Discovery of a Novel Smectic-C^* Liquid-Crystal Phase with Six-Layer Periodicity

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We report the discovery of a new smectic-C^* liquid-crystal phase with six-layer periodicity by resonant x-ray diffraction. Upon cooling, the new phase appears between the SmC^*_α phase having a helical structure and the SmC^*_{d4} phase with four-layer periodicity. This SmC^*_{d6} phase was identified in two mixtures which have an unusual reversed SmC^*_{d4}-SmC^* phase sequence. The SmC^*_{d6} phase shows a distorted clock structure. Three theoretical models have predicted the existence of a six-layer phase. However, our experimental findings are not consistent with the theories.

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The smectic-C^* (SmC^*) phases [1,2] are interesting because they show a variety of structures and are utilized in many applications such as electro-optical devices. These phases are usually formed by chiral rodlike molecules arranged in layers. Within each layer, there is no positional order and the molecules tilt from the layer normal in the same direction as shown in Fig. 1(a). Different SmC^* phases are distinguished by the evolution of azimuthal orientations of the molecular tilt along the layer normal. Figure 1(b) summarizes the SmC^* variant phases that have been discovered so far. In the SmC^*_α (SmC^*) phase, the molecular orientation forms an incommensurate helical structure of pitch length on the order of 10 (100) layers. The SmC^*_{d4} and SmC^*_{d3} phases [3] have distorted four- and three-layer structure. The SmC^*_A phase is an antiferroelectric phase with molecules tilting in opposite directions between adjacent layers. All these SmC^* phases have an optical pitch on top of their unit cell. These phases are somewhat similar to antiferromagnetic (helical) phases found in rare earth metals [4]. The structures of SmC^* variant phases have been investigated by many experimental techniques such as ellipsometry and resonant x-ray diffraction (RXRD) [5–9]. The rich variety of these phases provides a perfect system to study the intermolecular interaction in various phases. A number of theoretical models have been proposed to explain the structures of these phases [10–15]. Among them, three [10,13,15] predicted the existence of a SmC^* phase with six-layer periodicity. However, this phase had never been experimentally observed before this work.

In this Letter, we report the discovery of a SmC^*_{d6} phase with six-layer periodicity in two different mixtures. There are three experimental observations supporting our discovery. First, the pitch shows a clear jump at the SmC^*_α-SmC^*_{d6} phase transition and stays locked-in to six layers in the SmC^*_{d6} phase. Discontinuity in the layer spacing was also observed in one of the mixtures at the transition. Second, the split resonant x-ray peaks in the SmC^*_{d6} phase reveal a distorted biaxial structure, which distinguishes it from the uniaxial SmC^*_α phase characterized by a single resonant peak. The third experimental observation is the coexistence of the SmC^*_{d6} and SmC^*_α phases near the SmC^*_α-SmC^*_{d6} transition temperature, indicating a first order phase transition.

The chemical structures and phase sequences of the studied compounds are shown in Fig. 1(c). The two mix-

