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Experimental Determination of the Curvature-Induced Reduction in the Smectic A-Nematic Transition Point†

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On the basis of an analogy between smectic A-nematic and superconductor-normal metal transitions, de Gennes has predicted that a twist or bend distortion should reduce T_{AN} with respect to that of a curvature-free sample. We report measurements of the reduction of T_{AN} on samples prepared in two different geometries. In the first, a magnetically induced twist distortion has been used to obtain preliminary data on 8 OCB and CBOOA samples. In the second, a wedge-shaped twisted nematic cell has been used to get quantitative data on the reduction of T_{AN} of CBOOA as a function of twist distortion.

INTRODUCTION

Recognizing the similarity in the role of the phase of the layers in smectic A and the phase of the wave-function in superconductors, de Gennes constructed a Landau-Ginsburg free energy to describe the second-order smectic A-nematic (AN) transition.[1] The analogy between the AN and superconductor-normal transitions led him to make two important predictions: (i) T_{AN}, the AN transition temperature, should be reduced if a twist or bend distortion is imposed, just as a magnetic field reduces the superconductor-normal transition temperature, and (ii) the twist (k_{22}) and bend (k_{33}) elastic coefficients of the nematic phase should exhibit pretransitional anomalies as the temperature is reduced to T_{AN}. The second prediction has been the subject of a large number of quantitative experimental investigations (for a review, see Ref. 2). In contrast, there have

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been very few experimental studies regarding prediction (i), which is the subject matter of the present paper.

We shall first summarize the theoretical results. The detailed phase diagram of |curl n| against T_{AN} depends on the parameter $k = \lambda/\xi$, where λ is the penetration depth of a |curl n| type of distortion into the medium, and ξ the coherence length over which any perturbations influence the smectic order. If $k > 1/\sqrt{2}$ (i.e. materials of type II), under a |curl n| distortion, the A and N phase regions are separated by a 'Shubnikov phase'. However, most liquid crystalline materials appear to have $k < 1/\sqrt{2}$ (i.e. belong to type I); in that case, the |curl n| distortion leads to a reduction of T_{AN} and the transition becomes first order in character. The threshold curve is given by[1]

$$\frac{A^2}{2B} = \frac{1}{2} k_{ii}(\text{curl } n)^2, \qquad i = 2 \text{ or } 3 \tag{1}$$

where $A \simeq a(T - T^*_{AN})$ (in the mean field approximation) and B are the usual parameters of the Landau free energy. For distortions lower than the threshold, an 'intermediate state' with coexisting A and N regions is expected to occur.

To our knowledge, there have been only two experiments in which this theoretical prediction has been taken into account to explain some observations. In the first one by Cladis and Torza,[3] a 'striped' texture was observed when *N-p*-cyanobenzylidene-*p'*-octyloxyaniline (CBOOA) with a strong bend distortion was cooled to T_{AN}, and was interpreted in terms of the intermediate state. More recently, similar observations have been made by Hinov[4] on a CBOOA sample with a bend deformation induced by an electric field. It is fair to say that there has been no experimental determination of the phase diagram, i.e. the dependence of T_{AN} on |curl n|.

In this paper, we present the first experimental determination of the phase diagram of the type mentioned above, on samples with a twist deformation. Two experimental geometries have been used for this purpose. In the first, the deformation is induced by a magnetic field applied to a homogeneously aligned sample. The experiment will be described in the next section. It is difficult to accurately estimate the value of |curl n| in this case. Hence we have used another geometry in which the twist deformation is induced by surface treatment as in a twisted nematic cell. Experiments on a twisted nematic cell constructed in the form of a wedge can be used to obtain a reasonably good phase diagram. These results will be discussed in the last section.

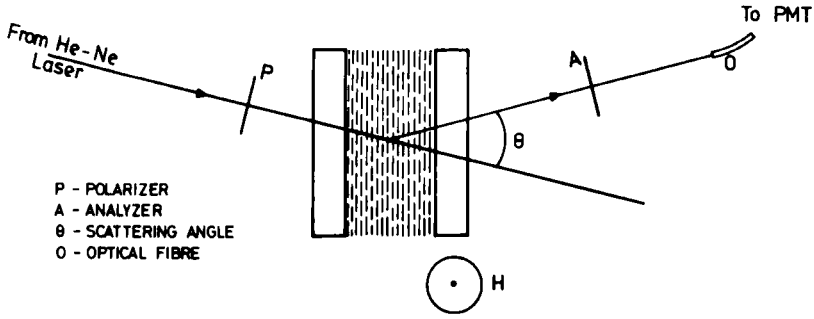

FIGURE 1 Schematic diagram of the experimental setup to detect light scattered by bend fluctuations. The magnetic field H applied perpendicular to the plane of the paper produces a twist distortion in the medium. For the sake of clarity, the thickness of the sample is very much exaggerated compared to that of the glass plate.

