

## Smectic- $C^*$ liquid crystals with six-layer periodicity appearing between the ferroelectric and antiferroelectric chiral smectic phases

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We found a subphase with a six-layer periodicity which appears between the ferroelectric  $SmC^*$  and the antiferroelectric  $SmC_A^*(q_T = 0)$  phases. The six-layer periodic structure is directly determined by the microbeam resonant x-ray scattering measurement. Furthermore, considering the dielectric constants, this phase was found to be ferroelectric, assigned as  $SmC_A^*(q_T = 2/3)$ . This subphase indicates the importance of the competition between the ferro- and the antiferroelectric phases and, in that point, it is essentially different from the previously observed six-layer phase. The relation between current theories and our present experimental results has been studied and discussed.

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Tilted chiral smectic phases have attracted much attention and accordingly, they have been extensively investigated for many years. In particular, the successive phase transition between synclinc  $SmC^*$  [1] and anticlinic  $SmC_A^*$  [2] is one of the most interesting subjects, in which the appearance of some subphases has been experimentally determined [3] and the existence of further subphases has been theoretically predicted based on the long-range interlayer interaction and the frustration of clinicity (synclinc or anticlinic) [4]. The molecular arrangement of the subphases was defined by the ratio of the synclinc ferroelectric ordering to the anticlinic antiferroelectric ordering in the unit structure, i.e.,  $q_T = \{[F]/([F] + [A])\}$ , where  $[F]$  and  $[A]$  are the number of synclinc ferroelectric and anticlinic antiferroelectric orderings, respectively [3]. It is very interesting that this kind of complex successive phase transition occurs in such a thermally fluctuating soft matter system with no long-range positional order. Several theories have been proposed to clarify the origin of the successive phase transition [5–8], however, between the  $SmC^*$  and the  $SmC_A^*$  phases, which until now are based on the competition between the ferroelectric and antiferroelectric orders. So far, only the subphases possessing a three-layer ( $q_T = 1/3$ ) or four-layer ( $q_T = 1/2$ ) periodic structure have been experimentally verified by the resonant x-ray scattering (RXS) [9–11]. In some previous papers [3, 12, 13], the existence of other subphases was pointed out based on the results of the electro-optic measurements, but they could not yet be directly verified by RXS measurements. Recently Wang *et al.* have reported the smectic phase with a six-layer periodicity [14]. This phase is new but represents a specific case, because it appears between the  $SmC^*$  and  $SmC\alpha^*$  phases, not between ferroelectric  $SmC^*$  and antiferroelectric  $SmC_A^*$ . Hence, the origin for the appearance of two  $SmC^*$  variants is essentially different, as will be discussed later in detail.

In this Rapid Communication, we report on the discovery of a third subphase with six-layer periodicity in between  $SmC^*$  and  $SmC_A^*$ , assigned as  $SmC_A^*(q_T = 2/3)$ , that is directly confirmed by RXS. The relation between hitherto existing theories and our experimental results is discussed in this paper.

We also discuss the essential difference between our observed subphase and the phase found by Wang *et al.*

The sample used is a mixture of (*S,S*)-bis-[4'-(1-methylheptyloxycarbonyl)-4-biphenyl] 2-bromoterephthalate (compound 1), with a bromine atom in the central core part [15], and 10 wt % of (*S,S*)- $\alpha,\omega$ -bis(4-{[4'-(1-methylheptyloxycarbonyl)biphenyl-4-yl] oxycarbonyl}phenoxy)hexane (compound 2) [16,17], whose chemical structures and phase sequences are shown in Fig. 1(a). Dielectric measurements were carried out using an LCR meter (HIOKI, LCR HiTESTER 3532-50) [15]. The mixture was inserted into a 16- $\mu\text{m}$ -thick planar cell, of which temperature was controlled using a temperature control unit (Chino, DB1230). The oscillation amplitude was 0.1 V p.p.