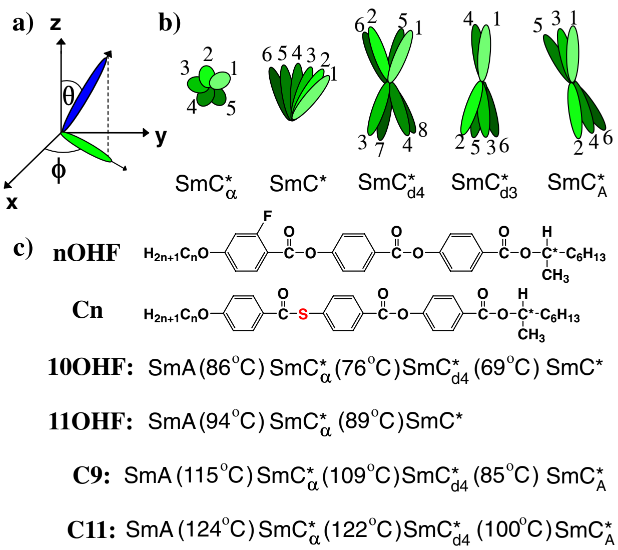

FIG. 1 (color online). (a) Schematic representation of the average molecular tilt in a SmC^* layer. θ and ϕ are the tilt and azimuthal angles. (b) Intermolecular layer arrangements in the SmC^*_α, SmC^*, SmC^*_{d4}, SmC^*_{d3}, and SmC^*_A phases. Ellipses, numbered by layer indices, represent the projections of the molecules onto the layer plane. In the SmC^*_α phase, the tilt angle is usually small compared to the other phases. (c) The chemical structures and phase sequences (upon cooling) of the homologous series nOHF and Cn. The sulfur atoms in the Cn compounds are essential for the RXRD experiments.

tures that show the SmC^*_{d6} phase are ternary mixture $(73\%10\text{OHF-}27\%11\text{OHF})_{0.85}\ C9_{0.15}$ (mixture A) and binary mixture 89%10OHF-11%C11 (mixture B) [16]. Preliminary optical and RXRD results of these two mixtures can be found in Refs. [17,18]. The primary compound in these two mixtures is 10OHF. 10OHF is unique because it is the only pure compound that shows a reversed SmC^*_{d4}-SmC^* phase sequence upon cooling [19,20]. To date, almost all the antiferroelectric liquid-crystal compounds display the following phase sequence: SmA-SmC^*_α-SmC^*-SmC^*_{d4}-SmC^*_{d3}-SmC^*_A, with some of the phases missing for a given compound. However, 10OHF exhibits the SmC^*_{d4} phase at a higher temperature than the SmC^* phase. Both mixture A and mixture B also exhibit this unusual phase sequence.

RXRD is the most powerful tool in characterizing the structures of the SmC^* variants [7]. Unlike conventional x-ray diffraction, RXRD can reveal the orientational order in chiral smectic phases. The studied compounds must contain a heavy element with accessible resonant energy in its core part, e.g., the sulfur atom in the Cn compounds in our case. For a structure with n-layer periodicity, in addition to principal peaks at $Q_z/Q_0 = l\ (l = 1, 2, \ldots)$ there are satellite peaks ($m = \pm1, \pm2$) at $Q_z/Q_0 = l + m\ (1/n \pm \epsilon)$. $Q_0 = 2\pi/d$ and d is the layer spacing. $\epsilon = 2\pi/p$ where p is the optical pitch [21]. Thus, from the data, information about the layer spacing and pitch (related to n) can be obtained. The RXRD experiments were conducted at beam line X-19A of the National Synchrotron Light Source. The mixtures were characterized in freestanding film geometry. The x-ray energy E was tuned to 2.471 keV, near the sulfur's K absorption edge. Figure 2 summarizes the results from pitch and layer spacing measurements in mixture A and mixture B.

In mixture A, the pitch in the SmC^*_α phase decreases almost linearly from 6.49 to 5.39 layers upon cooling [22]. At $T = 81.43\,^\circ$C, there is an abrupt jump to 6.00 layers. A sudden decrease in the layer spacing is also observed at this temperature. Then the pitch stays locked-in to 6.00 layers for a temperature range of approximately 1 K. The lock-in of the pitch to six layers is a clear evidence of the existence of the SmC^*_{d6} phase. The jump implies that the SmC^*_{d6} phase and the SmC^*_α phase are two different phases and the transition between them is first order. From the layer spacing data we can also see that the tilt angle nearly saturates around the SmC^*_{d6} phase. It is interesting how the pitch evolves with temperature. Upon cooling, it decreases smoothly through six layers and then jumps up to six. There are two structures with six-layer periodicity in this mixture: (i) a uniaxial SmC^*_α structure with a pitch value of six existing near $T = 87.72°$ C and (ii) a biaxial SmC^*_{d6} structure over a temperature range of about 1 K. These two structures show very different resonant peaks.

