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Possibility of twist-grain-boundary structure in nonchiral liquid crystals

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Recent studies of highly chiral liquid crystals suggest that twist in smectic phases can be supported by the introduction of periodic twist grain boundaries that would produce a helical structure formed by smectic blocks that are twisted with respect to each other. Here, we examine the possibility of observing such a structure in nonchiral smectic liquid crystals. Experimental results suggest that such structures may be obtained by confining ordinary nonchiral liquid crystals in a cell in which the directors at the two surfaces are nonparallel.

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The recent discovery of the Abrikosov flux lattice analog in liquid crystals has produced much excitement in both experimental and theoretical research. This analogy is based on the observation by de Gennes [1], that the nematic to smectic liquid crystal phase transition is very similar to the metal to superconductor phase transition. Extending this analogy further, Renn and Lubensky predicted the existence of a flux-lattice-like phase in chiral liquid crystals which they called the twist-grain-boundary (TGB) phase [2]. Independent of this prediction, the experimental observation of a very unusual phase with properties resembling those of nematic and smectic liquid crystals had been observed [3,4]. Careful subsequent experiments have established that this unusual phase is the predicted TGB phase [5]. This unusual phase has since been observed in numerous compounds [6,7].

The structure of the Abrikosov analog in liquid crystals is often referred to as the twist-grain-boundary phase because it consists of regularly spaced grain boundaries of screw dislocations that are parallel to each other within the grain boundary, but are rotated by a fixed angle with respect to the screw dislocations in adjacent grain boundaries. Thus each smectic block is separated by a twist grain boundary that allows one smectic layer to be angularly offset from the neighboring block. In chiral materials, the twisting is induced by the chirality of the system. Thus in nonchiral liquid crystals the intrinsic TGB phase vanishes. In all the cases reported so far, the TGB structure has been observed only in chiral liquid crystals. It should be possible however, as we show in this paper, that chirality may not be necessary to observe the TGB structure.

Consider a nematic liquid crystal confined in a cell whose surface is parallel to the x-y plane, and the cell surfaces have been rubbed along the x axis at the bottom surface and the y axis at the top surface. For nematic liquid crystals confined in such a cell, the director rotates from one surface to the other at a constant rate to produce a uniformly twisted nematic structure. In the case of strong anchoring, quite typical for nematic liquid crystals, the director at the surface is pinned along the rubbing axes and the twist angle is equal to the difference between the rubbing direction at the two surfaces. For weak anchoring, assuming a surface anchoring energy of the form $A\sin^2\phi$, the twist angle is reduced by 2ϕ, where $\sin(2\phi) = K\pi/dA$, and K and d are the elastic constant and the cell thickness, respectively [8]. If for the moment we assume strong anchoring and if the material possesses a smectic A phase, the question is what would happen if such a twisted nematic structure is cooled into the smectic phase? It is known that the twist elastic constant K_2 diverges at the nematic to smectic phase transition temperature, and therefore the twist of the smectic layer is forbidden. Thus ordinarily it would be expected that the sample upon cooling into the smectic phase would break up into two domains in which the layer normal coincides with either the x axis or the y axis. On the other hand, if the material has a tendency to form a TGB phase then it is possible that the material would spontaneously break up into small smectic blocks separated by twist grain boundaries with the block rotation axis which is perpendicular to the smectic layers.

