreover, the three-dimensional F phase exhibits long range in-plane bond orientational order, similar to the three-dimensional analog of the two-dimensional hexatic phase [5]. Thus, the F phase is necessarily characterized by two order parameters : a tilt parameter  $\Phi = \Phi_0 e^{i\phi}$  and a six-fold bond orientational parameter  $\Psi = \Psi_0 e^{6i\psi}$ . Solving a particular model of the coupled tilt and bond orientations in the mean-field approximation, Bruinsma and Nelson [6] have shown that the smectic C phase must also exhibit a degree of in-plane bond orientational order. On the other hand, they showed that a non-zero value of  $\langle \Psi \rangle$  cannot induce a finite tilt.

Motivated by the foregoing experimental and theoretical work, we have undertaken an optical

study of the material 90.4, which is thought to exhibit a smectic A (A) to F phase transition. Unlike the A-C transition which has been experimentally characterized by only a tilt order parameter, and the A-hexatic transition which is characterized by a bond order parameter [7], the A-F transition should strongly exhibit the simultaneous onset of both types of order. The purpose of this work, then, was to study the effects, if any, of the coupling between bond and tilt order on their respective pretransitional behaviours. (We know of no material which undergoes a transition from hexatic to F upon cooling, although crystalline smectic B-F transitions are known to occur [8].) In this experiment we measured the temperature dependence of the birefringence, as well as the molecular tilt induced by a strong magnetic field above the A-F transition. This represents the first observation of the pretransitional behaviour associated with an A-F transition.

Samples of 90.4, the only known material thought

to exhibit an A-F transition, were obtained from Dr. Terrance B. Tripp of the University of Maine at Presque Isle, and used without further purification. Most microscopic, miscibility, and X-ray studies indicate that this material possesses an F phase [9-11], although these identifications were made before the smectic I phase was discovered. There is some suggestion in the X-ray intensity profile that the phase in question may be smectic I [2]. The latter phase differs from the F phase primarily in the direction of tilt of the quasi-hexagonal molecular packing. In addition, some form of smectic I phase is thought to exhibit algebraic decay of positional correlations, as opposed to exponential decay characteristic of an F phase [2, 4].

The material was placed between two microscope slides separated by  $125 \pm 5 \mu\text{m}$  thick mylar spacers. The glass was coated with the surfactant hexadecyltrimethyl ammonium bromide to induce perpendicular (homeotropic) alignment. The sandwich was then inserted into a 3.8 cm diameter brass cylinder which served as the oven. Light portholes, which were 3 mm in diameter, were covered by glass windows. Temperature was controlled by means of a Yellow Springs Instrument Model 72 proportional controller with a pair of Fenwal UUA33J4 thermistors ( $3\,000 \Omega$  at  $25^\circ\text{C}$ ), which exhibit a small magnetoresistance [12]. One thermistor was used for feedback to the controller circuit and one for temperature measurement. Long term stability was about 5 mK in a constant field.

The birefringence apparatus, which is based upon a compensation scheme utilizing a modulated Pockels cell, is described in detail elsewhere [13]. In this experiment the modulation frequency was 20 kHz and phase sensitivity between the extraordinary and ordinary polarization components was better than  $10^{-3}$  rad.

The sample was first heated into the isotropic phase; it was then slowly cooled across the isotropic-smectic A phase transition temperature in the presence of a magnetic field  $H = 50$  kOe applied perpendicular to the glass, inducing a uniform homeotropic alignment. Confirmation of the alignment was made visually. The sample was then rotated by  $45^\circ$  about an axis perpendicular to the field, resulting in the experimental geometry shown in figure 1. The incident laser polarization was given by  $(\mathbf{y} + \mathbf{z})/\sqrt{2}$  and the director orientation in zero field by  $(\mathbf{x} + \mathbf{z})/\sqrt{2}$ , i.e.,  $45^\circ$  with respect to the incoming beam. In this configuration a magnetic field  $H$  applied along  $\mathbf{z}$  exerts a torque on the molecular director, inducing a small tilt  $\Phi_0$  of the director (Fig. 1b). For sufficiently small  $\Phi_0$  (a few tenths of a degree),  $\Phi_0 \propto H^2$ . Moreover, as the director tilts, a change in phase difference at the detector  $\Delta\delta [\equiv (\delta(H) - \delta(0))]$  between the ordinary (parallel to  $\mathbf{y}$ ) and extraordinary (parallel to  $\mathbf{z}$ ) polarization components occurs, where  $\Delta\delta \propto \Phi_0$ . Here  $\delta(0)$  is the optical phase difference between the two polarization components at zero field and  $\delta(H)$

