From The Cover: Giant-block twist grain boundary smectic phases


PNAS 2005;102;14191-14196; originally published online Sep 21, 2005;
doi:10.1073/pnas.0500664102

This information is current as of May 2007.
Giant-block twist grain boundary smectic phases

J. Fernsler†, L. Hough†, R.-F. Shao‡, J. E. Macleennan†, L. Navailles†, M. Brunet‡, N. V. Madhusudana‡, O. Mondain-Monval†, C. Boyer, J. Jasadzinski‡, J. A. Rego†, D. M. Walba‡, and N. A. Clark†‡

†Department of Physics and Liquid Crystal Materials Research Center, University of Colorado, Boulder, CO 80309-0390; ‡Department of Chemistry and Biochemistry and Liquid Crystal Materials Research Center, University of Colorado, Boulder, CO 80309-0215; †Department of Chemical Engineering, University of California, Santa Barbara, CA 93106; ˚Centre de Recherche Paul Pascal, Centre National de la Recherche Scientifique, Avenue Albert Schweitzer, 33600 Pessac, France; ‡Raman Research Institute, Bangalore 560080, India; and ˚Groupement de Droit Compare, Unites Mixtes de Recherche 5581, Universite Montpellier II, F-34095 Montpellier Cedex 05, France

Edited by Tom C. Lubensky, University of Pennsylvania, Philadelphia, PA, and approved August 15, 2005 (received for review March 9, 2005)

Study of a diverse set of chiral smectic materials, each of which has twist grain boundary (TGB) phases over a broad temperature range and exhibits grid patterns in the Grandjean textures of the TGB helix, shows that these features arise from a common structure: “giant” smectic blocks of planar layers of thickness \( b > 200 \text{ nm} \) terminated by GBs that are sharp, mediating large angular jumps in layer orientation between blocks (60° < \( \alpha < 90° \)), and lubricating the thermal contraction of the smectic layers within the blocks. This phenomenon is well described by basic theoretical models applicable in the limit that the ratio of molecular tilt penetration length-to-layer coherence length is large, and featuring GBs in which smectic ordering is weak, approaching thin, melted (nematic-like) walls. In this limit the energy cost of change of the block size is small, leading to a wide variation of block dimension, depending on preparation conditions. The models also account for the temperature dependence of the TGB helix pitch.

The nearly simultaneous prediction of the twist grain boundary (TGB) phase, the liquid crystal (LC) analog of the Abrikosov type II superconductor (1), and its discovery in the nP1M7 series of chiral smectics (2) has led to a class of soft-matter phases exhibiting particularly striking manifestations of chirality. Although fluid-layered smectics in general tend to expel twist of the layer normal, the TGB phases adopt a state of layer twist, driven by molecular chirality in a way analogous to the accommodation of magnetic field by the formation of flux vortices in a type II superconductor. In the LC case twist is enabled by formation of GBs, which behave as arrays of screw dislocations, mediating change in layer orientation between blocks of planar smectic layers, and acting as the “flux tubes” in Gennes’ smectic/superconductor analogy (3).

The early TGBs (2, 4, 5) exhibited a set of common characteristics, including narrow TGB phase temperature (\( T_g \)) ranges, \( T_g \approx 1°C \), small angular jumps in layer orientation at the GBs (5), and Grandjean-like textures of the director rotation (TGB) helix (2). However, beginning with the 1993 report of the nitrotolane system having homologs with TGB phase ranges of up to 100°C (6), a distinct class of TGB materials has emerged (6–11) characterized by a ratio \( \alpha = \theta \delta/\ell \) of twist penetration length, \( \alpha \), to smectic layer correlation length \( \ell \) (Fig. 1a) that is very large, approaching \( \alpha \approx 100 \), with \( 1/\alpha < \ell \approx 2\pi/\rho \), where \( \rho \) is the preferred pitch of the twist of the director \( \mathbf{n} \), the mean local molecular long axis orientation, without smectic layering.

