

A three-dimensionally modulated structure in a chiral smectic-C liquid crystal

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In this article we report the discovery of a new twist grain boundary phase. This phase is characterized by a 2-dimensional undulation of the smectic-C*-like blocks in the form of a square lattice. We suggest that this three-dimensionally modulated structure, which was not anticipated by theory, owes its origin to chiral interactions.

The formal analogy between superconductors and smectic liquid crystals was invoked by De Gennes¹ to predict the possibility of an intermediate phase with a lattice of dislocations in smectics. Goodby *et al.*² discovered such a structure in a highly chiral liquid crystal. This twist grain boundary (TGB_A) phase consists of a helical stack of blocks of smectic-A (S_A) liquid crystal, separated by grain boundaries made of an array of screw dislocations (Figure 1*a*), in accordance with a structure which had been worked out by Renn and Lubensky³. Unlike superconductors, smectic liquid crystals can have other modifications like the smectic-C (S_C) in which the molecules are tilted with respect to the layer normal and the smectic-C* (S_C*) in which the tilt direction has a helical arrangement about the layer normal. Although TGB phases with S_C-like blocks (TGB_C) (Figure 1*b*) and S_C-like blocks (TGB_C*) have been theoretically

predicted^{4,5}, only the TGB_C phase has been experimentally characterized in some detail^{6,7}. Liquid crystals are rather soft, and can exhibit novel geometrical structures. We have found in a binary mixture a new TGB phase which has a 2D undulation of the S_C blocks in the form of a square lattice.

Experimental

The new phase was found in binary mixtures of the chiral compound 4-(2'-methyl butyl phenyl 4'-*n*-octyl biphenyl-4-carboxylate (CE8)) and 2-cyano-4-heptyl-phenyl-4'-pentyl-4-biphenyl carboxylate (7(CN)5) which have very similar lengths and molecular structures. On heating, CE8 exhibits the phase sequence (with temperature in °C): crystal 67 S_T, 70 S_C, 85 S_A, 134.6 N* 140.5 I, where N* stands for chiral nematic and I for isotropic phases. On the other hand, 7(CN)5 has a wide nematic range (crystal 45 N 102 I) and X-ray studies have shown that it has a strong skew cybotactic (S_C-like) short range order⁸. The phase diagram of the binary mixtures is shown in Figure 2. The TGB phases are found only in mixtures with ~5 wt% to 45 wt% of 7(CN)5. Most of the physical studies were conducted on a mixture with about 36 wt% of 7(CN)5, which

exhibits the following (known) phases on cooling: I 121.7 N^* 76.8 TGB_A . Observations using a polarizing microscope show that as the sample is cooled further to 63°C, there is a distinct transition from the TGB_A phase to another phase, in which large patches develop a square grid pattern. As the temperature is lowered below 59°C the grid becomes less distinct.

In a cell whose glass plates are pretreated with polyimide and unidirectionally rubbed so that the nematic director has a planar alignment, the TGB_A phase exhibits a Grandjean plane texture¹ similar to the cholesteric phase. In such a sample the boundary condition ensures that the helical axis is perpendicular to the glass plates. The local changes in the cell thickness produces sympathetic variations in the helical pitch producing the Grandjean plane texture. As the director alignment is fixed on the glass surfaces, only an integral number of half pitches can be accommodated between the plates. The number changes by unity across each Grandjean Cano (GC) dislocation line. As the temperature is lowered the texture goes over to a well-aligned square grid pattern, one of the axes of which is parallel to the rubbing direction. In wedge-shaped samples, the GC lines are seen in both the TGB_A (Figure 3 a) and the new phase with the square grid (Figure 3 b), demonstrating that there is a helical twist normal to the plates in both the cases. As the temperature is lowered to

59°C, the GC lines become highly distorted and appear to get anchored at surface irregularities. The spacing between GC lines increases only down to 59°C below which the irregular lines are not affected by temperature. The square grid is a pseudomorphic (or metastable) texture below 59°C and is erased by a displacement of the cover slip, to produce a texture characteristic of the S_C phase. As the temperature is increased, the square grid texture is recovered at 59°C, as are the distinct and straight GC lines in the wedge-shaped sample. These observations show that there is a new phase which occurs between the TGB_A and S_C phases. It is characterized by a helical arrangement whose axis is normal to the glass plates for planar alignment and a square grid modulation in the orthogonal plane. It is a thermodynamically distinct phase which appears both on cooling from the TGB_A phase and on heating from the S_C phase.