In order to establish the possibility of TGB like structures, one has to establish at least two things: (1) that there are smectic layers, and (2) that they are twisted. In the absence of detailed x-ray studies, the presence of smectic structure can be deduced from the observation of the slight change in texture as the material is cooled into the smectic-A phase as is the case for the samples that we have examined. The twist in the structure can be established by using polarized light, and analyzing the state of the output light, for example, by examining whether the polarization is rotated with respect to the input light polarization. Barring polarization rotation due to optical activity, which is generally small, and identically equal to zero for nonchiral materials, there exists only one case where the polarization of the light can appear to have been rotated by a uniform nontwisted birefringent material. In this case, however, the rotation would occur only when the input polarization of the light with respect to the director at the entrance surface of the cell is at 45° and the cell thickness is such that the phase difference for the two eigenmodes is an exact odd multiple of π for a particular wavelength. Furthermore, when the polarization direction coincides with the director at the surface, there would be no polarization rotation. This shows that if the polarization of the light is rotated by a birefringent structure over a broad wavelength region, then the structure must be twisted, and the twist has to be gradual so

as to allow adiabatic following of the polarization of the light. This twist in the structure can also be determined by using monochromatic light if the polarization rotation is not very sensitive to the direction of the input polarization with respect to the director axis at the surface. The slight sensitivity arises because of the incomplete waveguiding in the twisted structure.

We have attempted to observe TGB like behavior in a number of nonchiral liquid crystals. Here we present results for 4-cyano-4′-*n*-octyloxybiphenyl) (M24), a commercial cyanobiphenyl material from British Drug Houses (BDH). We have chosen to use a sample that has been prepared in a particular way so as to provide a built-in reference. This was done by spatially controlling the surface alignment of the same sample cell into four regions, two of which produced twisted structure of opposite twist and two reference regions with no twist. The procedure for preparing such a sample has been described previously [9]. The director orientation in these four regions is as follows: (a) the director lies along the x axis on both the top and the bottom surface, (b) the director lies along the x axis on the top and along the y axis at the bottom, (c) the director lies along the y axis on both surfaces, and (d) the director is along the y axis at the top and along the x axis at the bottom. The reference control areas which show the common smectic A structure would be in regions (a) and (d). The TGB structure is expected to be observed in regions (b) and (d).

When the sample in its nematic phase is viewed between polarizers such that the polarizers and the analyzer are crossed and are along the x and y axis, respectively, one observes that regions (a) and (d) appear dark while regions (b) and (c) appear bright (see Fig. 1). This is easily understood by noting that the optic axis in regions (a) and (d) lies either along the polarizers or the analyzer and hence these regions would appear dark. Similarly the other two regions appear brighter, because of at least partial optical waveguiding which causes the polarized light to rotate through 90°. On approaching the smectic A phase the apparent viscosity of the material increases which can be inferred by gently resting the sample cell and observing the flow. At the onset of the smectic transition, characteristic oriented focal conic fans become visible in all four regions, marking the onset of the smectic phase transition. However, this structure is most easily seen by observing the edges of the sample. These changes result from the formation of the smectic layers. The transmitted light intensity, however, does not appear to change significantly at least close to the nematic to smectic phase transition in any of the four regions, suggesting that the twisted structure in regions (b) and (c) is retained even when the material is cooled into the smectic phase (see Fig. 2). There is very little change in the transmitted light intensity as the sample is rotated with respect to the plane of polarization of the input light. Thus we have to conclude that structure in the smectic phase in regions (b) and (c) must be twisted and similar to the continuously twisted structure in the nematic phase since the polarization light transformation deduced by measuring the light transmission intensity above and below the phase transition is almost identical.

In order to quantify the optical observations, we have measured the light transmission in these regions (b) and (c) as a function of temperature. Since the changes were identical in these two regions, data for only one region are shown in Fig. 3. While the onset of the smectic A transition is evident by a slight change in the transmitted intensity, it does not change significantly when the temperature of the sample crosses the N-A transition temperature. This clearly indicates that the structure in regions (b) and (c) must be twisted, similar to that in the nematic phase. Note that in the absence of the TGB like structure, the transmission through regions (b) and (c) would have changed dramatically if the structure had changed from being twisted in the nematic phase to being untwisted in the smectic phase. The light transmission through regions (a) and (d), that is the untwisted regions, remains practically zero throughout the temperature range that was investigated and is not shown. For the data in Fig. 3, the slight decrease in the light intensity with decreasing temperature may be due to the change in the sample birefringence which produces less waveguiding and also due to increased scattering from the focal conic defects. However, the dramatic change in the