Materials and Methods

FFEM was carried out by quenching the LC, sandwiched between \( 2 \times 2 \text{-mm} \) Cu planchette, from various temperatures in the TGB range to 77 K by rapid immersion in liquid propane and fracturing it cold in a vacuum. Transmission electron microscopy of Pt-C fracture face replicas revealed topographies having the global structure of layer surfaces and layer steps familiar from the study of fluid thermotropic and lyotropic smectics (13, 14). FFEM thus provided a direct measure of the layering block structure of TGB phases, enabling direct visualization, with \( \sim 2\text{-nm} \) resolution, of the mediation of layer twist by screw dislocations, the latter identifiable as terminations of layer steps (4). XRD studies of the structure factor \( h u, q v \) of W371 and W376, where \( q \) is the scattering vector (see Fig. 3), were also carried out on 20- to 30-µm-thick Grandjean-oriented samples (TGB helix axis normal to the surfaces) contained between kapton films (W371) or \( \sim 100-\text{-µm-thick glass plates} (W376) \).

W371, W376, and a SO14/CE8 mixture were studied. SO14 is 2-cyano-4-heptyl-phenyl-4’-pentyl-4-biphenyl carboxylate (7), and CE8 is 2’-methyl-butyyl-phenyl-4’-n-octyl pphenylcarboxylate (7). The phase sequence of the 36% SO14/64% CE8 mixture used is isotropic (I) to chiral nematic (CN) at \( T = \sim 122°C \), CN to GTGBT smectic A (GTGBTA) at \( T = \sim 77°C \), and GTGBTA to GTGBT smectic C (GTGBTC) at \( T = \sim 63°C \). W371 is 4-[4-(1-hexyloxy-carbonyl-ethylamino)-3-nitro-phenylethynyl]-benzoic acid 4-(9-cis-12-cis-octadecadienyl)-oxy-phenyl ester (compound 9 in ref. 6). The phase sequence of W371 is I to CN at \( T = \sim 73°C \), CN to GTGBTA at \( T = \sim 60°C \), and GTGBTA to GTGBTC at \( T = \sim 47°C \). W376 is 4-[4-(1-hexyloxy-carbonyl-ethylamino)-3-nitro-phenylethynyl]-benzoic acid 4-dodecloyx-phenyl ester (compound 8 in ref. 6). The phase sequence of W376 is I to CN at \( T = \sim 98°C \), CN to GTGBTC at \( T = \sim 62°C \), and GTGBTC to crystal at \( T = \sim 48°C \). Helix pitches were measured from Grandjean line spacing in wedge cells with the helix axis normal to the plates.

Results

Fig. 2 shows examples of FFEM images of the GTGBT layering in S1014/CE8 and W376. The fracture faces exhibit domains of well-ordered TGB helix (Fig. 2 a, b, and d), areas where the helix is

This paper was submitted directly (Track II) to the PNAS office.

Abbreviations: LC, liquid crystal; SmA, smectic A; SmC, smectic C; GB, grain boundary; TGB, twist GB; MGB, melted GB; GTGB, giant-block TGB; GTGBTA, GTGBT smectic A; GTGBTC, GTGBT smectic C; FFEM, freeze-fracture electron microscopy; XRD, x-ray diffraction; CN, chiral nematic.

†To whom correspondence should be addressed. E-mail: noel.clark@colorado.edu.

∥To whom correspondence should be addressed. E-mail: noel.clark@colorado.edu.

© 2005 by The National Academy of Sciences of the USA

www.pnas.org/cgi/doi/10.1073/pnas.0500664102

PNAS | October 4, 2005 | vol. 102 | no. 40 | 14191–14196
jumps between blocks and repeats in both GBTGB materials studied. With such large angular jumps involving macroscopic distances, the director tilts non-negligibly with respect to the y-z plane (16, 17). The XRD experiments provide additional evidence for these key GBTGB structural features in W371 and W376. The scattering from W371 is especially interesting as it has a CN–GBTGBA–GBTGBC structural sequence, where the A-layer spacing, $d_A$, is nearly T-independent, and the C-layer spacing, $d_C$, exhibits a continuous contraction caused by molecular tilt, $\theta$, of the nematic director in the y-z plane (16, 17). In previous studies of the TGBA–TGBBC-phase sequence, where the A-layer spacing, $d_A$, is nearly T-independent, and the C-layer spacing, $d_C$, exhibits a continuous contraction caused by molecular tilt, $\theta$, of the nematic director in the y-z plane (16, 17). In previous studies of the TGBA–TGBBC-phase sequence, where the A-layer spacing, $d_A$, is nearly T-independent, and the C-layer spacing, $d_C$, exhibits a continuous contraction caused by molecular tilt, $\theta$, of the nematic director in the y-z plane (16, 17). In previous studies of the TGBA–TGBBC-phase sequence, where the A-layer spacing, $d_A$, is nearly T-independent, and the C-layer spacing, $d_C$, exhibits a continuous contraction caused by molecular tilt, $\theta$, of the nematic director in the y-z plane (16, 17). In previous studies of the TGBA–TGBBC-phase sequence, where the A-layer spacing, $d_A$, is nearly T-independent, and the C-layer spacing, $d_C$, exhibits a continuous contraction caused by molecular tilt, $\theta$, of the nematic director in the y-z plane (16, 17).
The W376 sample is a monodomain exhibiting commensurate lock-in at $H_{9254}$ (Fig. 3).