For the present study, we used an x-ray microbeam source for RXS in order to investigate the local structure within uniform domains and at constant temperature as much as possible. X-ray microbeam experiments were performed at the beam line BL-4A of the Photon Factory (Tsukuba) [18]. For these measurements, the mixture was inserted into a 25- $\mu\text{m}$ -thick sandwich cell whose substrates are 80- $\mu\text{m}$ -thick glass plates coated with indium tin oxide that is used as an electrode. By rubbing one of the substrates coated with polyimide (JSR, AL1254), uniformly planar domains were obtained. By applying a square wave electric field (20–100 Hz,  $\pm 3.8$  V/ $\mu\text{m}$ ) at 105 °C and subsequently heating after stopping the field, we could obtain quasibookshelf structures in the  $SmC^*$  variant phases. The optical geometry has been shown in the previous papers except for the detector [18]. The incident beam was monochromatized using a double crystal monochromator, and then it was focused using a Kirkpatrick-Baez system down to a size of 3 (horizontal)  $\times$  4 (vertical)  $\mu\text{m}^2$  at the sample site. Figure 1(b) shows the x-ray fluorescence intensity of the mixture as a function of the incident energy ( $E$ ) around the Br  $K$  absorption edge (13.48 keV) with the incident beam energy being fixed to the first resonant peak (indicated by the arrow). We used a pixel array detector (DECTRIS, Pilatus-100K) as a two-dimensional x-ray detector [15], which is inherently free of dark current and readout noise. The sample-to-camera

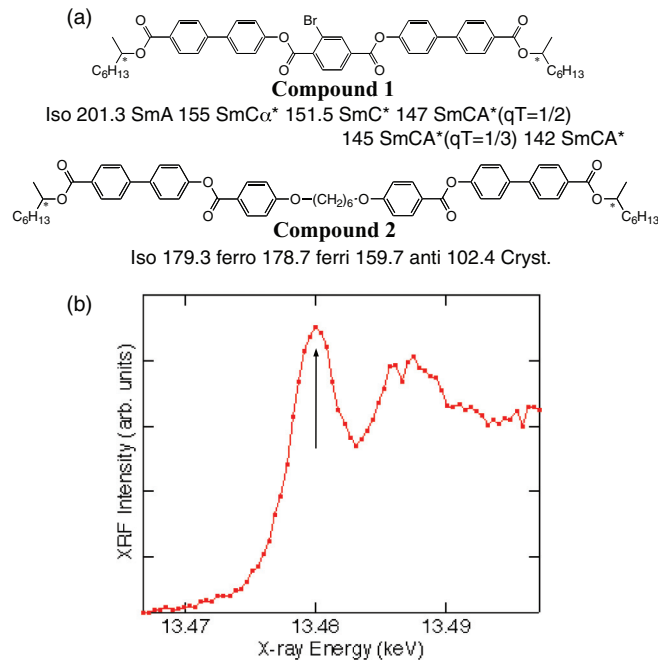


FIG. 1. (Color online) (a) Chemical structure and phase sequence of used compounds, and (b) the x-ray fluorescence intensity of the mixture (compound 1:compound 2 = 9:1) as a function of the incident energy ( $E$ ) around the Br  $K$  absorption edge (13.48 keV). The black arrow indicates the resonant peak energy.

distance was about 70 cm. To suppress the background intensity, the angular divergence of the incident beam was adjusted to the angular spread of the layer diffraction, and the path between the sample and the detector was evacuated to reduce air scattering. To minimize the radiation damage onto the sample, the incident x-ray intensity was limited to a photon flux of the order of  $10^7$  photons/s. The exposure time for a two-dimensional diffraction pattern was typically  $\sim 60$  min, depending on the signal intensity.

