A 3-dimensionally modulated structure in a chiral smectic-C liquid crystal

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Abstract:
In this article we report the discovery of a new Twist Grain Boundary phase. This phase is characterised 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.
Introduction:

The formal analogy between superconductors and smectic liquid crystals was invoked by de Gennes\textsuperscript{1} to predict the possibility of an intermediate phase with a lattice of dislocations in smectics. Goodby et al\textsuperscript{2} discovered such a structure in a highly chiral liquid crystal. This "Twist Grain Boundary" (TGB\textsubscript{A}) phase consists of a helical stack of blocks of smectic A (S\textsubscript{A}) liquid crystals, separated by grain boundaries made of an array of screw dislocations (Fig.1a), in accordance with a structure which had been worked out by Renn and Lubensky\textsuperscript{3}. Unlike superconductors, smectic liquid crystals can have other modifications like the smectic C (S\textsubscript{C}) in which the molecules are tilted with respect to the layer normal and the smectic C\textsuperscript{*} (S\textsubscript{C}\textsuperscript{*}) in which the tilt direction has a helical arrangement about the layer normal. Although TGB phases with S\textsubscript{C} like blocks (TGB\textsubscript{C}) (Fig.1b) and S\textsubscript{C}\textsuperscript{*} like blocks (TGB\textsubscript{C}\textsuperscript{*}) have been theoretically predicted\textsuperscript{4,5}, only the TGB\textsubscript{C} phase has been experimentally characterised in some detail\textsuperscript{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\textsubscript{C}\textsuperscript{*} 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-heptylphenyl-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\textsubscript{I} 70 S\textsubscript{C}\textsuperscript{*} 85 S\textsubscript{A} 134.6 N\textsuperscript{*} 140.5 I where N\textsuperscript{*} 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 Xray studies have shown that it has a strong skew cybotactic (S\textsubscript{C} like) short range order\textsuperscript{8}. The phase diagram of the binary mixtures is shown in Fig 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\textsuperscript{*} 76.8 TGB\textsubscript{A}. Observations using a polarising microscope show that as the sample is cooled further to 63°C, there is a distinct transition from TGB\textsubscript{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 polyamide and unidirectionally rubbed so that the nematic director has a planar alignment, the TGB_A phase exhibits a Grandjean plane texture\(^1\) 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 axis of which is parallel to the rubbing direction. In wedge shaped samples the GC lines are seen in both the TGB_A (Fig.3a) and the new phase with the square grid, demonstrating that there is a helical twist normal to the plates in both the cases (Fig.3b). 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 characterised 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 stabilising the modulated
structure. In order to characterise the structure in greater detail, we have conducted
the following experiments:

(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 (Fig 3c).

(b) In cells prepared with homeotropic boundary conditions in which the director
preferentially aligns normal to the glass plates, the TGB\textsubscript{A} phase is charac-
terised by a filamentary texture\textsuperscript{9}, each filament corresponding to a rotation of
the director by $\pi$ radians, and the width of the filament $\approx p/2$ where $p$ is the
pitch of the TGB helix\textsuperscript{9}. When the sample is cooled to 63°C, the filaments
very clearly develop an undulatory structure (Fig 3d) with a periodicity which
roughly corresponds to that of the square grid observed in the planar geo-
metry. As the temperature is lowered to 59°C, i.e, in the S\textsubscript{C}\textsuperscript{*} 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\textsubscript{C}\textsuperscript{*} 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) Xray scattering studies on 25μm thick aligned samples taken between etched
cover slips show that in the TGB\textsubscript{A} phase there is a relatively (compared to
N\textsuperscript{*}) sharp ring corresponding to the $S_A$ layer spacing\textsuperscript{2}. 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\textsubscript{C}\textsuperscript{*} 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.

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The effect of an external AC electric field was studied in different geometries. Under the action of a 10KHz field applied along the TGB helical axis in the planar geometry, the dark regions separating the bright ones (see Fig.3b) become very thin and straight and remain intact even at 30V/µm. In the homeotropic geometry, under an appropriate setting of crossed polarisers, 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 (1Hz) square wave voltage is applied between ITO coated plates in the same geometry, for a field \(~\sim 5V/\mu m\), 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 polariser 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 Fig. 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 solitons\(^1\) which appear like thin lines of the 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, ie., in the blocks. This is reminiscent of the blue phases exhibited by short pitched cholesterics close to the transition point to the isotropic phase. 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\textsubscript{C\textastriped} phase\textsuperscript{5}. Since the grain boundaries also undulate along with the entire structure, we call the new phase the undulated TGB\textsubscript{C\textastriped} (UTGB\textsubscript{C\textastriped}) 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 Fig 5 and Fig 6 respectively. The TGB pitch increases as the temperature is lowered, the rate of variation becoming very large in the UTGB\textsubscript{C\textastriped} phase. Measurements on the TGB\textsubscript{C} phase also show a similar trend\textsuperscript{6}. On the other hand, the lattice spacing of the square grid decreases quite sharply as the temperature is lowered from TGB\textsubscript{A} to UTGB\textsubscript{C\textastriped} transition point, and levels off at lower temperatures. Indeed the pitch in the S\textsubscript{C\textastriped} phase roughly corresponds to the lattice spacing at the lowest temperatures of UTGB\textsubscript{C\textastriped} phase.

The physical origin of the UTGB\textsubscript{C\textastriped} 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\textsubscript{A} phase itself has a considerable non-uniformity, with almost perfect S\textsubscript{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 block\textsuperscript{1}. 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 (Fig.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 dislocations\textsuperscript{10}. 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\textsubscript{C} structure in which there is neither a helical twist nor undulations in the blocks.

Thus the UTGB\textsubscript{C}\textsuperscript{*} phase is characterised by helical axes both along and normal to the S\textsubscript{C}\textsuperscript{*} layers and it naturally occurs between the TGB\textsubscript{A} in which the helical axis is parallel to the S\textsubscript{A} planes, and S\textsubscript{C}\textsuperscript{*} in which it is normal to the S\textsubscript{C}\textsuperscript{*} planes. Very recently we have found that the UTGB\textsubscript{C}\textsuperscript{*} 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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Figure Legends

Fig.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). $\mathbf{N}$ is the layer normal and $\mathbf{n}$ is the director. $\tau$ is the helical axis.

Fig.2 Phase diagram of the binary mixtures of CE8 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.

Fig.3a Photograph of the Grandjean Cano lines seen in the TGB$_A$ phase in a wedge shaped sample with pretreated glass plates as explained in the text.

Fig.3b Photograph of the square grid pattern (grid spacing $\sim 2.5$ $\mu$m) seen in the new phase at 60$^\circ$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.

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

Fig.3d Photograph of the 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 polarisers, periodicity of the undulation $\sim 4$ $\mu$m).

Fig.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 wavevectors. 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’.
Fig. 5 Temperature variation of the pitch in the three helical phases, viz., $N^*$, $TGB_A$ and $UTGB_{C^*}$.

Fig. 6 Temperature variation of the lattice spacing in the square grid phase.
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Fig. 5

Pitch (µm) vs. Temperature (°C)

Key:
- UTGBc*
- Sc*
- TGB_A
- N*