Deformation of the layer contraction, the layer normals remain perpendicular to the TGB helix axis. The W371 sample is fundamentally different behavior, with peak intensity in $T$ at $\Delta = 0$° and has a maximum half-width-at-half-height $\delta_0 = 10$° at $T = 20$°C in the GBTGBC phase.

This difference may indicate that the GBs are melted in W371. Materials such as 11F2BTFO1M7 (16). However, W371 shows fundamentally different behavior, with $I(a, b)$ exhibiting resolution-limited scattering peaks vs $\omega$ on arcs of constant $\omega = 2\pi/d$ as $\Theta$, the angle between $a$ and the $c$ plane, is varied, with maximum peak intensity in $I(a, b)$ at $\Theta = 0$° at all $T$s in the A and C phases. (Fig. 3b). This scattering structure indicates that diffraction broadening $\Delta_\omega = 1/b$ is negligible, a result of the large block size, and that $I(a, b)$ is the result of a mosaic probability distribution of smectic layer normals $P(w_c) \propto I(q, \Theta)$, where $P(w_c)$ is peaked at all $T$ at $\omega_0 = 0$° and has a maximum half-width-at-half-height $\delta_\omega = 10$° at $T = 20$°C in the GBTGBC phase.

The difference may indicate that the GBs are melted in W371. Materials such as 11F2BTFO1M7 have low-angle (C $\approx 0$) GBs across which layers are connected by dilute screw dislocations (20), spaced by $b$. For layers to shrink without tilting about y, the screw dislocation spacing must correspondingly change ($\omega \approx b$), requiring nucleation of new dislocations and dislocation motion. By contrast, in the MGB case, the GB is a melted nematic-like film that isolates layers from those in adjacent blocks with respect to their translational displacement along N, effectively providing a lubricated interface.

The scattering from the W371 Grandjean samples was found to be independent of sample orientation about the TGB helix axis in the GBTGBA (Fig. 3d) and GBTGBC phases, even for $T < 35$°C, where the square grid modulation, indicative of $\Delta = 90$° lock-in in the GBTGBA has appeared. This apparent isotropy was because the W371 modulation pattern was polydomain within the $1 \times 1$ mm illuminated area. However, it was possible to illuminate single modulation domains in W376, and these exhibited a 6-fold intensity modulation pattern indicative of $\Delta = 60$° lock-in. Like W371, the scattering from W376 in the GBTGBC phase is also peaked at $\Theta = 0$°.

Fig. 3c shows a distribution of block sizes in W376 at $T = 60$°C, obtained from sampling $\Delta = 0$° domains in the FFEM images, along with $L_b$ obtained from optical measurement of the TGB helix pitch $p_{opt}$ of a $\Delta = 60$° domain in a wedge-shaped Grandjean cell, and use of $L_b = p_{opt}/\Delta$ (21). Tilt of the fracture plane with respect to the TGB axis tends to make the FFEM $L_b$ values appear to be larger.