For $78.9°\ \text{C} < T < 80.2°$ C, the pitch is not well defined because there are multiple weak and noisy peaks spread

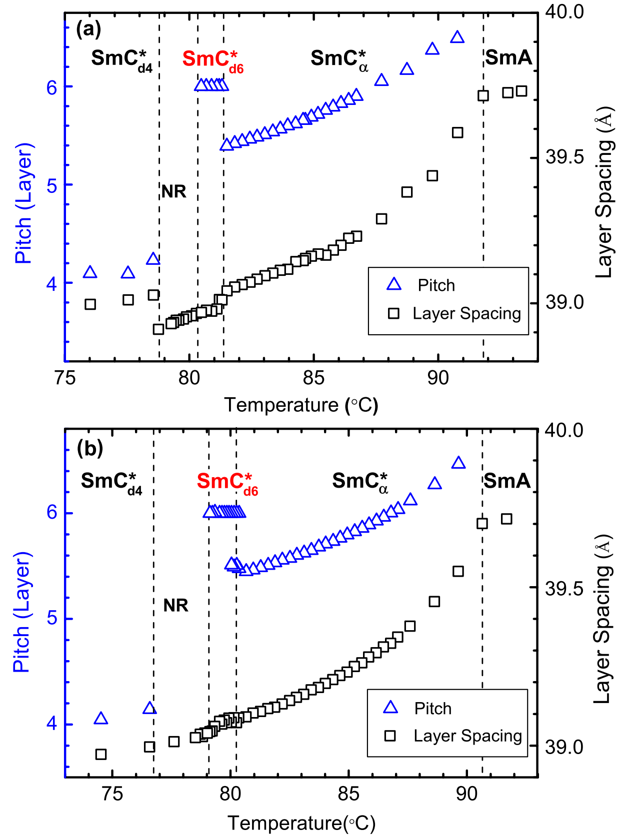

FIG. 2 (color online). Temperature dependences of pitch (triangles) and layer spacing (squares) for (a) mixture A and (b) mixture B. Different phases are divided by dashed lines. Noisy resonant signals are obtained in the regions between the SmC^*_{d6} and SmC^*_{d4} phases. They are called noisy region (NR). No pitch data are given in these regions.

over a wide range in Q space (much broader than the full width at half maximum of the SmC^*_α and SmC^*_{d6} resonant peaks). At the same time, the shapes of the nonresonant principal peaks do not change at all. The resonant peaks become sharp again in the SmC^*_{d4} phase, accompanied by a discontinuity in the layer spacing. This behavior suggests that during the transition from the SmC^*_{d6} to SmC^*_{d4} phase, the layer structure remains well established but the orientations of the molecules are in a complex state. How to extract the information about the orientational order from these noisy peaks in this region remains an important research project for us in the future.

In mixture B, the temperature evolution of the pitch is similar to that of mixture A. The temperature range of the SmC^*_{d6} is slightly larger. A "noisy region" also exists between the SmC^*_{d6} and SmC^*_{d4} phases. There are coexistences of the SmC^*_{d6} and SmC^*_α phases near the transition between them. One major difference from mixture A is that there exists no observable jump in layer spacing.

Figure 3 displays a typical x-ray intensity versus Q_z at $T = 80.89°$ C within the SmC^*_{d6} phase of mixture A. The data clearly show split peaks centered at $Q_z/Q_0 = 1.167$

