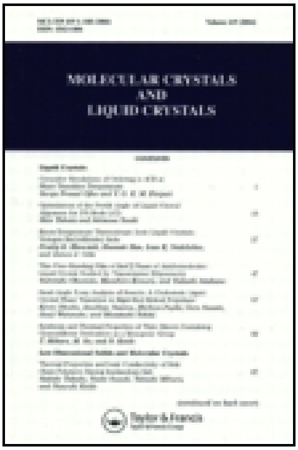

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# Phase Diagram Involving the Twist Grain Boundary Phase in the Vicinity of a Virtual Cholesteric-Smectic A-Smectic C*Point

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# Phase Diagram Involving the Twist Grain Boundary Phase in the Vicinity of a Virtual Cholesteric–Smectic A–Smectic C* Point

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We report the first detailed study of the phase diagram in the vicinity of a virtual Cholesteric–Smectic A–Smectic C* point in a binary liquid crystal system. The occurrence of the *Twist Grain Boundary* phase, which is the liquid crystal analog of the Abrikosov flux lattice in type II superconductors, is established by optical microscopy, X-ray and selective reflection measurements. The study affords a direct comparison between the experimental phase diagram and the theoretical scenario as envisaged by Renn and Lubensky.

*Keywords: Twist grain boundary, selective reflection, phase diagram*

## INTRODUCTION

The nature of the nematic–smectic A–smectic C (NAC) meeting point has been the subject of extensive experimental studies.[1,2] These studies have been made all the more interesting by the recent predictions[3] of the chiral version of the Chen–Lubensky model.[4] Different topologies emerge depending on the strength of chirality and relative magnitudes of different elastic constants. When the chirality is zero one gets the usual NAC multicritical point. Turning the chiral field on leads to a rich variety of phase diagrams with the appearance of a new type of phase,[3] namely, the "twist grain boundary" (TGB) phase which preempts the occurrence of the chiral nematic (cholesteric or Ch)-smectic A (A)-chiral smectic C (C*) meeting point. The TGB phase is the liquid crystal analog of the Abrikosov flux lattice in superconductors. On the experimental side, the zero chirality case—the NAC multicritical point—is, as remarked earlier, well established.[6] For the chiral version two different types of meeting points, viz., a triple point[7] and a multicritical point[8] have been reported. However, the TGB phase, recognised to be identical[9] to the A* phase discovered by Goodby *et al.*,[10] has not been found near the Ch–A–C* meeting point. In this paper we report the first observation of a phase diagram in which the TGB phase appears, as expected by the theory, near a virtual Ch–A–C* meeting point.

## MATERIALS AND METHODS

We present results of experiments carried out on binary mixtures of 4-(2′-methyl butyl)phenyl 4′-*n*-octyl biphenyl-4-carboxylate (CE8-from BDH) and 4-*n*-dodecyloxy biphenyl-4′-(2′-methyl butyl)benzoate (C12).[11] The occurrence of the TGB phase in the vicinity of a virtual Ch–A–C* meeting point is established by optical microscopy, X-ray diffraction and selective reflection measurements.

## RESULTS AND DISCUSSION

The partial temperature–concentration ($T$–$X$) phase diagram, obtained using a Mettler hot stage in conjunction with a polarising microscope, is shown in Figure 1. It is seen that for $X < 0.32$ ($X$ is the weight fraction of C12 in CE8) there is a direct Ch–A transition. For $X > 0.32$, a new phase appears which grows at the expense of the A phase and gets bounded near $X = 0.7$. Optical microscopic studies show that on cooling, the Ch phase transforms into the A phase through an intermediate phase. The microphotograph obtained for $X = 0.6$ at 118°C is shown in Figure 2. The transition to the intermediate phase is signalled by the appearance of the filament texture, characteristic of the TGB phase.[10,13] As the temperature is lowered to the A phase this pattern vanishes resulting in a homeotropic texture. On further cooling the A phase goes to a C* phase. Moreover, the plane texture (molecular director parallel to the substrate) of the mesophase shows that it has a helical structure, and the helix axis lies in a direction parallel to the layers of the phase. Thus, the intermediate phase has a twisted layer structure. Selective reflection measurements confirming the structure will be described later. For $X > 0.62$, there is no A phase and for mixtures with $0.62 < X < 0.7$ the sequence Ch-TGB-C* is seen . It is interesting to note that for any concentration the