Depolarized transmission light microscopy observations in different cell geometries enable optical study of the TGB helix and smectic block structure under a variety of confinement conditions. In cells with the LC in a wedge-shaped gap between glass plates, Grandjean lines can be used to measure the TGB helix pitch, which increases with decreasing $T$ in all of the materials studied (7). However, for thinner cells with the LC between rubbed nylon on indium tin oxide-coated glass plates, the behavior is quite different, as exemplified by the textures obtained with S1014/CE8 in a $T = 4$° thick gap (Fig. 4c and d). In these cells the CN aligns in a Grandjean texture but, upon cooling, the appearance of smectic order at $T \approx 75$°C unwinds its helix nonuniformly, with the spontaneous formation of minority domains with no helix, i.e., with a single block (bookshelf alignment, $N_b = 1$) between the plates, and the majority of the cell with two blocks, $N_b = 2$, as shown in Fig. 4d. A $t = 4$° thick cell with the bulk pitch should have $N_b = 14$ blocks. Layer orientation of the blocks formed near the CN–SmA is developed and the SmC* helix (21) appears within the blocks, the notation denoting the presence of the helix, the chiral precession of $n$ around the tilt cone of angle $\theta$ (Fig. 1a). The SmC* helix not only renders the layer orientation visible (Fig. 4), but also, with electric field application to unwind the helix (22, 23), enables counting of the number of blocks, $N_b$. Thus, in the $N_b = 2$ domains two unwinding transitions are observed, generally with
different threshold fields, indicating that the two blocks have different thickness since the field unwinding threshold depends on block thickness, decreasing with decreasing $b_0$ (24). Block thickness is nonuniform, i.e., the position of the block-block interface between the plates varies across the cell, as is also the case for the two smectic blocks that appear in chiral SmA materials with a large surface electroclinic effect (25). In the two-block domains the layers of the two blocks are generally oriented symmetrically with respect to the rubbing direction (Fig. 3d), but this preference is weak, with local structures in some areas of the cell varying continuously to other regions with different angular jumps in orientation between the blocks ranging over $0 < \Delta < 90^\circ$ (Fig. 4c). Areas with either $\Delta = 60^\circ$ or $\Delta = 90^\circ$ are also observed, in agreement with the FFEM observations. In $N_b = 2$ domains the TGB helix is maintained in a partially unwound condition by the influence of the rubbed polymer layers on the director. The possibility of accommodating such reduced twist along the TGB helix axis in the SmA by introduction of a single high-$\Delta$ GB provides direct evidence that $\lambda$ is large ($\lambda b_0 \approx 1$), as will be discussed below. The $W_{376}$ 2D lattice structures (Fig. 4a) are similar to that found in planar preparations of S1014/CES (ref. 7 and Fig. 4d). $W_{376}$ and W371 also showed Grandjean textures similar to those of S1014/CES in $t < 5$-$\mu$m cells. For example, Fig. 4a shows a $t \approx 2$-$\mu$m-thick $W_{376}$ Grandjean cell (planar alignment on the surfaces) with distinct areas of different block number exhibiting square and nearly hexagonal lattices.

It was also possible to obtain cells of $W_{376}$ between plates coated for homeotropic orientation of the director that gave the TGB helix parallel to the glass. This optical texture, smooth focal conic arrays in the CN phase as expected for a short-pitch CN, enabled the local CN helix axis to be determined unambiguously. These cells develop distinct quasiperiodic bands running normal to the CN helix upon cooling into the TGBA phase, which we interpret as the appearance of blocks to form a TGB helix (Fig. 4b). Upon further cooling in the TGBA phase a second set of stripes, the SmC* helix, appears normal to the first (Fig. 4b). This texture shows regions of distinct correlation in SmC* helix position through a distance of many TGB blocks along the TGB helix axis, suggestive of lock-in to a commensurate structure of the TGB block orientation. The resulting texture (Fig. 4b), however, is quite spatially inhomogeneous, which we ascribe to the spatial variation of $\lambda$ and $b_0$, and perhaps lock-in with different $\Delta$ values in different places.

Discussion

Development of a model for GBTGBA behavior begins by noting that the CN elastic energy is lowered as the nematic-preferred twist elastic constant, and the third term is the transverse part of $F_{GB}$ in which $K/\lambda^{2} = \psi_{0}(\xi_{0}^{2})^{2}$ is the susceptibility for tilt of $\mathbf{n}$ from N. For $\lambda \rightarrow \infty$, $F_{GB} = -K\xi/k_{0}$, the nematic energy of the ideal helix relative to the unwound smectic state. Assuming an isolated chiral SmA block in the absence of external surface torques on $\mathbf{n}$ gives $\theta(x) = (\Delta/2)\sin([\beta/2 - x/\lambda])\sin(\beta/2)$, which was taken to be at the block edge, as sketched in Fig. 1a, and $F_{GB}(\Delta, b_0, \lambda)$ is minimized for $\Delta_{\min}(b_0, \lambda) = 2\tan(\beta/2)$, with $\alpha = k_{0}b_0$. In this model the MGBs transmit no torque on the director, the director field within the blocks depending only on $b_0$ once $k_{0}$ and $\lambda$ are specified.