We have also prepared cells whose glass plates are coated with a thin layer of glycerine which produces a degenerate planar anchoring. Again the square grid texture appears in both the heating and cooling runs. Of course, in a wedge-shaped sample no GC lines form due to the degeneracy in the boundary condition, and the lattice spacing of the square grid is found to be independent of the thickness of the sample. Thus, surface anchoring is not important in stabilizing the modulated structure. In order to characterize the structure in greater detail, we have conducted the following experiments:

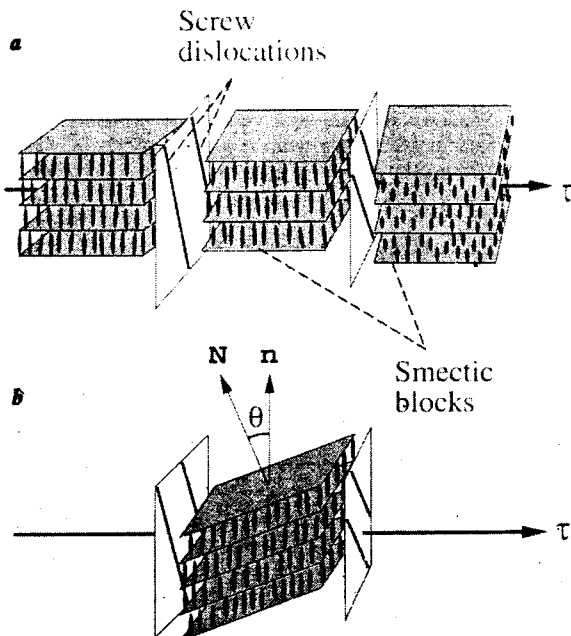


Figure 1. a, Schematic representation of the TGB_A structure. The direction of the average orientation of the molecules (director) is along the local layer normal. b, Schematic representation of the TGB_C structure (after reference 7). 'N' is the layer normal, and 'n' is the director. 'τ' is the helical axis.

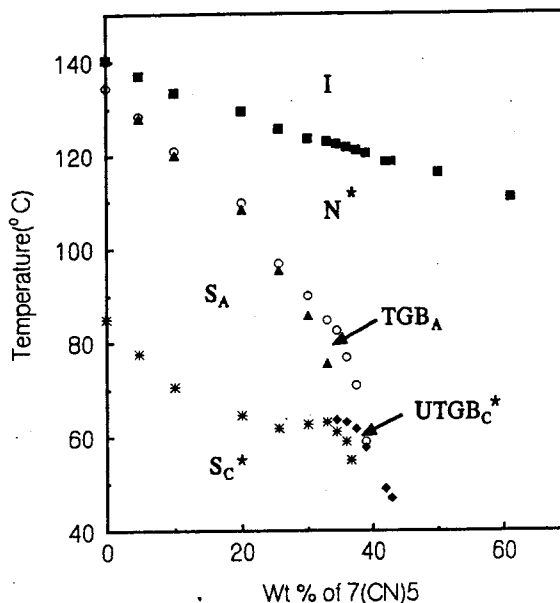


Figure 2. Phase diagram of the binary mixtures of CEB and 7(CN)5. Note that the TGB phases occur only in the mixtures and the new phase ($UTGB_C$) occurs in a narrow range of compositions.