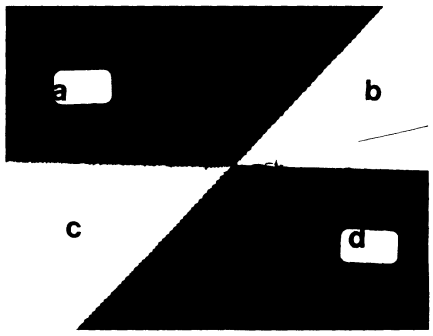

FIG. 1. A microphotograph taken with the sample between crossed polarizers. The four regions (a)–(d) are determined by orientation of the director at the two surfaces (see text for details). The photograph is taken at 70 °C in the nematic phase.

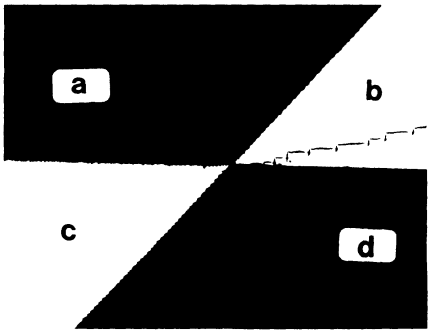

FIG. 2. A microphotograph taken with the sample between crossed polarizers. The four regions (a)–(d) are determined by orientation of the director at the two surfaces (see text for details). The photograph is of the same region shown in Fig. 1, taken at 65 °C in the smectic phase.

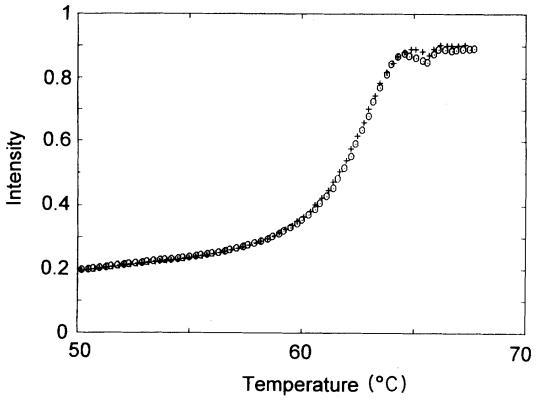

FIG. 3. Light transmission through the twisted region as a function of temperature. The symbol (○) represents the data during the cooling cycle while the symbol (+) represents the data during the heating cycle. The data are taken with the sample between crossed polarizers, and the angle between the directors at the two surfaces is 90° in the nematic phase.

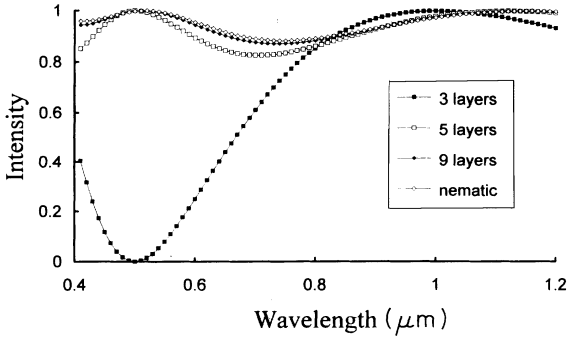

FIG. 4. Calculated light transmission through a 90° twisted liquid crystal structure. Three curves are for the twisted smectic block structure with three, five, and nine blocks and the fourth is for the continuous nematiclike structure. For these calculations the cell thickness $d = 10$ μm, and birefringence $\Delta n = 0.1$.

intensity several degrees below the transition clearly cannot be due to change in the material birefringence alone. These changes may be due to the changes in the anchoring strength at the surfaces or due to the increase in the size of the smectic blocks with decreasing temperature.