Figure 2 shows the temperature dependence of the dielectric constants at 1 kHz during heating, in which the dielectric

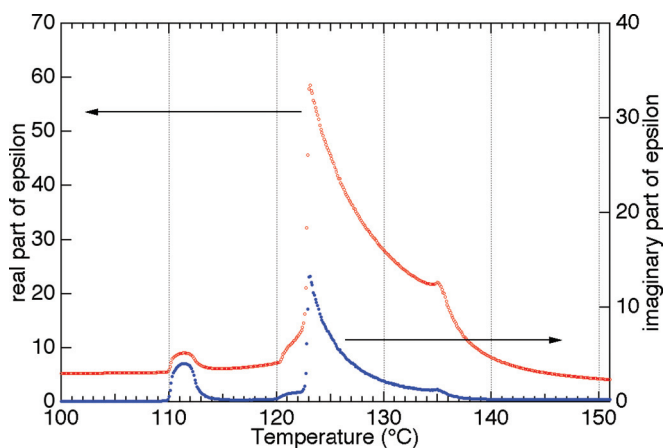


FIG. 2. (Color online) Temperature dependence of dielectric constants of the mixture (compound 1:compound 2 = 9:1) at 1 kHz on the heating process. Red and blue symbols indicate the real and imaginary parts of dielectric constants, respectively.

constants are considered to reflect the net spontaneous polarization of each phase [19]. Just above 123  $^{\circ}\text{C}$ , large dielectric constants with values close to those in the SmC\* phase of a pure compound 1 [15] are observed. Thus in this temperature region, the presence of the ferroelectric SmC\* phase is ascertained. Moreover, the dielectric constants were almost zero below 110  $^{\circ}\text{C}$ , suggesting the antiferroelectric SmC $_A$ \*( $q_T = 0$ ) phase because of the zero net spontaneous polarization. Note that in the intermediate temperature region between the SmC\* and the SmC $_A$ \*( $q_T = 0$ ) phase; three regions (110–113.5  $^{\circ}\text{C}$ , 113.5–120.5  $^{\circ}\text{C}$ , and 120.5–123  $^{\circ}\text{C}$ ) with different dielectric constants are clearly observed. Three such regions were also confirmed by microscope observations using polarized light to visualize the temperature gradient of the homeotropic cells. Hence, it can be safely concluded that at least three subphases exist between SmC\* and SmC $_A$ \*( $q_T = 0$ ).

Figure 3 shows the two-dimensional microbeam RXS profiles at various temperatures. Each individual pattern was obtained by satisfying the Bragg condition of one of the satellite peaks as much as possible. In Fig. 3(a),  $1 \pm 0.5$  satellite peaks are clearly observed at 105  $^{\circ}\text{C}$ , reliably indicating an antiferroelectric phase with a two-layer superstructure. A very

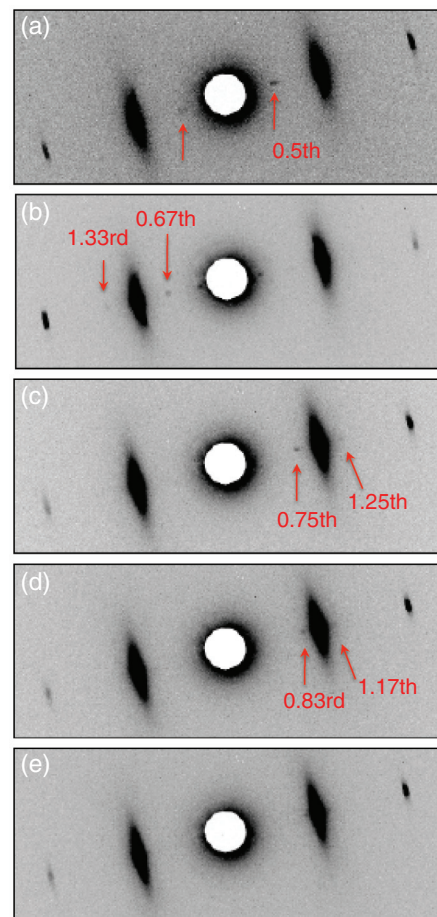


FIG. 3. (Color online) Two-dimensional microbeam resonant x-ray scattering profiles at various temperatures: (a) 105  $^{\circ}\text{C}$ , (b) 111  $^{\circ}\text{C}$ , (c) 118  $^{\circ}\text{C}$ , (d) 121  $^{\circ}\text{C}$ , and (e) 124  $^{\circ}\text{C}$ . Red arrows indicate the satellite peaks.