- a) The diffraction pattern of a laser beam from the structure brings out the underlying square grid distortion which results in a periodic variation of the effective refractive index (Figure 3 c).
- b) In cells prepared with homeotropic boundary conditions in which the director preferentially aligns normal to the glass plates, the TGB_A phase is characterized by a filamentary texture⁹, each filament corresponding to a rotation of the director by π radians, and the width of the filament $\approx p/2$, where p is the pitch of the TGB helix⁹. When the sample is cooled to 63°C, the filaments clearly develop an undulatory structure (Figure 3 d) with a periodicity which roughly corresponds to that of the square grid observed in the planar geometry. As the temperature is lowered to 59°C, i.e. in the S_C phase, the filaments disappear, but on reheating they reappear with the undulatory

structure. The structure straightens out when the temperature is raised to 63°C.

- c) When small drops of the liquid crystal are deposited on a glass plate treated for homeotropic alignment, in the S_C phase concentric GC rings are seen. As the temperature is raised to 59°C, undulatory filaments grow as arcs with their centres at the geometric centre of the drop.
- d) X-ray scattering studies on 25 μm thick aligned samples taken between etched cover slips show



Figure 3 a. Grandjean-Cano lines seen in the TGB_A phase in a wedge-shaped sample with pretreated glass plates as explained in the text.



Figure 3 c. Diffraction pattern of a He-Ne laser beam produced by the square lattice of the type shown in Figure 3 b.

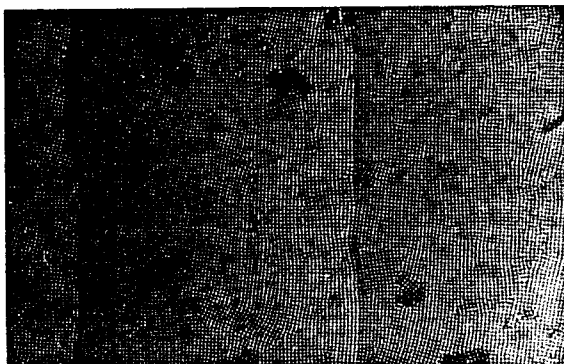


Figure 3 b. Square grid pattern (grid spacing $\sim 2.5 \mu\text{m}$) seen in the new phase at 60°C in a wedge-shaped sample. Note the two vertical Grandjean-Cano lines which are characteristic of a helical arrangement normal to the plane of the figure.

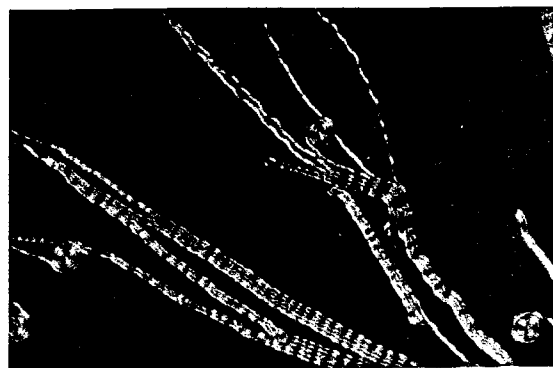


Figure 3 d. Filamentary texture just below the transition to the $UTGB_C$ phase exhibited in samples whose walls are pretreated for homeotropic alignment. Note the undulations in the filaments (crossed polarizers, periodicity of the undulation $\sim 4 \mu\text{m}$).

that in the TGB_A phase there is a relatively (compared to N^*) sharp ring corresponding to the S_A layer spacing². As the temperature is lowered below 63°C, the ring expands showing that the molecules are now tilted in the layers. Below 59°C, in addition to the ring, four relatively strong spots are also seen. Probably they indicate an unwound region of S_C liquid crystal near the glass surfaces. In the present experiment, we are unable to verify if the TGB structure in the new phase is commensurate or otherwise.