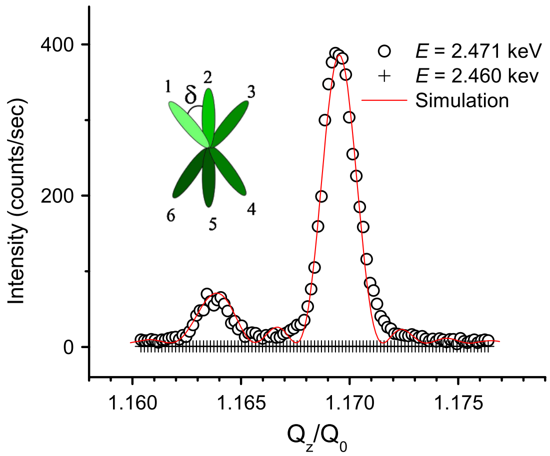

FIG. 3 (color online). The resonant satellite peak (circles) from mixture A at 80.89° C and the simulation (line). Crosses are off-resonance data obtained at $E = 2.460$ keV. The center of the split peaks is located at $Q_z/Q_0 = 1.167$, corresponding to a pitch of six layers. The split peaks indicate a distorted structure. The positions and intensities of the two peaks give an optical pitch of 350 layers (1.36 μm) and a distortion angle δ of $27 \pm 2°$. The simulation has been normalized to match the measured intensities. The illustration is the structure used in our fitting.

($n = 6$, $l = 1$, $m = 1$). It indicates that the SmC^*_{d6} phase is a biaxial six-layer phase. The fact that resonant satellite peaks disappear at $E = 2.460$ keV demonstrates the resonant nature of the split peaks. The illustration in Fig. 3 depicts the structure we propose for the SmC^*_{d6} phase [23]. This structure has been discussed by Osipov and Gorkunov [24] based on symmetry arguments. We carried out numerical simulations based on Levelut and Pansu's work [21]. Our results show that if $\delta = 0°$ (planar structure), the two peaks are of equal intensity. If $\delta = 60°$ (uniaxial structure), there is only one single peak. Two peaks of different intensities suggest that the SmC^*_{d6} phase has a distorted clock structure. The simulation that fits our data yields $\delta = 27° \pm 2°$. Split peaks centered at $Q_z/Q_0 = 0.833$ ($l = 1$, $m = -1$) were also observed. The distortion angle of the SmC^*_{d6} phase does not have a strong temperature dependence. In both mixture A and mixture B, δ changed by less than 4° throughout the entire SmC^*_{d6} phase.

Details of the coexistences of the SmC^*_{d6} and SmC^*_α phases in mixture B are illustrated in Fig. 4. At $T = 80.36°$ C, the main peak of the SmC^*_{d6} appears and coexists with the single peak of the uniaxial SmC^*_α phase of 5.48 layers. The intensity of the SmC^*_{d6} (SmC^*_α) peak increases (decreases) upon cooling. At $T = 80.04°$ C, the split peaks of the SmC^*_{d6} phase are well developed. The data at this temperature again show that the SmC^*_{d6} phase and the SmC^*_α phase coexist. At $T = 79.94°$ C, the SmC^*_α peak disappears and the entire film is in the SmC^*_{d6} phase.

Another question we would like to address is the relationship between the SmC^*_{d6} phase and the reversed

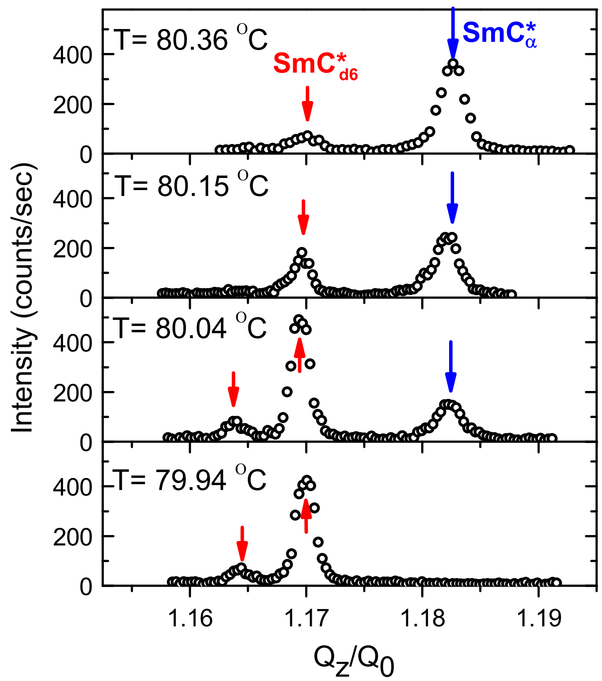

FIG. 4 (color online). X-ray intensity scans from mixture B at four different temperatures during the SmC^*_α-SmC^*_{d6} transition. Short red arrows and long blue arrows point to the peaks of the SmC^*_{d6} phase and the SmC^*_α phase, respectively. The temperature range of the coexistence of the SmC^*_α and the SmC^*_{d6} phases is about 0.4° C for mixture B. In mixture A, we did not identify the coexistence region experimentally.