The structure of the single GB in the $N_b = 2$ domains of Fig. 4c and $d$ can now be obtained by letting $b_0 \rightarrow \infty$ in the above expression and noting that, in the block at the remaining single GB near $x = 0$ (Fig. 1a), the net director twist is $\Delta/2 = \alpha = \lambda k_{0}$, thus, in this case the preferred net twist across the single $N_b = 2$-domain GB, i.e., including the boundaries of its two blocks, will be $2\lambda k_{0}$. Experimentally then, $\pi/3 < 2\lambda k_{0} < \pi/2$, requiring $\lambda k_{0} \approx 0.5$. Since in the TGB structure with nearly the preferred CN pitch (e.g., the TGBA of S1014/CES) we must necessarily have $k_{0} = \lambda b_0$, we immediately find that $\lambda = b_0/2$ for the observed GBTGB values of $\Delta \approx 1$. Thus, in the GBTGBs studied here the twist penetration length is comparable to the giant block size.

The energy density of a bulk TGB phase, a periodic array of such twisted smectic blocks, is the sum of the nematic elastic and GB contributions:

$$F(\lambda, \beta, b_0) / K \xi^2 = \left[ 1/2 \left( \tan(\beta/2) / (\beta/2) \right) \right][\Delta / \Delta_{\min}]^2$$

$$- 2 \Delta / \Delta_{\min}^2 + 2\pi(\xi/\lambda(1/\beta)),$$

where $\epsilon = \epsilon_{0}(\xi_{0}^{2}) / K \xi^2$ is the ratio of smectic-to-nematic energy scales, $F(\lambda, \beta, b_0) / K \xi^2$, plotted in Fig. 1b vs. $\Delta$ and $\alpha b_0 = \psi_{0} k_{0}$, for several values of $\alpha$, $\psi_{0} = 0.5$, $K = 3 \times 10^{-8}$ J/m, and $\epsilon = 0.06$; although too simple to be considered as anything more than an elementary TGB description, nonetheless it illustrates several important features of TGB energetics relevant to the GBTGBs. Specifically, for the range of $\Delta$ of interest ($0.15 < \Delta < 1.5$ rad), $F(\Delta, \beta, b_0)$ exhibits a minimum $F_{\min}(\Delta(\alpha b_0))$ along the line $k_{0}b_0 = \lambda$ (see the blue line in Fig. 1b), corresponding to the preferred CN twist. $F_{\min}(\Delta(\alpha b_0))$ increases at small $\Delta$ because of the increasing number of GBs, and at large $\Delta$ because of increased deviation of $\mathbf{n}$ from the ideal linear helix (see red curves in Fig. 1b). While the minimum in $F(\Delta, \beta, b_0)$ vs. $b_0$ is deep (see the black curve in Fig. 1b along $\Delta = 2$ rad), the minimum in $F_{\min}$ along the line of preferred twist is comparatively quite weak (note the reduced energy scale at left for the red curves in Fig. 1b), especially for $\lambda \approx 1/k_{0}$ and $\lambda \approx \lambda_0$, in which case there is little energetic penalty to pay for increasing $b_0$ along the line of preferred twist to $b_0 \approx \lambda$. For larger $b_0$, untwisted regions appear in the middle of the blocks at $|x| > \lambda$ from the GBs and the energy increases rapidly. This energy analysis and the observation of thick blocks in the $N_b = 2$ domains of S1014/CES suggest that the GBTGB structure has $b_0$ comparable to a few $\lambda$. The assumption that the GBs are melted and thus that GB energy is independent of $\Delta$ is likely to be met only for large angle GBs $\Delta \approx 1$). For small $\Delta$ the screw dislocation interactions must be accounted for (1, 27).
director twisted state (9, 28), as well as by spatial variation azimuthal reorientation, $kC$ director tilt appear upon entering the GBTGBC. For a TGBC block with perturbations of the basic GBTGBA structure of Fig. 1 divided by its value $C$ equals $G$ and Martinot-Lagarde (24) can be applied to the case of smectic blocks (9, 30–32). The structure and energetics of SmC*-helixed TGBs (9, 30–32). The condition for helix unwinding in the block is $\Delta = 0.2(\text{V}/\mu\text{m})$ at the SmA–SmC transition (6), comparable to the largest values of $e$ observed over wide T ranges (36–38), and $e = 0.2(\text{V}/\mu\text{m})$ in S1014/CE8 (39). These observations were made in the SmA state after unwinding the TGBA helix with an electric field (6). The fact that the helix can be unwound by applied field, also observed in W376, is itself a feature of large electroclinic response. A universal aspect of such large-$e$ electroclinic materials is saturation of $\theta(E)$ at large $E$ (38–40), typically at $\theta = 30^\circ$, indicating that $(\partial\theta/\partial a)$ or other higher-order terms that act to limit $\theta$ need to be added to the harmonic Landau–deGennes expression for $\phi(z)$ above. Such terms will similarly act to limit $\Delta$ and would also influence the spatial gradients of $\partial\phi(\zeta)$ and thus the effective correlation length $\xi$. In the harmonic Landau–deGennes approximation, since $\lambda = \xi^{-1}$, large $\lambda$ implies small $x$. For the $\lambda$ values observed ($\lambda C = 1$), we find the ratio of smectic-to-nematic energy scales $x = 1$, therefore $q_{\lambda} = 1$, implying that $\xi < d$, the layer spacing. The addition of higher order $\partial\phi/\partial a$ terms would bring $\xi$ into a more physically reasonable range ($\xi = d$).