- e) The effect of an external AC electric field was studied in different geometries. Under the action of a 10 kHz field applied along the TGB helical axis in the planar geometry, the dark regions separating the bright ones (see Figure 3 b) become very thin and straight and remain intact even at 30 V/μm. In the homeotropic geometry, under an appropriate setting of crossed polarizers, the undulatory filaments are seen to have periodic dark and bright bands along the length. If the filament is roughly parallel to a pair of wires between which a transverse electric field is applied, the dark bands expand and the bright ones shrink. When a very low frequency

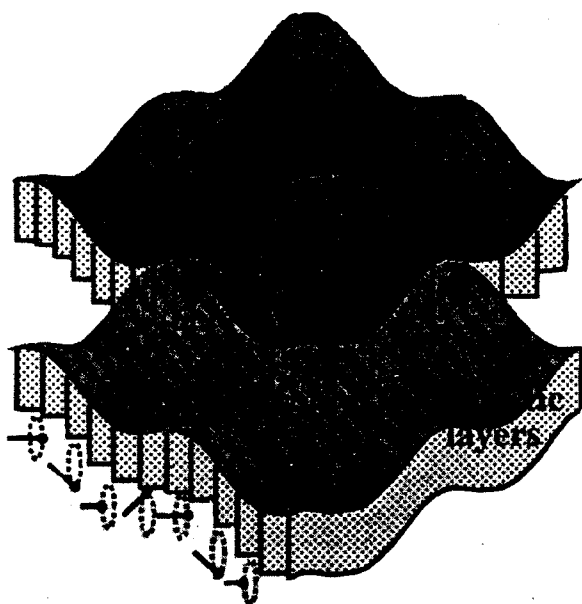


Figure 4. Schematic diagram of the geometrical arrangement of two neighbouring smectic-C* blocks in the proposed structure in the new phase. Note that the 2D-undulations in both the blocks have the same orientations of the wave vectors. The orientation of the smectic layer normal (large arrows) is different in the two blocks, which are separated by a grain boundary (not shown explicitly). The dotted areas representing smectic layers have undulations only in the vertical plane. The helicity of the director in the lower smectic-C* block is shown by that of the 'nails'.

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(1 Hz) square wave voltage is applied between ITO-coated plates in the same geometry, for a field ~ 5 V/μm, the filaments become broader and straight. Further, a narrow dark band in the *centre* of the filament shows a spatially periodic intensity modulation along the length which responds at the frequency of the applied voltage. This is best seen when the polarizer is set nearly orthogonal to the 'axis' of the filament. On the other hand, a similar voltage applied to a TGB_A filament shows a continuous dark band in the centre.

Discussion

Based on the above observations, we propose that the intermediate phase is TGB_C in nature, i.e. there is a helical arrangement of tilted molecules within each S_C like block. In addition, these TGB_C -blocks have a two-dimensionally undulating structure such that it forms a square grid. A schematic diagram of such a structure is shown in Figure 4.

The two-dimensional modulation with a square lattice is a consequence of the uniaxial nature of the TGB phase which has a helical twist. The electric field experiments on the material with negative dielectric anisotropy can be understood if there is a helical twist *within each block*, the field-induced unwinding of which produces solitons¹, which appear like thin lines of the

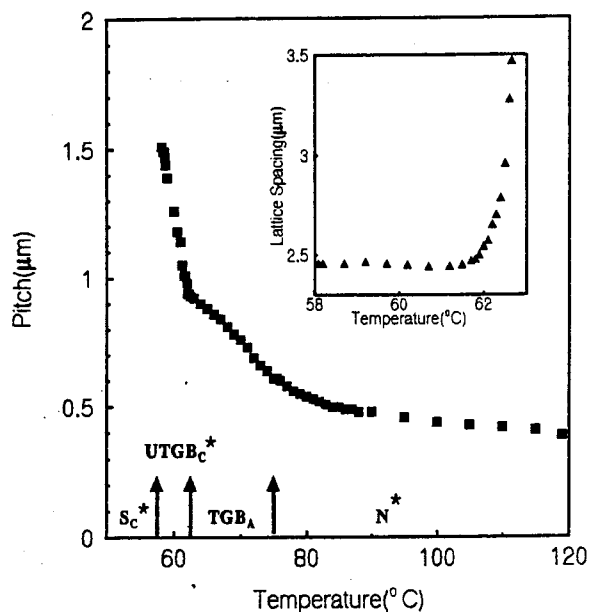


Figure 5. Temperature variation of the pitch in the three helical phases, viz. N^* , TGB_A and $UTGB_C$. The inset shows the temperature variation of the lattice spacing of the square grid.