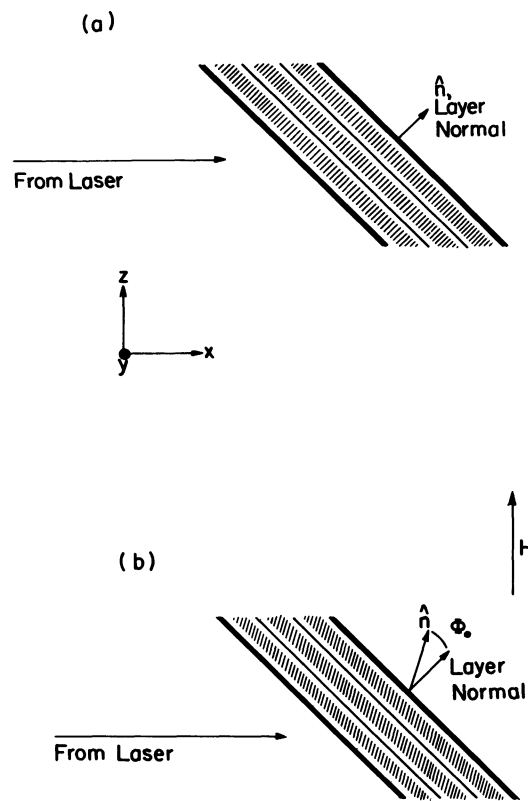


Fig. 1. — Experimental geometry. The sample is oriented at  $45^\circ$  with respect to both the incoming laser and the magnetic field. a)  $H = 0$ ; b)  $H \neq 0$ . Molecules tilt by angle  $\Phi_0$  with respect to layer normal.

is the phase difference in the presence of a strong magnetic field. Thus, the tilt susceptibility  $\chi \equiv d\Phi_0/dH^2|_{H=0}$  is proportional to  $d(\Delta\delta)/dH^2|_{H=0}$ . Fields varying between 50 and 100 kOe were utilized, sufficient to induce an increase in phase difference  $\Delta\delta$  varying between 0.05 and 0.2 rad, corresponding to a few tenths of a degree of tilt. At each temperature  $d(\Delta\delta)/dH^2 \propto \chi$  was obtained from measurements of  $\Delta\delta$  vs.  $H^2$ , and measurements were always made upon cooling.

The largest component of error arose from drift in temperature as the field was increased. Since a change in temperature affects the nematic order parameter  $S$  and thus the sample birefringence, the effective phase difference  $\delta$  varied by approximately  $-2 \times 10^{-4} \text{ mK}^{-1}$ . In the presence of a field, a shift in temperature of 8 mK from the temperature at which the zero field reading was made could be equivalent to a 4 to 5% error in  $\Delta\delta$  (and thus  $\chi$ ) far above the transition temperature  $T_c$ . Closer to  $T_c$ , where smaller fields were used and  $\Delta\delta$  was larger, the fractional error was smaller, scaling approximately as  $\chi^{-1}$ . The primary source of this temperature drift was two-fold: magnet heating affecting the ambient temperature sensed by the heater feedback circuit and magnetoresistance in the feedback thermistor. To mitigate these affects, the oven was insulated

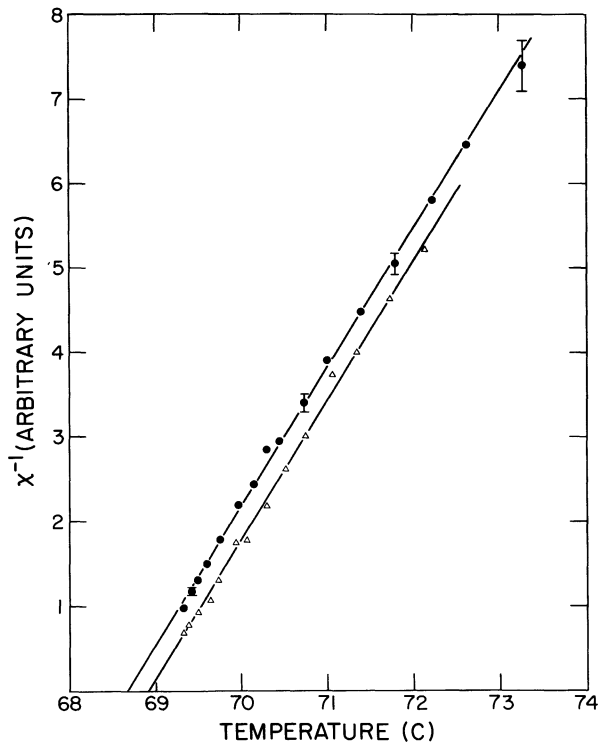


Fig. 2. — Inverse of susceptibility vs. temperature for two separate runs. Lines represent a two parameter, weighted least-squares fit to data, and are scaled to yield same slope. Characteristic error bars are shown at various temperatures.

