FREEZE-FRACTURE TEM OF THE HELICAL SMECTIC A* PHASE

K.J. Ihn, R. Pindak* and J. A. N. Zasadzinski

Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106
* AT&T Bell Laboratories, Murray Hill, NJ, 07974

A new liquid crystal (called the smectic-A* phase) that combines cholesteric twist and smectic layering was a surprise as smectic phases preclude twist distortions. However, the twist grain boundary (TGB) model of Renn and Lubensky predicted a defect-mediated smectic phase that incorporates cholesteric twist by a lattice of screw dislocations. The TGB model for the liquid crystal analog of the Abrikosov phase of superconductors consists of regularly spaced grain boundaries of screw dislocations, parallel to each other within the grain boundary, but rotated by a fixed angle with respect to adjacent grain boundaries. The dislocations divide the layers into blocks which rotate by a discrete amount, Δθ, given by the ratio of the layer spacing, d, to the distance between grain boundaries, l₀; Δθ = d/l₀ (Fig. 1).

The SmA* phase has been observed in 1-methylheptyl 4'-[[4''-tetradecyloxyphenyl]propioloyl]oxy] biphenyl-4-carboxylate (+14P1M7) between 90° C and 94° C. The helical pitch is 0.5 microns and X-ray diffraction has shown that the layer spacing is 4.3 nm, and that the layers are parallel to the pitch axis. Although these observations are consistent with the TGB model, they cannot distinguish between microscopic models for the molecular organization. This requires freeze-fracture TEM. To prepare the SmA* phase for TEM, a 0.5 μl drop was heated to the isotropic phase between two copper planchettes. The sandwich was plunged into liquid propane from 92.5° C and fractured and replicated at -170° C.

Fig. 2 shows a typical fracture of the SmA* phase. The surface has a regular asymmetric undulations similar to cholesteric phases. The helical axis is roughly vertical and the pitch is about 0.5 μm. In addition to the undulations, smectic layers are visible at the arrows. They are parallel to the helical axis as predicted by the TGB model. At each trough of the undulating fracture surface (open arrow), the layers are roughly normal to the fracture direction, and the 4.1 spacing (Fig. 4) is consistent with X-ray diffraction. At the crests, the layers are almost parallel to the fracture surface, and the fracture has the typical pattern of a dense array of screw dislocations. These dislocations are oriented normal to the fracture surface, and hence perpendicular to the helical axis, as shown in higher magnification in Fig. 3. The screw dislocations have a Burgers vector of a single layer, which is consistent with the TGB model.

Fig. 4 shows the optical transform of a selected area of Fig. 2. The pairs of strong reflections correspond to the layer spacing and longer spacings in the image. These reflections indicate that the apparent layer spacing changes discontinuously along the helical axis, which is what we would expect for a fracture plane that cuts the discretely rotating blocks of the TGB model of the SmA* phase at an oblique angle to the helix axis. From measurements of the 5 pairs of spots' position in reciprocal space, and their angles, we can determine both the rotation of the layers and the spacing of the screw dislocations. For the TGB model, these angles should be a multiple of the twist angle, nΔθ = nd/l₀.

We find that the twists between layer blocks are 330° ± 30°, 450° ± 30°, 640°±20°, and 760°± 20°, which gives Δθ = 150° ± 16°. Hence, the spacing between grain boundaries is 15 - 16 nm, consistent with the observed screw dislocation density in Fig. 3. These measurements conclusively show that the TGB model is appropriate for the SmA* phase, and that this phase is the liquid crystal analog of the Abrikosov phase in superconductors.

FIG. 1. Schematic representation of the TGB model of the SmA* phase. Blocks of smectic-A layers of spacing $d$ are separated by regularly spaced twist grain boundaries separated by a distance $l_b$. The angles of the smectic planes separated by a grain boundary differ by $\Delta \theta = d/l_b$.

FIG. 2 Freeze-fracture morphology of SmA* phase. At open arrows, layers are normal to the fracture direction and spaced 4.1 nm apart. Full arrows mark the signature fracture pattern of screw dislocations.

FIG. 3 Twist grain boundary of screw dislocations in the SmA* phase. From measurements of the shadow width, these screw dislocations have a Burgers vector of a single layer step.

FIG. 4. Optical diffraction pattern of a selected area near the center of Fig. 2.