SmC^*_{d4}-SmC^* phase sequence. We have studied another ternary mixture $(73\%10\text{OHF-}27\%11\text{OHF})_{0.75}$ $C9_{0.25}$ by RXRD. The concentration of compound $C9$ is increased from 15% in mixture A to 25% in this mixture. The phase reversal is still clearly visible but the SmC^*_{d6} disappears. The pitch decreases from 6.03 to 5.03 layers in the SmC^*_α phase and then drops to 4.08 layers in the SmC^*_{d4} phase. Pure 10OHF has the reversed phase sequence. However, by reviewing our high-resolution null transmission ellipsometry data of pure 10OHF [19], there is no indication of the SmC^*_{d6} phase. Both mixtures exhibiting the SmC^*_{d6} phase also display the phase reversal behavior. However, at least one mixture showing the reversed phase sequence does not have the SmC^*_{d6} phase. Is the reversed phase sequence required for the SmC^*_{d6} phase? Is there a certain route we have to follow in the phase diagram in order to see the SmC^*_{d6} phase? More work regarding the SmC^*_{d6} phase is needed to answer these and many related questions.

To date, the liquid-crystal phase having six-layer periodicity has been proposed by three research groups. Yamashita [10] predicted a six-layer phase as a part of the devil's staircase structure which has not been confirmed experimentally. By relaxing the requirement of the uniformity of tilt angles among different layers, the theoretical advance by Dolganov *et al.* [13] yielded a mesophase having six-layer periodicity. So far, the layer spacing variation among different layers has not been observed experimentally. In particular, our acquired layer spacing variations (see Fig. 2) do not support such an assumption. Finally, the results from Hamaneh and Taylor [15] do not offer any structural information of the six-layer phase. In summary, our observed SmC^*_{d6} phase has not been theoretically predicted.

The nature of the long-range interaction in liquid crystals has been a long-standing question in condensed matter physics. Two research groups have tried to address the physical origin of the long-range order and establish the stability of phases having periodicity larger than 4 layers. Hamaneh and Taylor [15] propose that thermal fluctuations in the shape of the smectic layers translate into an effective long-range interaction. However, we cannot map the acquired pitch evolution from either mixture shown in Fig. 2 into their phase diagram without varying two relevant parameters nonmonotonically, which is clearly forbidden in the model. The long-range interaction proposed by Emelyanenko and Osipov [14] is induced by the "discrete" flexoelectric effect. The importance of flexoelectric effect in stabilizing the SmC^* variant phases was first discussed by Cepic and Zeks [11]. Unfortunately, in the Emelyanenko-Osipov model only mesophases with periodicity of 8, 5, 7, and 9 layer are predicted between the SmC^* and SmC^*_A phases upon cooling. The six-layer phase is absent which is contradictory to our experimental findings. Thus the physical origin of the long-range interaction for phases with a long periodicity (e.g., SmC^*_{d6} phase) remains unsolved.

In conclusion, we have discovered a novel biaxial six-layer SmC^*_{d6} phase. Although a phase with 6-layer periodicity was predicted, its measured biaxial structure and phase behavior were unexpected and beyond the current theoretical understanding. The discovery of this phase extends the range of the commensurate long-range order in the SmC^* variant phases from four layers to six layers. Our findings point out the need for a theory that could describe the structures of all SmC^* variant phases including the SmC^*_{d6} phase and generate a phase diagram that explains the associated phase sequence.

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