TWIST DEFORMATION INDUCED BY A MAGNETIC FIELD

The experimental configuration is shown in Figure 1. The homogeneously aligned sample was taken between two glass plates whose inside surfaces were coated at an oblique angle with silicon monoxide. The thickness of the sample x_0 was in the range of 20 to 50 μ. In the nematic phase, if a magnetic field (H) is applied in the plane of the glass plates but perpendicular to the initial orientation of the director ($\mathbf{n}$), for a field strength $H > H_c$ the Freedericksz threshold, the sample acquires a twist deformation $|\text{curl } n| = d\phi(x)/dx$. The threshold field is given by

$$H_c = \frac{\pi}{x_0}\sqrt{\frac{k_{22}}{\Delta\chi}} \tag{2}$$

where $\Delta\chi$ is the anisotropy of the volume diamagnetic susceptibility of the medium.

$|\text{curl } n|$ at any given point (x) for a field $H(>H_c)$ is given by

$$\frac{d\phi(x)}{dx} = \frac{\pi}{x_0}\cdot\frac{H}{H_c}[\sin^2\phi_m - \sin^2\phi(x)]^{1/2} \tag{3}$$

where $\phi_m(H)$ is the maximum angle of twist at the midplane. $|\text{curl } n|$ takes the largest value near the boundaries and reduces to zero at the midplane. The maximum value is given by

$$\left(\frac{d\phi}{dx}\right)_{\max} = \frac{\pi}{x_0}\cdot\frac{H}{H_c}\sin\phi_m(H) \tag{4}$$

One can easily evaluate the average value of |curl n| over the entire sample thickness:

$$\left(\overline{\frac{d\phi}{dx}}\right) = \frac{\pi}{x_0} \cdot \frac{H}{H_c} \cdot \frac{\sin^2 \phi_m}{\phi_m} \cdot \left[\left(1 - \frac{1}{\sin^2 \phi_m}\right)\frac{\pi}{2} \cdot \frac{H}{H_c} + \frac{1}{\sin^2 \phi_m} E\left(\sin \phi_m, \frac{\pi}{2}\right)\right] \quad (5)$$

where $E(\sin \varphi_m, \pi/2)$ is the complete elliptic integral of the 2nd kind. For $H < 2.5H_c$, $(\overline{d\varphi/dx}) > \frac{2}{3}(d\varphi/dx)_{max}$. As the magnetically deformed sample is cooled below T_{AN}, one expects that the A phase is formed at the midplane (where |curl n| = 0) and grows toward the boundaries at lower temperatures. Our visual observation clearly showed the reduction of T_{AN} on application of a sufficiently strong field. (In all our experiments, the temperature was measured to an accuracy of 0.01° using a copper constantan thermocouple and a Keithley 181 digital nanovoltmeter.) If the sample is cooled under the field to a temperature slightly lower than T^0_{AN} (the superscript 0 standing for $H = 0$), and H is reduced to zero, the transition to the A phase occurred immediately. The N–A front could be moved by changing the value of H. Further, on careful observations it was noticed that the N–A transition under the field was really complete only when the temperature is lowered by a considerable value. For example, if $d \simeq 25\ \mu$, $H \simeq 15{,}000$ G, the transition is complete only for $T \simeq T^0_{NA} - 2$. The large temperature range of the "intermediate state" is probably due to the continuous increase in the value of |curl n| as the growing smectic layer squeezes the nematic region into a progressively thinner region as the temperature is lowered. We could also observe the reduction in T_{AN} in the heating mode, under the action of H. The transition point was detected by monitoring the light scattered by bend fluctuations in the sample[5] (Figure 1). The field dependences of T_{AN} for CBOOA (which has almost a second order A–N transition[6]) and *p-n*-octyloxy-*p'*-cyanobiphenyl (8 OCB, which has an extremely weak first order AN transition[7]) are shown in Figures 2 and 3, respectively. Though we get the correct trend in both cases, it is difficult to estimate the actual value of |curl n| for the following reasons: (a) $d\varphi/dx$ is nonuniform across the sample, as discussed earlier, and (b) the value of H_c is difficult to estimate at T_{AN} (H_c is expected to tend to ∞ as $k_{22} \to \infty$ at T_{AN}). Hence this method is not suitable for determining the phase diagram quantitatively.

