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PUBLICATIONS
S. Jaradat, *et al.*, "Unexpected Field-Induced Phase Transitions Between Ferrielectric and Antiferroelectric Liquid Crystal Structures," *Phys. Rev. E*, **77**: 010701 (2008).

Z.Q. Liu, *et al.*, "The Unique Pitch Evolution in the Smectic-C_α* Phase," *Phys. Rev. Lett.*, **99**: 077802 (2007).

P. Fernandes, *et al.*, "Polarization Studies of Resonant Forbidden Reflections in Liquid Crystals," *Phys. Rev. Lett.*, **99**: 227801 (2007).

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Investigating Orientational Order of Liquid Crystals

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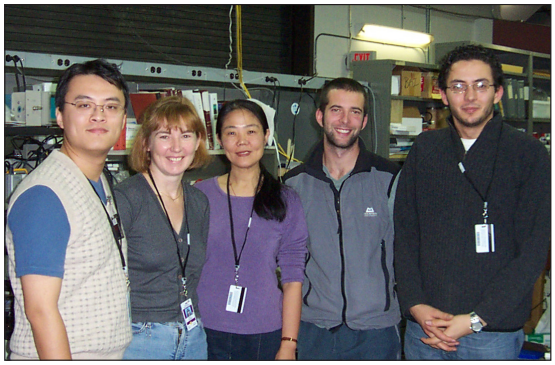
Orientational order enables technological applications for liquid crystals as positional order does for crystals. Three groups, headed by Cheng-Cher Huang from the University of Minnesota, Helen Gleeson from The University of Manchester, and Philippe Barois from Bordeaux University, collaborated with NSLS scientists Ron Pindak and Suntao Wang to use the technique of resonant x-ray scattering for measuring orientational order in layered liquid crystal phases with periodicities from nanometers to micrometers. The layered phases were comprised of molecules tilted with respect to the layer normal, which were either chiral, rod-shaped molecules, or banana-shaped molecules. Because of the chirality or banana-shape of the molecules, the tilted, layered, liquid-crystal phases lack a mirror symmetry, which allows the existence of an in-plane polarization perpendicular to the tilt-plane of the molecules and along the bow in the banana-shaped molecules like an arrow in a bow. Depending on how the direction of the in-plane polarization varies between layers, the phases can be ferro-, ferri-, heli-, or antiferroelectric and an applied electric field can induce changes in orientation or, if sufficiently high, changes in phase. Electric-field-induced reorientation of the large optical anisotropy of the molecules has been utilized in applications from high-resolution camera viewfinders to large-area monitors. These three research groups each made significant discoveries regarding the behavior of these intriguing and technologically important phases.

Authors (from left) Ron Pindak, Suntao Wang, Paulo Fernandes, and Philippe Barois



Authors (from left) Zengqiang Liu, Helen Gleeson, Winnie Wang, Nicholas Roberts, and Shaden Jaradat

The class of tilted, layered phases formed by chiral rod-shaped molecules is referred to as Smectic-C* (SmC*) phases. Because of the molecular chirality, the phases exhibit a slow helical change in tilt or polarization direction that can be unwound by surface treatments of thin sample cells. Neglecting this slow helical change, the basic SmC* phase has a uniform tilt direction (synclinic) and is ferroelectric, but there are a number of variations on this theme resulting in new SmC* type phases. In earlier work, the researchers demonstrated that a key feature exhibited by the new SmC* type phases was a rapid helical change in tilt-direction, and hence in-plane polarization, between layers with

the pitch of the helix varying from two to tens of molecular layers. Specifically, as illustrated in **Figure 1**, they are: a SmC^*_α variation in which the helical pitch is short but incommensurate with the layer spacing; a SmC^*_3 and a SmC^*_4 variation exhibiting a lock-in of the unit cell to three and four molecular layers, respectively, forming a distorted helical structure; and finally, a SmC^*_A variation with alternating tilt and polarization giving an antiferro-electric response.

