Comment on "Optical and Resonant X-Ray Diffraction Studies Confirm a SmC^*_{FI2} − SmC^* Liquid Crystal Phase Sequence Reversal"

Recently, Wang *et al.* [1] reported phase reversal of the SmC^*_{FI2} − SmC^* phase sequence in 10OHF investigated by null transmission ellipsometry (NTE). SmC^*_{FI2} can occur in between SmC^* and SmC^*_α, rather than below SmC^*. Prior to this Letter, the known phase sequence generally was SmC^*_A − SmC^*_{FI1} − SmC^*_{FI2} − SmC^* − SmC^*_α. [2], while other phases were also reported [3]. The exact structures of these phases were determined by resonant x-ray diffraction (RXRD) technique [4]. The SmC^*_{FI1} and SmC^*_{FI2} subphases show 3- and 4- layer periodic structures, respectively, and SmC^*_α has temperature-dependent periodicity varying from 5 to 8 layers.

The existence and structure of the high-temperature SmC^*_{FI2} phase was observed in a binary mixture of 10OHF with 25% of the sulfur-containing component C9, which enables RXRD measurements [1]. Then, the other binary mixtures (10%–50% of C9), as well as pure 10OHF, were also studied by NTE and the obtained phase sequences were further extrapolated to the pure 10OHF compound. Thus they conclude the existence of the reversed phase sequence: SmC^* − SmC^*_{FI2} − SmC^*_α.

We studied the pure 10OHF sample using several techniques including polarizing microscopy, spontaneous polarization, and birefringence. Here we present only the results on dielectric permittivity, $\varepsilon_\perp'$ at 1 kHz due to page limitations, while the findings are also confirmed by other techniques (to be published later). Our results, in general, support their conclusion on existence of high-temperature SmC^*_{FI2}. Nevertheless our results also reveal some new features, not covered in [1]. Figure 1(a) shows the temperature dependence of $\varepsilon_\perp'$ on both cooling and heating for 26 μm planar cell. The results on cooling support the phase sequence obtained in [1]. The temperature range 62 °C–70 °C, where the SmC^*_{FI2} was observed [1] shows low $\varepsilon_\perp'$, which is expected for antiferroelectric phases. Nevertheless the data obtained by heating from SmC^* show a large $\varepsilon_\perp'$ in the same temperature range. Hence we conclude that SmC^*_{FI2} is a monotropic phase. The results on heating from the crystalline (Cr) state show the phase transition directly to SmC^*_α; therefore SmC^* is also monotropic. Moreover, pure 10OHF samples kept overnight in either SmC^* or SmC^*_{FI2} phases were always crystallized.

Figure 1(b) shows the dependence of $\varepsilon_\perp'$ on bias voltage measured at 1 kHz. Initially the cell is cooled from the SmA phase in the absence of a bias voltage to guarantee SmC^*_{FI2} phase. Then the bias voltage is increased from 0 to 40 V and then decreased back to 0 V. The data show that once the cell is transformed from SmC^*_{FI2} (low $\varepsilon_\perp'$) to unwound SmC^* by applying bias it does not return to its initial state by removing the bias but stays in the SmC^* (high $\varepsilon_\perp'$). Therefore, the SmC^*_{FI2} phase is in a metastable state.

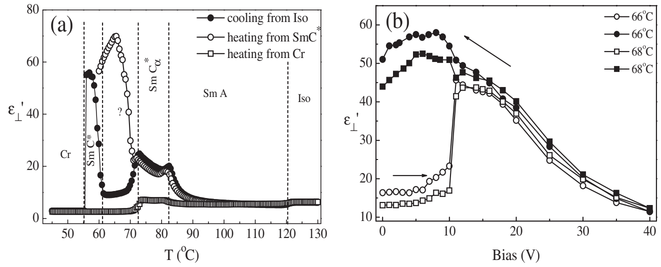

FIG. 1. Dependence of $\varepsilon_\perp'$ on temperature (a) and bias voltage for the phase (?) (b); (open and filled symbols: bias increasing and decreasing, respectively).

Summarizing, we find that (i) both SmC^* and the high-temperature SmC^*_{FI2} are monotropic phases appearing on cooling only, and (ii) SmC^*_{FI2} is also metastable disappearing on the application of electric field and crystallizing with time. Therefore it is not clear whether a thermodynamically stable high-temperature SmC^*_{FI2} phase does really exist at least in the pure compound. We cannot judge the stabilities of these phases in the mixtures (Fig. 3b, [1]) because the authors did not apply such a sufficient electric field. The question arises as to whether they are justified in extrapolating the phase sequence from thermotropic mixtures (25% and higher) to monotropic on cooling (pure 10OHF) via again monotropic on heating (10% mixture) (Fig. 3b in [1]). More experiments and theory are needed to shed further light on this.

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