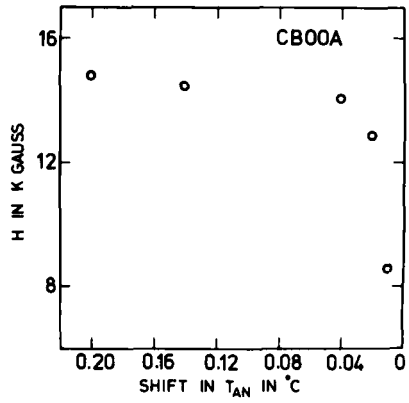

FIGURE 2 Magnetic field dependence of the shift in T_{AN} for a 25 μm thick sample of CBOOA.

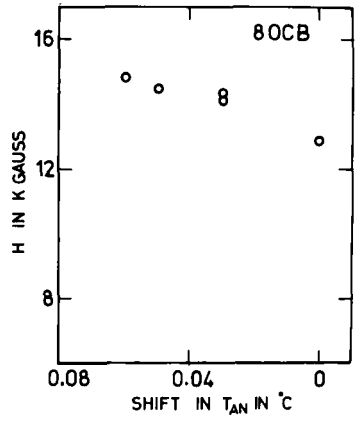

FIGURE 3 Magnetic field dependence of the shift in T_{AN} for a 25 μm thick sample of 8 OCB.

STUDIES ON "TWISTED NEMATIC" CELLS

Two glass plates whose inside surfaces are coated with silicon monoxide at an oblique angle are arranged in a twisted nematic configuration. The

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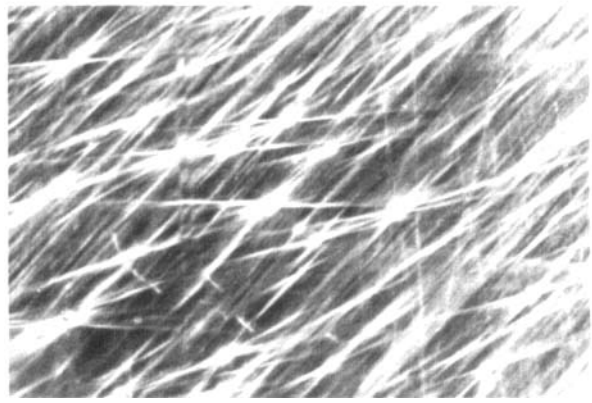
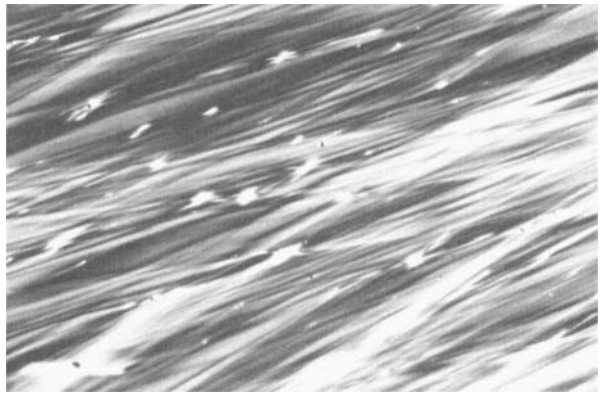


(*b*)

FIGURE 4 Photographs of various aspects of "twisted nematic" samples of CBOOA cooled below T^0_{AN} (polarizers adjusted to get a relatively dark field of view). (*a*) A sample of thickness 50 μm at 82.7°C. Focused on the bottom plate: notice that the A phase has started to appear in the form of folds which are aligned along the diagonal from the top left corner to the bottom right corner, corresponding to the orientation of the molecules on the bottom plate (400×). (By focusing the microscope on the top plate, similar folds aligned in a different direction corresponding to the orientation of the molecules on the top plate could be seen.) (*b*) Another sample (thickness = 15 μm) at 82.4°C focused on the midplane. The easy axes of the molecules on the top and bottom plates are nearly vertical and horizontal respectively. Folds and strong fluctuations of the director were seen simultaneously in the field of view, indicating the coexistence of A and N phases. (*c*) Same sample as in (*b*) but at 78.6°C. The entire sample is filled with folds of the A phase. No fluctuations are seen, indicating that the transition to the A phase is complete. Notice that the average alignment of the folds is ~45° to the vertical.