The large linear electroclinic susceptibility at low $\theta(E)$ and nonlinear saturation at large $\theta(E)$ suggests an even simpler extreme nonlinear “square well (SW)” model of the GBTGB structure, wherein the energy cost of tilt within a block is assumed to be zero (infinite tilt susceptibility) for $\theta(E)$ in the range $-\theta_{\text{sat}} < \theta(E) < \theta_{\text{sat}}$ and to be infinite for $\theta(E) > \theta_{\text{sat}}$, where $\theta_{\text{sat}}$ is a property of the smectic layering. We assume again that the blocks are bounded by MGBs that transmit no torque on the director, so that the reorientation across each block is always from $-\theta_{\text{sat}}$ to $+\theta_{\text{sat}}$. Within the blocks this model yields simple twist of the director of wavevector $k = (\partial\phi/\partial z)(2\theta_{\text{sat}}/L_0)$, and an angle jump $\Delta = 2\theta_{\text{sat}}$ at the MGBs. Assuming MGBs of energy $E_{\text{MGB}}(\theta_{\text{sat}}/L_0) = \delta Gk_0^2L_0$, where $\delta G$ is the CN–SmA free energy difference and $\xi$ the CN–SmA interface thickness, the free energy $F_{\text{MGB}}(\theta_{\text{sat}}/L_0)$ results

$$F_{\text{SW}}(\theta_{\text{sat}}/L_0) = (K/2)[(2\theta_{\text{sat}}/L_0)^2 - k_0^2] + \delta Gk_0^2L_0$$