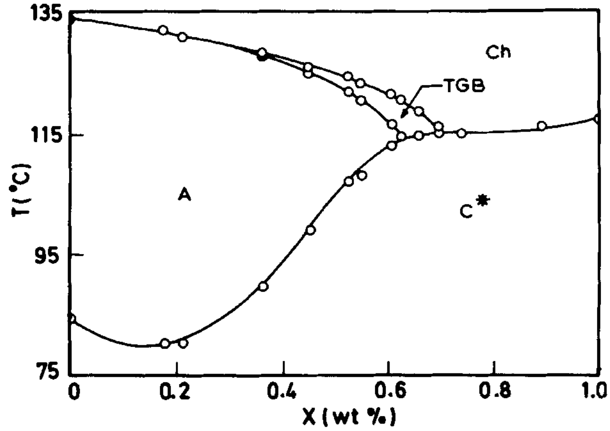

FIGURE 1 Partial temperature–concentration ($T$–$X$) diagram for binary mixtures of 4-(2′-methyl butyl) phenyl 4′-*n*-octyl biphenyl-4-carboxylate or CE8 and 4-*n*-dodecyloxy biphenyl -4′-(2′-methyl butyl)benzoate or C12. $X$ is the concentration (by weight) of C12 in the mixture. The solid lines are meant to serve as guide to the eye. (The symbols used for different phases are explained in the text).

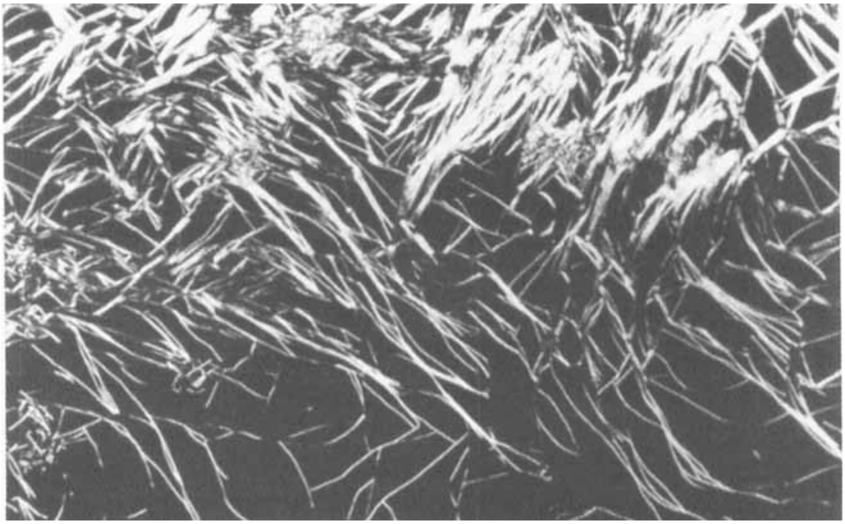

FIGURE 2 The filament texture characteristic of the TGB phase as seen when the sample is cooled from the cholesteric phase. The photograph was taken at 3.6°C below the Ch-TGB transition point in an $X = 0.6$ sample (Magnification: $X$ 125).

TGB phase occurs at temperatures above the A and/or the C* phase, a feature observed earlier[13] and also predicted by the theory.

The differential scanning calorimeter scan for $X = 0.6$ and 0.66 are showm in Figure 3a and 3b. It is observed that the Ch-TGB transition is quite strong but relatively broad.[14] In constrast, the TGB-A transition is extremely weak, nevertheless clear on an enlarged scale (see inset of Figure 3a). The A-C* transition is sharp and appears to be second order while the TGB-C* transition is quite strong. All these

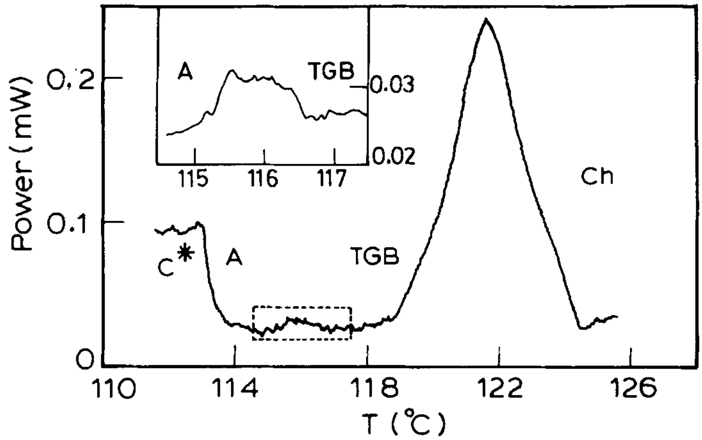

FIGURE 3 Differential scanning calorimeter scans obtained on heating (heating rate is 5°C/min) for (a) $X = 0.6$ and (b) $X = 0.66$ mixtures. In Figure 3a, the region enclosed in dashed lines is shown on an enlarged scale as an inset.