The goal of the research by the Manchester group was to use chiral additives to extend the temperature range of the intermediate SmC^*_3 and SmC^*_4 phases, making them potentially useful for electro-optic devices, and then study the behavior of aligned samples of these intermediate phases under applied electric fields in device cells. In order to study changes in the orientational periodicities of these phases, the x-ray energy was tuned to the resonant peak of a selenium atom within the rigid core of the molecules. Since the polarization process of the resonant electrons is essentially anisotropic, it follows that the associated structure factor possesses a tensor symmetry, which strongly affects the polarization state of the scattered x-rays. At resonance, the four-layer and three-layer periodicities of the SmC^*_4 and SmC^*_3 phases exhibit Bragg diffraction peaks respectively at a quarter- and third-order values of the scattering wavevector Q when plotted in units of $Q_0=2\pi/L$, where L is the layer spacing. The surprising discovery of the researchers was the existence of a five-state switching sequence for the SmC^*_4 phase under applied fields. As demonstrated by the resonant x-ray scans shown in the insert to **Figure 1**, the antiferroelectric SmC^*_4 phase first undergoes a transition to the ferrielectric SmC^*_3 phase and then to the ferroelectric SmC* phase. This sequence occurs for each sign of applied field giving the five distinct states.

The focus of the work by the Minnesota group involved a study of the nature of the SmC^*_α phase with an incommensurate helical pitch (INHP)>four layers and a second phase with an INHP<four layers, that had been observed respectively in compounds A and B. Their molecular structures are given in **Figure 2**. Recent theories predicted that a continuous phase evolution should exist between these two SmC^*_α phases. The predicted behavior was observed by preparing binary mixtures $A_xB_{(1-x)}$. The symbol x indicates the weight percent of compound A in the binary mixture. The compound A contained a sulfur atom in its core. Sulfur-edge resonant x-ray scattering could be used to measure the INHP. **Figure 2** shows the temperature dependence of the measured INHP for different mixtures. The mixture x=0.25 has the SmC^*_α phase with INHP<four, while mixture x=0.75 has the SmC^*_α phase with INHP>four layers. The mixtures of x=0.45, 0.50 and 0.53 have INHP evolving across INHP=four layers. The results clearly show a continuous evolution of the INHP through the four-layer lock-in region in agreement with theory. However, the data also show a significant change in curvature at INHP=four layers, which is not explained by any theory.

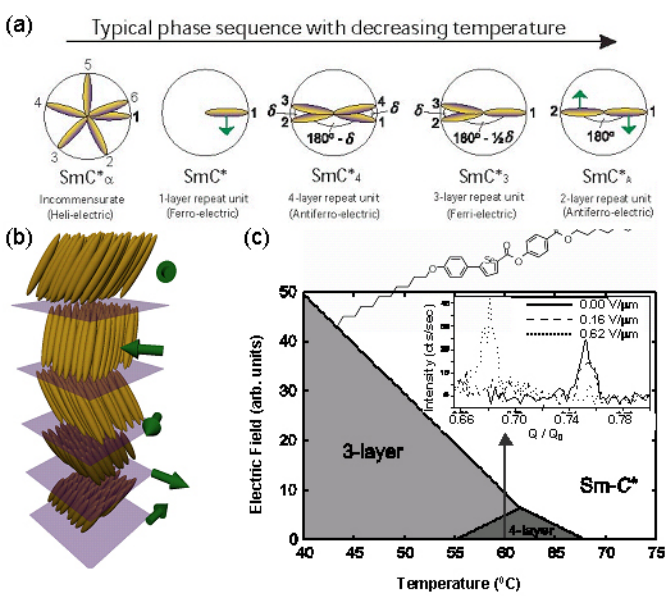


Figure 1. *(a) View of the SmC* phases along their layer normal showing the molecular projections in sequential layers labelled 1,2,3,… The in-plane polarization direction is shown by the green arrows for the SmC* and SmC_A* phases. (b) Side view of the SmC^*_α phase, the green arrows indicate the heli-electric polarization. (c) Schematic showing the dependence of the induced SmC* phases on applied electric field and temperature. Insert shows the change in resonant x-ray scattering features for increasing electric field at a fixed temperature indicated in the phase diagram by an arrow.*