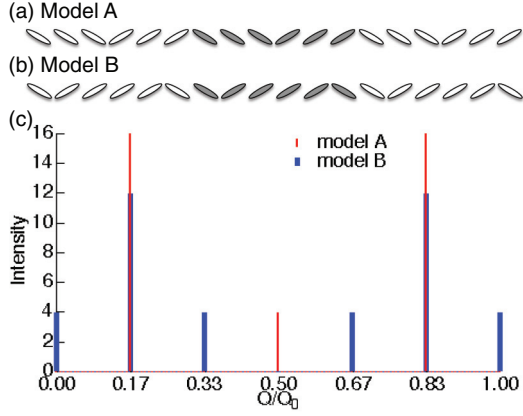


FIG. 4. (Color online) Two models of six-layered periodic structures (a) and (b), and calculated satellite peak intensities of two types of six-layered structures (c). Unit periodicity of each structure is marked in gray.  $Q_0$  is the corresponding wave number of the fundamental layer spacing.

slight splitting of the satellite peaks, which is not clearly visible in Fig. 3(a), was observed in agreement with the existence of a long-wave helical pitch superposed onto the superstructure. Moreover,  $1 \pm 0.33$  and  $1 \pm 0.25$  reflection peaks are observed at  $111^\circ\text{C}$  [Fig. 3(b)] and  $118^\circ\text{C}$  [Fig. 3(c)], respectively, which indicate  $\text{SmC}_A^*(q_T = 1/3)$  and  $1/2$  with corresponding three-layer and four-layer periodic superstructures, respectively. Most notably, as shown in Fig. 3(d),  $1 \pm 0.17$  satellite peaks are observed, which clearly indicate a six-layer periodic superstructure just above of the  $\text{SmC}_A^*(q_T = 1/2)$  phase. These  $1 \pm 0.17$  reflection peaks are observed at  $121, 122,$  and  $123^\circ\text{C}$ . Additionally, at  $124$  and  $125^\circ\text{C}$ , weak satellite peaks appear very close to the first-order diffraction peak, as shown in Fig. 3(e), which corresponds to the  $\text{SmC}^*$  phase. From the satellite peak positions, the helical pitch in  $\text{SmC}^*$  seems to be short. Unfortunately, it was impossible to perform quantitative calculations because the weak satellite peaks strongly overlap with the tail of a much stronger first-order peak, but it does not contradict the dark homeotropically aligned texture. Above  $126^\circ\text{C}$ , the satellite peak position depends on the temperature and indicates a layer periodicity that is shorter than the helical pitch in  $\text{SmC}^*$ , suggesting the emergence of the  $\text{SmC}\alpha^*$  phase.

Let us consider the molecular arrangement of the subphase with six-layer periodicity. Using the ANNNXY (axial next-nearest-neighbor XY) model with biquadratic interaction, a six-layer periodic structure has already been theoretically predicted by Yamashita and Tanaka [20]. Likewise, Dolganov *et al.* also proposed a six-layer periodic structure by applying a discrete phenomenological model [21]. In the paper by Emelyanenko and Osipov [22], a six-layer periodic structure has not been discussed, but recently Osipov and Gorkunov [23] and Emelyanenko and Ishikawa [24] developed their theory further, and concluded that a six-layer subphase ( $q_T = 2/3$ ) should appear. The corresponding molecular arrangements, as resulting from the theoretical models, are shown in Fig. 4. Based on the paper written by Osipov and Gorkunov [23], we calculated the satellite peak intensity of the two types of six-layered structures illustrated in Figs. 4(a) and 4(b). Here, an Ising-like structure has been assumed for simplicity. In