$$F_{\text{SW}}(\theta)/Kc_0^2 = (1/2)(1/y - 1)^2 + \eta/y,$$

Fig. 5. Temperature dependence of $k/k_C$, the GBTG helix wavevector $k$ divided by its value $k_C$ at the CN/GBTGB transition in S1014/CE8 and W371. $k/k_C$ is approximately linear vs. $T$ with similar slopes in the two materials, with deviation from linearity associated with the appearance of the intrablock SmC helix in the GBTGB phase. Linear behavior indicates that $\eta = \delta G/k_C$, and thus $\delta G$ varies as $\delta G = F_{\text{SW}}(\theta_{\text{sat}}) - T$. In the GBTGB case, where local energy is minimized with $n$ tilted from N through some equilibrium angle $\theta_C$, i.e., lying on the tilt cone of angle $\theta_C$, the transblock twist is enabled both by azimuthal reorientation, $\phi(x)$, of $n$ into a polarization splayed/director twisted state (9, 28), as well as by spatial variation $n$ away from the equilibrium orientation, as in the GBTGBA when $\lambda$ is large. Detailed calculation of the twisted state with fixed $\theta_C = 0$, corresponding to free surfaces on a block (29) [in this reference ($\gamma_1 = \gamma_2 = 0$) with intrinsic twist $\psi_0 = 0$] shows that the twisted state is always the most stable (ref. 29 and Fig. 5). Thus, for the GBTGBCs studied here ($n/k_C = \lambda \approx 1$ and $n_C = \Delta$) the change in $\phi(x)$ across a block is $\pi$, as described by Brunet et al. (9) [$(\delta\phi(x)/\pi) = \eta/k_0$], and the energetics of the elasticity are not significantly different from that of the SmA, i.e., with $K_C$ and azimuthal orientation $\phi$, the energy density of the SmC* helix for the case of free boundaries is $F_{\text{SW}} = (K/2)(\delta\phi/\delta z)^2 - 2c_0(\delta\phi/\delta z)$, where $k_C = 2\pi/pc$ is the wavevector of the SmC* helix. The condition for helix unwinding in the block is obtained by comparing the resulting energy minimum of the wound helix, $F_{\text{SW}} = -(K/2)k_0^2$ with the cost of satisfying boundary conditions caused by the finite block size, assuming a SmC slab thickness $L_0 = \lambda C$, i.e., $k_0 = \lambda C$. For a SmC slab of thickness $L_0 = \lambda C$, i.e., $k_0 = \lambda C$, we obtain the approximate unwinding thickness $d_C = \sqrt{\lambda C}$. This is the result of comparing the energy gain of winding the helix with the energy cost of the cores (of dimension $\lambda$) and the bulk distortion in $\lambda$ of the resulting required line disclinations, leading to the condition expressed on page 1707 of ref. 24. However, in the GBTGB case $\phi$ at the block boundaries is not fixed, but determined by a finite anchoring energy of strength $U = K/\lambda C$, i.e., with a surface interaction length $L_0$ also given by $\lambda C$. Since the helical winding of the director in a given block provides little energy relief in its neighbors (since their difference in layer normal orientation is $\Delta > 60^\circ$), the deformation caused by this block relaxes away in a distance $\lambda$ away from the block, effectively making each block thickener by $\lambda C$ at each of its two interfaces with a GB. In this picture, each block has its own SmC helix, with “tails” decaying over a distance roughly $\lambda C$ into its neighboring blocks. If $\lambda_C = n_C/2$, then the effective Brunet and Martinot-Lagarde slab thickness is $d_C = 4\lambda_C$ and the SmC* helix will be present as long as $pc < 16\lambda$. For the $L_0$ of the materials studied this will be $pc$ up to $pc = 2\mu$m, comparable to that found in W376 (Fig. 4) and S1014/CE8 (7). The nematic orientation in each GB is modulated to be commensurate with the helices in both adjacent blocks. As discussed by Pramod et al. (35), this is a likely mechanism for the observed transverse periodic undulation in the $x$-position of the GBs (7). In this case, the dark/light stripes shown in figure 4d of ref. 7 are caused by a $\Delta = 90^\circ$ structure of blocks alternating between having N parallel to and normal to the image plane. The coupling of $\phi(x)$ between neighboring blocks also provides a possible mechanism for the preference of $\Delta = 60^\circ$ or $90^\circ$ orientational jumps, either by coupling of fluctuations in GBs or SmC* helix penetration. Given the energetic ambivalence with respect to the choice of $\Delta$ and $L_0$, indicated by Fig. 1b, even weak second-nearest neighbor interactions could stabilize commensurate lock-ins.
where \( y = k Bohr/2q_{\text{sat}} \) and \( \eta = \delta G \xi / (2\theta_{\text{sat}} K_{\theta}) \). This leads to a TGB state with pitch

\[
k(T) / k_0 = 1 - \eta(T)
\]

for \( \eta < 1 \), the unwound SmA state for \( \eta > 1 \), and \( y = 1 \) (\( k_0 = 2\theta_{\text{sat}} / k_0 \)) the block size in the limit of small \( G \). In this model, taking \( 2\theta_{\text{sat}} \approx 1 \), the basic condition for obtaining the GBTGB is \( 8G \xi < K_{\theta} \), the GB energy cost/area needs to be less than the helix twist energy gain/area. Eq. 2 yields qualitatively similar dependence of \( F / \kappa T_0 \) for the large \( \lambda \) model above. Helix pitch data on S1014/CE8 (\( T \)) and W371, plotted in Fig. 5, show that \( \eta(T) \approx T_{\text{N1GBA}} / T \) which is to be expected if the dominant \( T \) dependence of \( \eta \) is that of \( G \approx T_{\text{N1GBA}} / T \), where \( T_{\text{N1GBA}} \) is the CN/TGBA transition temperature. S1014/CE8 and W371 exhibit similar dependence on \( T \), indicating that \( \eta(T) \) grows to \( \approx 0.5 \) at \( T_{\text{N1A}} / T = 20^\circ \) in both materials.