square grid or a periodic intensity modulation along the length of the straightened filaments. Indeed the observed undulatory nature of the filament in the absence of field is a 'side view' of the 2-D undulating structure of the medium. The proposed structure is rather non-uniform with helical axes characteristic of a TGB smectic as well as in the orthogonal plane, i.e. in the blocks. This is reminiscent of the blue phases exhibited by short pitched cholesterics close to the transition point to the isotropic phase¹. However, the present structure is anisotropic and does not have cubic symmetry. As the smectic layer normals of the blocks rotate across the grain boundaries, the structure is highly non-uniform. The two dimensional undulation was not anticipated in the theoretical models of the TGB_C phase². Since the grain boundaries also undulate along with the entire structure, we call the new phase the undulated TGB_C (UTGB_C) phase.

The temperature variations of the TGB pitch (measured using the spacing between GC lines in a wedge-shaped sample) and the lattice spacing of the square grid (measured using the optical diffraction pattern) are shown in Figure 5. The TGB pitch increases as the temperature is lowered, the rate of variation becoming very large in the UTGB_C phase. Measurements on the TGB_C phase also show a similar trend⁶. On the other hand, the lattice spacing of the square grid decreases quite sharply as the temperature is lowered from TGB_A to UTGB_C transition point, and levels off at lower temperatures. Indeed the pitch in the S_C phase roughly corresponds to the lattice spacing at the lowest temperatures of UTGB_C phase.

The physical origin of the UTGB_C phase with its highly non-uniform structure is obviously of interest. It would appear that the elastic energy cost of the deformations involved would normally make such a structure unlikely. However, we must remember that the TGB_A phase itself has a considerable non-uniformity, with almost perfect S_A blocks separated by highly defected grain boundaries with screw dislocations. These two parts of the structure are so different that an anisotropic interfacial energy may be invoked between the blocks. The tilting of the molecules at the transition point may be expected to produce a helical twist along the smectic layer normal in a block¹. It is easy to see that the angle made by the director with the grain boundary varies along the layer normal if the grain boundary remains flat. This would cost extra energy which can be thought to arise from the fact that the director distortion across the grain boundary is no longer a pure twist. This

energy can be lowered if the grain boundary and with it the blocks undulate along the smectic layer normal (Figure 4). This ensures that the director is parallel to the grain boundary, reducing the grain boundary energy, and of course the helical twist in the block is favoured by the gain in the chiral energy. Note that the dislocations are no longer pure screw dislocations¹⁰. The undulation instability takes place along two mutually orthogonal directions in view of the uniaxial symmetry of the TGB structure. This means that in most of the blocks the smectic layer normal makes non zero angles with the two axes of the square grid. Indeed it is possible to show that for an appropriate set of parameters, i.e. the anisotropic grain boundary energy, the chiral term and the other elastic constants, the undulatory structure is energetically more favourable than the TGB_C structure in which there is neither a helical twist nor undulations in the blocks.

Thus the UTGB_C phase is characterized by helical axes both along and normal to the S_C layers and it naturally occurs between the TGB_A in which the helical axis is parallel to the S_A planes, and S_C in which it is normal to the S_C planes. Very recently we have found that the UTGB_C phase occurs in a couple of other systems. Detailed experimental and theoretical results on this phase, which is perhaps one of the most non-uniform liquid crystalline phases found as yet, will be published elsewhere.

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