each of two structures, the  $S$  factor, which is proportional to the satellite peak intensity in the experimental geometry of Ref. [21], is described as follows:

model A:

$$S_s^{(\sigma'/\pi)} = S_s^{(\pi'/\sigma)} = 2 \sin^2 2\Theta \sin^2 \beta \sin^2 \phi_0 \times \left[ 3 + 3 \cos \frac{\pi}{3}s - 3 \cos \frac{3\pi}{3}s - 2 \cos \frac{4\pi}{3}s - \cos \frac{5\pi}{3}s \right];$$

model B:

$$S_s^{(\sigma'/\pi)} = S_s^{(\pi'/\sigma)} = 2 \sin^2 2\Theta \sin^2 \beta \sin^2 \phi_0 \times \left[ 3 + \cos \frac{\pi}{3}s - \cos \frac{3\pi}{3}s - 2 \cos \frac{4\pi}{3}s + \cos \frac{5\pi}{3}s \right].$$

Here  $s = 1, 2, \dots, 5$  denotes the satellite number. Figure 4(a) shows an antiferroelectric ordering with zero net polarization, which represents the Ising-type version of the model considered by Osipov and Gorkunov [23], while Fig. 4(b) corresponds to the ferroelectric arrangement, whose structure is recently predicted by Emelyanenko and Ishikawa [24]. Calculated results of the satellite intensities are shown in Fig. 4(c), and it is found that the  $1 \pm 1/6$  peak has maximum values for both of the models. Considering that finite dielectric constants caused by a nonzero net spontaneous polarization are observed for the observed six-layer subphase ( $q_T = 2/3$ ), we conclude that the ferroelectric structure of Fig. 4(b) is considered to be more suitable to explain our experimental results. Recently, Dolganov *et al.* [25] proposed the phenomenological theory according to which an antiferroelectric phase with six-layer periodicity transforms into a ferroelectric structure with five-layer periodicity under a weak electric field. We performed RXS measurements under an applied ac field of 10 kHz. Even when an electric field with amplitude that is twice the amplitude of our dielectric measurements was applied, the observed RXS peaks corresponded to the six-layer periodicity. Therefore, it is conclusive that this subphase has a six-layer periodicity and ferroelectric properties under our present experimental conditions.

So far, the maximum number of layers forming a periodic superstructure of the subphase is four. This subphase is assigned as  $\text{SmC}_A^*(q_T = 1/2)$ . It has sometimes been argued that a subphase with more than a five-layer periodicity can hardly exist, because such a long-range interaction is difficult to develop, except in the case of helical structures. Recently, Wang *et al.* reported on a chiral smectic phase with the six-layer periodicity called  $\text{SmC}_{d6}^*$  [14]. Since this phase appears between  $\text{SmC}\alpha^*$  and  $\text{SmC}^*$ , clearly, the origin of the appearance of  $\text{SmC}_{d6}^*$  is essentially different from the present case of a six-layer subphase ( $q_T = 2/3$ ) between  $\text{SmC}^*$  and  $\text{SmC}_A^*$ . In this sense, our results represent the discovery of a subphase between  $\text{SmC}^*$  and  $\text{SmC}_A^*(q_T = 0)$  except for  $\text{SmC}_A^*$  with three-layer and four-layer periodic structures ( $q_T = 1/3$  and  $1/2$ , respectively). Considering the theory of Emelyanenko and Osipov [22], there is the possibility that other subphases, such as  $\text{SmC}_A^*(q_T = 1/5, 2/5, \text{ or } 3/5)$ , exist. Hence the research for other subphases

between  $\text{SmC}^*$  and  $\text{SmC}_A^*$  will be continued in future studies.