A further consequence of the significant twist within the blocks appearing as a result of the large tilt susceptibility in the GBTGBA is a substantial tilt \( \theta(x) \approx 30^\circ \) of \( N \) away from \( F \) at the edges of the blocks (Fig. 1a), but no tilt (\( \theta = 0 \)) in the middle of the blocks (Fig. 1a). One might then expect to find a variation in the layer thickness \( d(x) = dc\left[\frac{\theta(x)}{\kappa T_0}\right] \) across the block, especially in W371, which exhibits significant layer contraction at the A–C transition. How-\n\nnever, no such variation is seen, as the peaks in the radial wavevector x-ray scans through the TGB ring remain resolution-limited in the W371 and S1014/CE8, even though exhibiting significant shift in position upon passing from the SmA to the SmC phase, e.g., as in the W371 data in Fig. 3a. This may be an indication of “deVries”-type SmA behavior (37, 40), the azimuthal orientational ordering about the layer normal of already tilted molecules (requiring an explanation of the contraction found in the C phases), or it may reflect the energy cost of introducing edge dislocations into the blocks (requiring an explanation for why the tilt susceptibility is still so large at constant layer spacing).

Another interesting characteristic of the GBTGBs is their large TGB temperature ranges (10°C < \( T_a < 100^\circ \)). In the small block systems, the TGB phase gives way to a uniform untwisted smectic on cooling, a consequence of increasing energy cost of the GBs (\( E_{\text{GB}} \approx \sqrt{a} \) in the Landau–deGennes harmonic model), resulting in larger \( l_0 \)s as the smectic order strengthens. As \( l_0 \) increases beyond \( \lambda \), the increasing deviation of the twist from an ideal helix raises the overall energy above that of the untwisted smectic. However, the effect of increasing \( \lambda \) (for example, by decreasing \( \gamma \) at constant \( \delta G \xi / (2\theta_{\text{sat}} K_{\theta}) \)) is always to reduce the distortion in the twist of \( N \), making accommodation of the twist in the smectic easier by moving the nematic energy closer to the \( F_j = -\Delta k_{\phi}^2/2 \) of the ideal helix, behavior evident in the model calculation of Fig. 1b. Additionally the number of GBs required is reduced. These factors combine to make large \( \lambda \) TGB states more energetically favorable for a given \( k_0 \), rendering the TGB stable even with a saturated smectic order parameter.

Conclusion

To conclude, experiments on several examples of the subclass of chiral smectic LC materials exhibiting wide TGB phase ranges and TGBC phases with the SmC helix have enabled us to provide basic information on the origin of this behavior. We show that the key relevant properties of such materials are a large tilt susceptibility \( \lambda/\kappa \) and a large penetration length \( \lambda \) for tilt of the director, the latter being comparable to \( k_0^{-1} \), the inverse wavevector of the CN twist. This, in turn, leads to the bulk condition that the smectic blocks are giant, with thickness \( l_0 \) also comparable to \( \lambda \) and \( k_{\phi} \).

The GBs observed here are sharp and planar, mediating large angle jumps between flat layers, indicating that if the screw disloca-\n\ntions exist they are well ordered into periodic arrays [rather than strongly fluctuating (41)]. The data and analysis, however, do not produce a detailed understanding of the internal structure of the GBs, i.e., whether the average smectic order parameter becomes small enough in the GB centers to consider them melted, and to what extent there is electron density modulaton within the GBs because of screw dislocations. The types of few block cells presented in Fig. 4c may offer an opportunity to address the latter question with microbeam XRD experiments on single GBs. The model, based on MGBs, describes the general GBTGB phenomenology well, but answers to remaining questions, such as the origin of the \( \Delta = 60^\circ \) and 90° lock-in, will require a more complete theoretical description of the large \( \lambda \) limit.

We thank T. Sluckin and T. Lubensky for conversations. This work was supported by National Science Foundation Grants DMR 0072989 and DMR 0213918 (Materials Research Science and Engineering Centers).