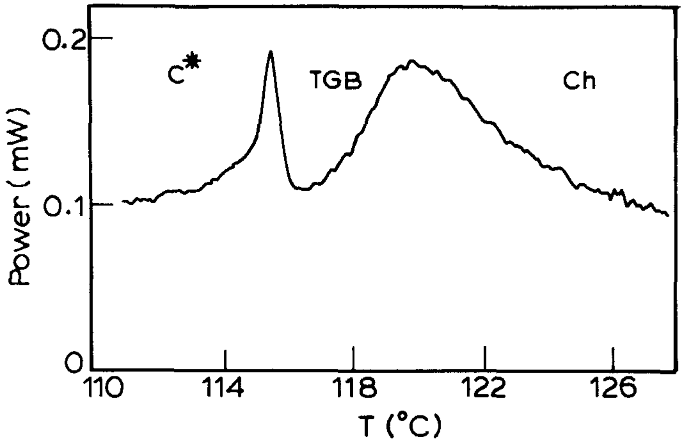

FIGURE 3 (*Continued*)

features are in good agreement with earlier observations.[10,12,13] Layer spacing (d) measurements were carried out using samples filled in Lindemann glass capillaries and employing a computer controlled Guinier X-ray diffractometer (Huber 644). The temperature dependence of *d* for $X = 0.6$ and 0.66 are shown in Figures 4a and 4b. On increasing the temperature *d* increases continuously in the C* phase, saturates in the A phase at a relatively constant value and continues to be so in the TGB phase also. The line profile in the C*, A and TGB phases were found to be comparable but increases in width on going to the Ch phase. In both A and TGB phases the *d*/*l* ratio (*l* being the length of the molecule) was found to be ~ 0.9, a value typical of a monolayer smectic A phase.

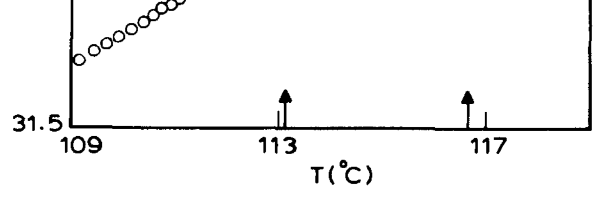

FIGURE 4 Temperature dependence of the smectic layer spacing (a) for $X = 0.6$. The arrows indicate the C*–A and A-TGB transition temperatures. (b) for $X = 0.66$. The arrow indicates the C*-TGB transition temperature.

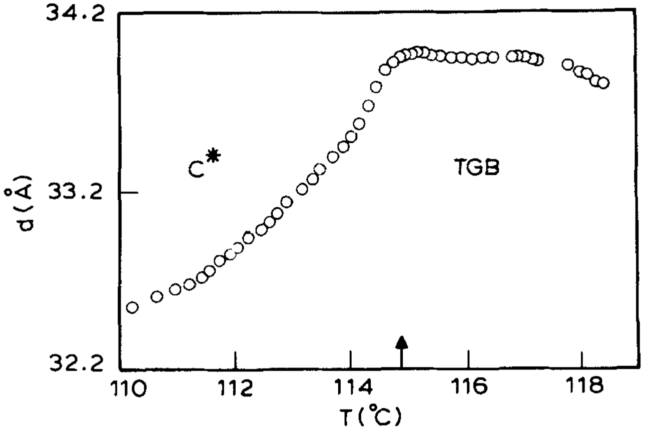

FIGURE 4 (*Continued*).

A necessary feature of the TGB phase is the simultaneous existence of smectic layering as well as a macroscopic helical structure with its axis parallel to the layer planes.[3] In order to demonstrate that the intermediate phase is indeed TGB, we have carried out transmitted light intensity measurements as a function of the incident beam wavelength. Experiments were done using a VIS/IR spectrophotometer (Hitachi U3400, wavelength range 400–2400 nm). Samples (thickness ~ 50 μm) were contained between glass plates coated with a polymer solution and unidirectionally buffed, a procedure which produces an alignment of the molecular director parallel to the plates. This in turn aligns the helical axis of the TGB phase to be perpendicular to the