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- [1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Physique Lett.* **36**, 69 (1975).
- [2] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **28**, L1265 (1989).
- [3] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.* **4**, 997 (1994).
- [4] J. Prost and R. Bruinsma, *Ferroelectrics* **148**, 25 (1993).
- [5] M. Yamashita, *Ferroelectrics* **181**, 201 (1996).
- [6] M. Čepič, E. Gorecka, D. Pocięcha, B. Žekš, and H. T. Nguyen, *J. Chem. Phys.* **117**, 1817 (2002).
- [7] M. A. Osipov, A. Fukuda, and H. Hakoi, *Mol. Cryst. Liq. Cryst.* **402**, 9 (2003).
- [8] A. Roy and N. V. Madhusudana, *Eur. Phys. J. E* **1**, 319 (2000).
- [9] R. Mach, R. Pindak, A. M. Levelut, P. Barois, H. T. Nguyen, C. C. Huang, and L. Furenliid, *Phys. Rev. Lett.* **81**, 1015 (1998).
- [10] L. S. Hirst, S. T. Watson, H. F. Gleeson, P. Cluzeau, P. Barois, R. Pindak, J. Pitney, A. Cady, P. M. Johnson, C. C. Huang, A. M. Levelut, G. Srajer, J. Pollmann, A. Seed, M. R. Herbert, J. W. Goodby, and M. Hird, *Phys. Rev. E* **65**, 041705 (2002).
- [11] L. S. Matkin, S. T. Watson, H. F. Gleeson, R. Pindak, J. Pitney, P. M. Johnson, C. C. Huang, P. Barois, A. M. Levelut, G. Srajer, and J. Pollmann, *Phys. Rev. E* **64**, 021705 (2001).
- [12] K. L. Sandhya, J. K. Vij, A. Fukuda, and A. V. Emelyanenko, *Liq. Cryst.* **36**, 1101 (2009).
- [13] A. D. L. Chandani, A. Fukuda, S. Kumar, and J. K. Vij, *Liq. Cryst.* **38**, 663 (2011).
- [14] S. Wang, L. D. Pan, R. Pindak, Z. Q. Liu, H. T. Nguyen, and C. C. Huang, *Phys. Rev. Lett.* **104**, 027801 (2010).
- [15] Y. Takanishi, I. Nishiyama, J. Yamamoto, Y. Ohtsuka, and A. Iida, *J. Mater. Chem.* **21**, 4465 (2011).
- [16] I. Nishiyama, J. Yamamoto, J. W. Goodby, and H. Yokoyama, *J. Mater. Chem.* **11**, 2690 (2001).
- [17] I. Nishiyama, J. Yamamoto, J. W. Goodby, and H. Yokoyama, *Liq. Cryst.* **29**, 1409 (2002).
- [18] Y. Takanishi, Y. Ohtsuka, Y. Takahashi, and A. Iida, *Phys. Rev. E* **81**, 011701 (2010).
- [19] K. Hiraoka, A. Taguchi, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **29**, L103 (1990).
- [20] M. Yamashita and S. Tanaka, *Ferroelectrics* **245**, 217 (2000).
- [21] P. V. Dolganov, V. M. Zhilin, V. K. Dolganov, and E. I. Kats, *Phys. Rev. E* **67**, 041716 (2003).
- [22] A. V. Emelyanenko and M. A. Osipov, *Phys. Rev. E* **68**, 051703 (2003).
- [23] M. A. Osipov and M. V. Gorkunov, *Liq. Cryst.* **33**, 1133 (2006).
- [24] A. V. Emelyanenko and K. Ishikawa, Abstracts of ILCC2012, ref. code 5551\_0237.
- [25] P. V. Dolganov, V. M. Zhilin, V. K. Dolganov, and E. I. Kats, *Phys. Rev. E* **86**, 020701(R) (2012).