For the TGB like structure, since the number of smectic blocks has to be an integer, the intensity might be expected to change in steps as the temperature is changed due to the changing number of blocks. However, no evidence of step changes in transmission is observed. This may be because of a small change in a large number of blocks. A rough estimate of the block size is expected to be the root mean square of the smectic layer thickness and the sample thickness [2]. In our case the layer thickness is of the order of 20 Å while the sample thickness is of the order of 10 μm which yields a block size of 1400 Å. These blocks therefore cannot be detected directly by visible light with a wavelength of about 5000 Å. This is, however, only a crude approximation and clearly the actual block size may be quite different and temperature dependent. Calculations of the optical properties of TGB like structure using 2×2 Jones matrices [10] suggests that the light transmission would be very similar to that for the twisted nematic liquid crystal as shown in Fig. 4. Careful optical observations of the samples, in the temperature regions several degrees below the transition, where the light intensity changes rapidly, show that the area being monitored becomes patchy in appearance with different birefringent colors developing across the measurement area. This indicates that the structure at these temperatures becomes spatially nonuniform and the smectic block size probably increases.

The observation, that the transmitted light intensity does not change when the twisted nematic structure is cooled into the smectic phase, indicates that the director in the smectic phase is also twisted. One explanation for this optical behavior is that there exists a TGB like structure in the smectic phase, where the smectic blocks are separated by the grain boundary of screw dislocations. It is also possible that the structure between the boundaries has a nematiclike structure which allows the two smectic blocks to rotate with respect to each other. It is not possible to optically distinguish between these two cases. The possibility that the director is somehow twisted within the smectic layers is unlikely since the smectic layer normal is parallel to the director and therefore rotating the director must also produce a rotation of the layers. Finally the possibility that the surface is nematiclike with the bulk being nontwisted smectic is unlikely. Consider, for example, two uniformly twisted surface nematic regions with a single untwisted smectic region in the middle. Using birefringence of 0.2, and probing the structure with 0.5 μm light, the nematic region has to be greater than 1.5 μm thick, which, while possible, seems unlikely. This possibility is further ruled out by applying an electric field across the sample and observing the electro-optic response. It is found that close to the phase transition temperature (~0–5 °C) the structure can be distorted. This distortion, however, is not due to the twisted surface nematic layer, because similar distortions are observed in the twisted (b) and (c) and the untwisted regions (a) and (d) at the same temperature. The electric field response in the two regions would have been different if there existed a thin nematic layer in regions (b) and (c).

Other liquid crystals with nematic to smectic A phase transition sequence were also found to have similar behavior, indicating the generality of the observations presented in this paper. However, in materials with isotropic to smectic A phase sequence, for example, in 4-cyano-4′-n-decyloxybiphenyl (10OCB), the TGB like structure was not observed, perhaps because of the lack of the nematic phase. This is an interesting observation which suggests that while the optical observations indicate a twisted structure, it may not be a TGB structure, but one in which the smectic blocks are separated by nematiclike regions. However, to account for the observed optical results, the number of smectic blocks has to be greater than 5 based on the data presented in Fig. 4.

This observation of the TGB like structure in nonchiral systems may allow a systematic control of the block

size by physically changing the amount of twist in the structure, by controlling either the angle between the director at the two surfaces or the sample thickness. Furthermore, this observation may provide the possibility of direct access to the observation of other twist-grain-boundary phases [11] such as the TGB_C which has recently been predicted and which has a structure analogous to the TGB_A phase but in which the smectic blocks have the structure of the smectic C phase instead of the smectic A phase. Furthermore, by doping these materials with chiral dopants, one has the further possibility of observing TGB_C^* which has a smectic block structure of smectic C^* phase instead of the nonchiral smectic C.

In conclusion, the optical observation appears to support TGB like structures in twisted nonchiral liquid crystals. Confirmation by x-ray studies would provide additional support, however the existence of the TGB structure in chiral or nonchiral systems can only be proved by providing evidence of the existence of the twist grain boundary itself.

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