and surrounded by a jacket of circulating water, substantially reducing thermal contact with the magnet. Moreover, at each field, the feedback resistor loop was manually corrected to account for magneto-resistance. Our effective confidence in relative temperature measurement was about 8 mK.

The inverse susceptibility  $\chi^{-1}$  vs. temperature data for two separate experimental runs are shown in figure 2. The data are scaled to exhibit the same slope, thus compensating for the effects of small differences in sample thickness and orientation in the oven. A third run, not shown here, yielded results consistent with those displayed. Several features are immediately obvious. First, the transition ( $T_c \approx 69.3$  °C) is strongly first order, unlike the A-C transition which in all cases has been found to be second order. The quantity  $T_c - T^*$ , where  $T^*$  is the temperature toward which the susceptibility appears to diverge before being cut off at  $T_c$ , is of the order of 400-600 mK. The first order nature of the transition has also been confirmed calorimetrically [14]. In light of this discontinuous transition, we must to some extent question the relevance of the Bruinsma-Nelson model [6] to this *particular* material. Their results are based upon positive fourth order terms in their free energy functional (Eq. (3.2), Ref. 6). These fourth order terms can conceivably become negative, however, by couplings to other variables such as density, although this possibility has yet to be fully explored.

A second observation is that the  $\chi^{-1}$  vs. temperature data follows a straight line, implying that the critical exponent  $\gamma$  characterizing the tilt susceptibility is  $1.00 \pm 0.04$ . Over the temperature range studied, no systematic deviation from this linear behaviour was observed. A similar mean-field behaviour was also recently observed in the second order A-C transition in butoxybenzylidene heptylaniline [15]. One must therefore conclude that coupling of the bond order to tilt order at most rescales the magnitude of the tilt susceptibility, leaving the functional form unchanged (excepting, of course, the first order behaviour) from that normally found in the A-C transition. This is not inconsistent with the predictions of Bruinsma and Nelson as they relate to a second order transition.

In figure 3 we show the phase difference  $\delta$  (to within an additive constant) vs. temperature in zero field for the geometry shown in figure 1. The phase difference is a qualitative measure of the temperature dependence of the nematic order parameter  $S$ . Such a measurement above the A-F transition is interesting because it has been observed that tilt fluctuations above the A-C transition suppress  $S$  [16], while short-range hexatic order fluctuations above the A-Hexatic transition in the material 650BC sharply enhance  $S$  [17]. Owing to this very large hexatic effect, one might expect a *net increase* in the anomalous part of  $\delta$  above  $T_c$  if bond fluctuations were to dominate the pretransitional behaviour. Nevertheless, in

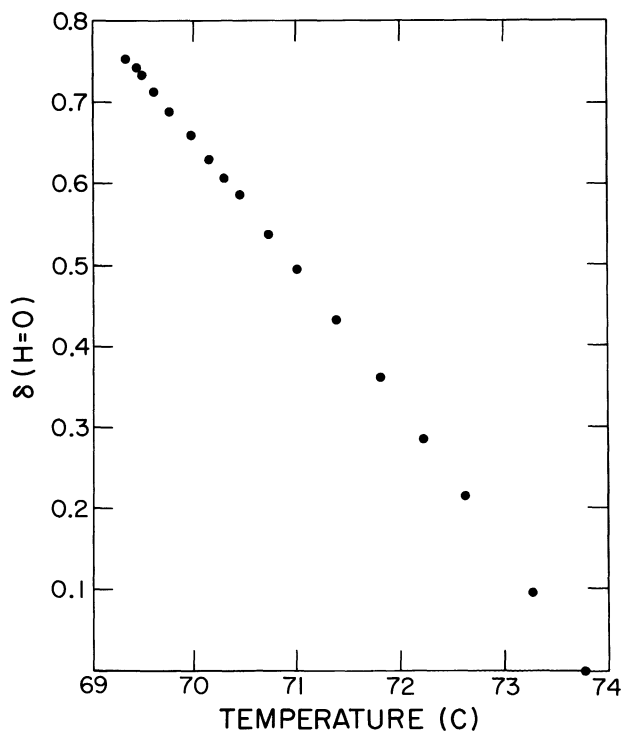


Fig. 3. — Phase difference  $\delta$  in rad at  $H = 0$ , to within an additive constant, between the extraordinary and ordinary components of light. As  $T$  decreases,  $\delta$  increases, indicative of an increase in the nematic order parameter  $S$ .