As demonstrated for magnetic systems, the tensor symmetry of the x-ray structure factor implies that the polarization state of the resonant scattered x-rays depends on the rotation angle ϕ of the sample about the scattering vector **Q**. In the helical phases studied in the preceding two projects, however, this ϕ-dependence is averaged out by the helical superstructure and gives no structural information. The challenging project of the Bordeaux group was to determine the structure of the non-helical B2 liquid crystal phase that is comprised of fluid layers of achiral banana-shaped molecules stacked in an antiferro-electric sequence. This constitutes the first example in liquid crystals of a structural determination that requires measuring the ϕ-dependence of the polarization of the resonant Bragg peaks for an unambiguous determination of the orientational structure.

Two possible structures had been proposed (synclinic SmCsPa or anticlinic SmCaPa, see **Figure 3**), undistinguishable from conventional crystallography. **Figure 3** shows the rotation omega (ω) of the polarization of the bilayer resonant Bragg peak vs. sample rotation ϕ. The solid curve is a fit of the experimental points to a tensor model of the structure factor derived for the SmCsPa structure. The dashed line calculated for the SmCaPa structure clearly rules out the anticlinic sequence.

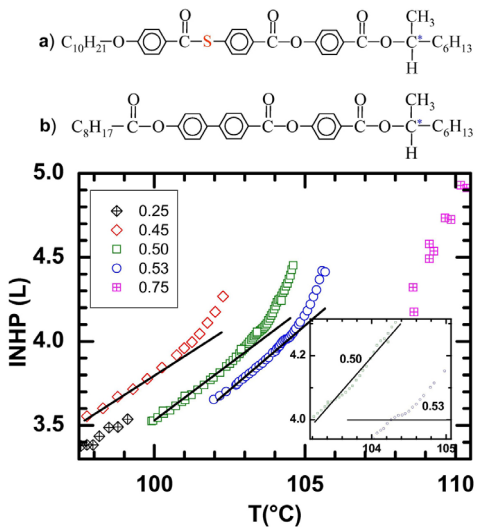


Figure 2. *INHP temperature evolution obtained from mixtures of the two liquid crystal compounds shown at the top of the figure. The inset shows the INHP evolution around 4 layers for the x=0.50 and 0.53 mixtures.*

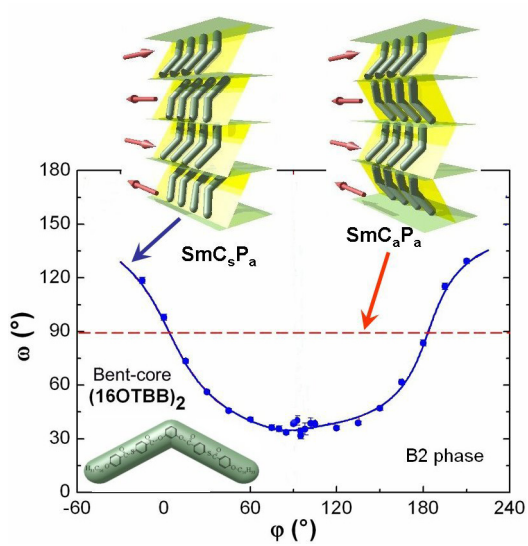


Figure 3. *Rotation ω of the polarization of the resonant Bragg peak vs sample rotation φ about the scattering vector* **Q**. *The upper insert shows the two possible structures for the antiferroelectric B2 phase and the lower insert shows the chemical structure and molecular shape.*