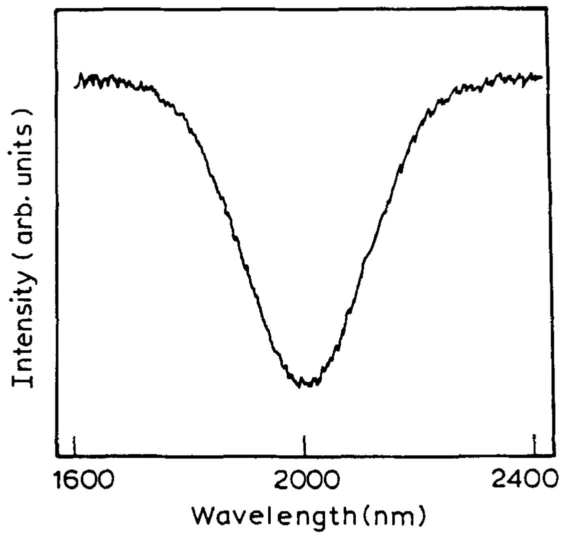

FIGURE 5 Typical optical transmission spectrum in the TGB phase for $X = 0.6$. The wavelength ($\lambda_{min}$) corresponding to the minimum in the plot is related to the pitch of the helical structure.

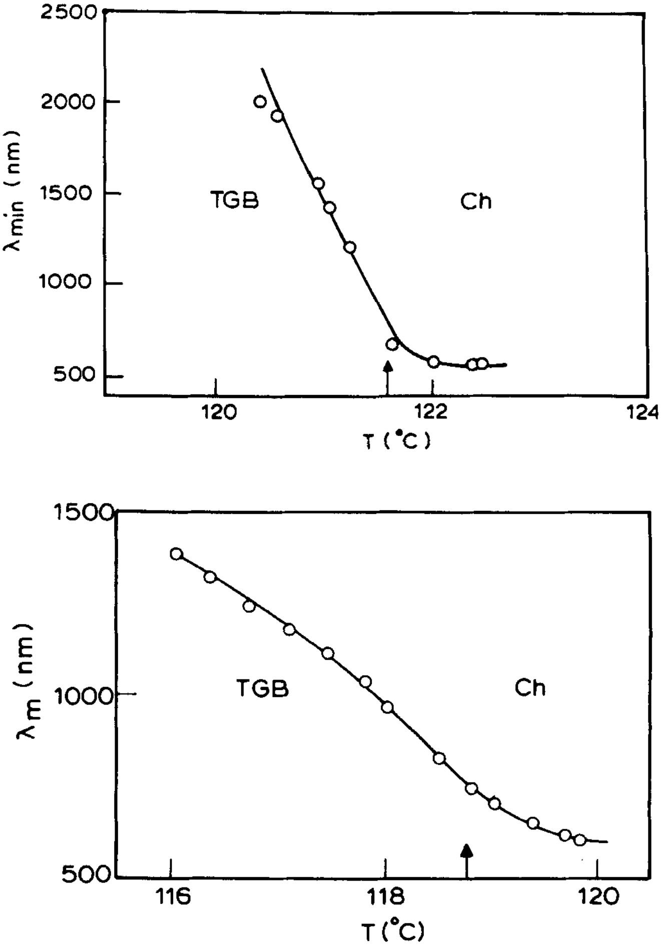

FIGURE 6 Temperature dependence of $\lambda_{\min}$ near the Ch-TGB transition for (a) $X = 0.6$ and (b) $X = 0.66$ mixtures. The arrow indicates the transition temperature.

glass surfaces. We have carried out optical transmission measurements at several temperatures in the Ch and TGB phases. During any run the temperature of the sample was kept constant to within +/− 25 mK. The spectrum obtained for $X = 0.6$ at 1.1°C below the Ch-TGB transition is shown in Figure 5. The minimum observed at 2000 nm represents the wavelength $\lambda_{\min}$ of selective reflection from the TGB phase. The thermal variation of $\lambda_{\min}$ for two concentrations $X = 0.6$ and 0.66 are shown in Figure 6. The trend observed (steady increase of $\lambda_{\min}$ as the temperature is lowered) and the value of the full width at half maximum of the spectra ($0.13\lambda_{\min}$) are in good agreement with the observations of Srajer *et al.*,[9] for TGB phase of + 14P1M7. These results, together with the X-ray and optical data presented above, confirm that this phase is the twist grain boundary phase. It must be mentioned here that unlike in the observed cases[15,16] of tilted TGB phases, the *d* values are not very much smaller than the *l* values measured in the most extended *all-trans* configuration using a Dreiding model ($l_{CE8} = 3.3$ nm and

$l_{C12} = 3.59\,\mathrm{nm}$). Hence, we believe that the TGB phase in our phase diagram is an orthogonal one.

In summary, we have reported the first observation of a phase diagram in which the TGB phase intervenes between the cholesteric and smectic A phases near a virtual chiral NAC point. The existence of this TGB phase in such a phase diagram validates the theoretical expectation of the Renn–Lubensky model.

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