(*c*)

nematic sample taken in such a cell has a uniform $|\text{curl } n| = (\delta\varphi/\delta x) = (\varphi_1 - \varphi_2)/x_0$ where $(\varphi_1 - \varphi_2)$ is the twist angle which is usually about 75°.

Observations were first made on *homogeneously* aligned samples having thickness in the range 20 to 50 μ under a polarizing microscope (Leitz ortholux Model II POL–BK). As T_{AN} was approached from higher temperatures, fluctuations in the intensity of light in the field of view increase considerably, and stop abruptly at T_{AN}. (The increase in fluctuation is somewhat surprising in view of the divergence of k_{22} and k_{33} as T_{AN} is approached and we have no explanation for this observation.)

In twisted nematic cells of uniform thickness x_0, the N–A transition was first noticed as "folds" which developed near the boundaries (see photograph *a* in Figure 4). However, fluctuations in the intensity of light could also be seen ,indicating the coexistence of A and N phases. The "intermediate state" (see photograph *b* in Figure 4) again lasted down to $\sim T_{AN} - 3$°C, for reasons already mentioned. When the entire sample was transformed to the A phase (photograph *c* in Figure 4), the folds corresponded to an orientation midway between φ_1 and φ_2. In thin samples sometimes one could see small islands in which the general alignment is different from the surroundings, probably due to defective coating and/or nonuniformity of the glass surfaces.

In order to determine T_{AN} as a function of $(\delta\varphi/\delta x)$, we used a twisted nematic cell in the form of a wedge (Figure 5). The twist angle $(\varphi_1 - \varphi_2)$ was about 75° and could be measured exactly under the polarizing microscope when the sample was in the nematic phase. The wedge angle was

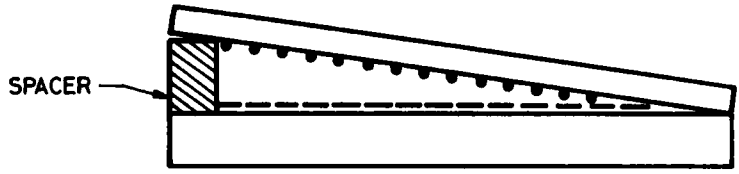


FIGURE 5 Schematic diagram of the wedge-shaped twisted nematic cell used to determine the dependence of T_{AN} on |curl n|. The dots and dashes represent the easy axes of alignment. In the actual experiment, the twist angle is $\simeq 75°$.

about 0.001 radian. The thickness of the cell was determined at various points by using a channeled spectrum technique before the sample was filled. By careful observations, the temperature at which the folds just appeared (as in Figure 4*a*) at any given point is noted down. This temperature is taken to be the value of T_{AN} corresponding to the initial value of |curl n| at that point. The results on CBOOA are shown in Figure 6. Using a dimensional argument, one can write[3]

$$T_{AN}^{t} = T_{AN}^{0} - lT_{AN}^{0}|\text{curl } n| \tag{6}$$

where the superscript t indicates the value for the twisted region and l is a molecular dimension. Using the data near T_{AN}^{0}, we find that $l \simeq 45$ Å. For the twist deformation, l should be compared to a transverse dimension of the molecules, and the large value that we obtain may mean that l represents

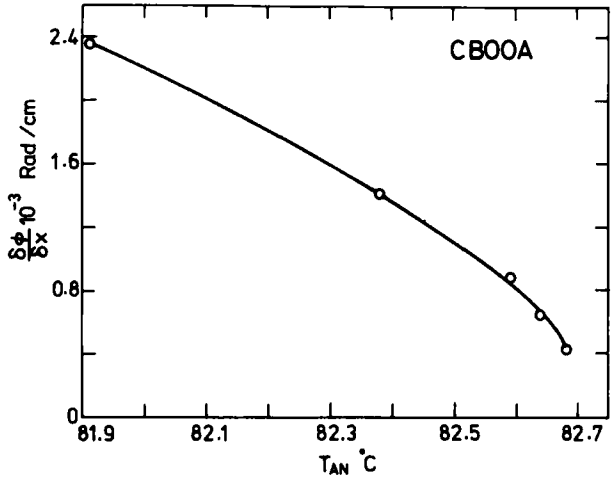


FIGURE 6 Variation of T_{AN} with $(\delta\varphi/\delta x)$ for CBOOA.

the dimension of a short-range ordered group. The antiparallel correlations between the strongly polar CBOOA molecules give rise to strong short-range order effects even far above T_{AN}.

We are refining this technique, and the results along with those on samples with a bend deformation will be reported elsewhere.

Acknowledgments

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