figure 3 it is seen that  $\delta$  increases smoothly with decreasing temperature, showing no appreciable pretransitional behaviour associated with either bond or tilt fluctuations above  $T_c$ . It is also possible, however, that the value of  $T_c - T^*$  may have been sufficiently large to preclude the observation of pretransitional effects in  $S$ .

In summary, we have performed a birefringence measurement of the magnetically induced molecular tilt to study the susceptibility above a smectic A-smectic F transition. The tilt susceptibility  $\chi$  exhibits a mean-field-like divergence similar to that observed above an A-C phase transition [15], although the divergence is cut off by a first order transition at  $T_c \simeq T^* + 0.5$  K. We conclude that the bond-tilt

coupling at most only rescales the magnitude of  $\chi$  and does not affect the exponent  $\gamma$  in the temperature regime studied. On the other hand, no pretransitional behaviour in the zero field birefringence due to either tilt or bond order fluctuations has been observed.

**Acknowledgments.** — We are grateful to Dr. David Nelson and Dr. Georgia Papaefthymiou for useful discussions, Dr. Terrance Tripp for the 90.4 samples, and Dr. C. C. Huang for the calorimetry data. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation, and one of us (JTH) is supported by NSF grant DMR 8019985.

### References

- [1] BENATTAR, J. J., DOUCET, J., LAMBERT, M. and LEVELUT, A. M., *Phys. Rev. A* **20** (1979) 2505.
- [2] GANE, P. A. C., LEADBETTER, A. J., BENATTAR, J. J., MOUSSA, F. and LAMBERT, M., *Phys. Rev. A* **24** (1981) 2694.
- [3] GANE, P. A. C., LEADBETTER, A. J. and WRIGHTON, P. G., *Mol. Cryst. Liq. Cryst.* **66** (1981) 274.
- [4] BENATTAR, J. J., MOUSSA, F., LAMBERT, M. and GERMAINE, C., *J. Physique Lett.* **42** (1981) L-67.
- [5] PINDAK, R., MONCTON, D. E., DAVEY, S. C. and GOODBY, J. W., *Phys. Rev. Lett.* **46** (1981) 1135.
- [6] BRUINSMAN, R. and NELSON, D. R., *Phys. Rev. B* **23** (1981) 402.
- [7] HALPERIN, B. I. and NELSON, D. R., *Phys. Rev. Lett.* **41** (1978) 121.
- [8] GOODBY, J. W., GRAY, G. W., LEADBETTER, A. J. and MAZID, M. A., *J. Physique* **41** (1980) 591.
- [9] GOODBY, J. W. and GRAY, G. W., *Mol. Cryst. Liq. Cryst.* **56** (1979) 43.
- [10] LEADBETTER, A. J., MAZID, M. A. and RICHARDSON, R. M., in *Liquid Crystals*, ed. by S. Chandrasekhar (Heyden, London) 1980.
- [11] GOODBY, J. W., GRAY, G. W., LEADBETTER, A. J. and MAZID, M. A., in *Liquid Crystals of One- and Two-Dimensional Order*, ed. by W. Helfrich and G. Heppke (Springer-Verlag, Berlin) 1980.
- [12] ROSENBLATT, C., *Phys. Rev. A* **24** (1981) 2236.
- [13] ROSENBLATT, C., TORRES DE ARAUJO, F. F. and FRANKEL, R. B., *Biophys. J.* **40** (1982) 83.
- [14] HUANG, C. C., private communications.
- [15] ROSENBLATT, C. and LITSTER, J. D., *Phys. Rev. A* **26** (1982) 1809.
- [16] LIM, K.-C. and HO, J. T., *Phys. Rev. Lett.* **40** (1978) 1576.
- [17] ROSENBLATT, C. and HO, J. T., *Phys. Rev. A* **26** (1982) 2293.