

Layer modulated smectic-*C* phase in liquid crystals with a terminal hydroxyl group

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We investigated local layer structures of the three smectic-*C* phases (Sm*C*, Sm*C'*, and Sm*C''*) in a liquid crystal with the terminal hydroxyl group using high resolution and microbeam x-ray diffraction. It is found that Sm*C* is the conventional Sm*C*₁ phase and Sm*C''* is the bilayer Sm*C*₂ phase. The Sm*C'* phase forms an in-plane modulation structure, so that this phase is the smectic-*C* antiphase. From the Fourier transform infrared spectroscopy, it is suggested that the intermolecular hydrogen bonding is important to induce the Sm*C'* and Sm*C''* phases.

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I. INTRODUCTION

Although liquid crystals have weak intermolecular interaction because of strong thermal fluctuation, the dipolar interaction between neighboring molecules frequently induces a specific structure in the liquid crystalline phase. The first smectic-*A* (Sm*A*) to smectic-*A* phase transition was observed by Sigaud *et al.* in 1979 [1]. However, this transition was detected only by differential scanning calorimetry (DSC) measurement, and their results did not contain sufficient experimental knowledge to test a speculation for a polar interaction as they said. The first experimental evidence of the structure difference between two Sm*A* phases was reported by almost the same authors, and lower Sm*A* has a bilayer structure, which speculates the interlayer dipolar interaction [2]. Later, a new type of (third) Sm*A* with in-layer modulation was found [3]. This phase appears in the binary system in which both constituent molecules have a terminal cyano group, and they suggested that the layer modulation was induced by the frustration between the normal monolayer structure and the bilayer structures caused by the dipolar interaction [3]. Since then, many studies for multiple Sm*A* phases have been performed experimentally and theoretically [4–6].

Intermolecular hydrogen bonding can also enhance the dimerization of molecules, and induce smectic phases with bilayer or modulated (antiphase) layer structures [7]. Nishizawa *et al.* reported the synthesis and phase behavior in a homologous series of liquid crystal molecules with a hydroxyl group at the end part, 4-[4-(7-hydroxyalkoxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (*I-n*) [8], and found that this molecule exhibits monolayer to bilayer structure depending on the alkyl chain length [9]. In both cases [7,9], in the molecules with a hydroxyl group at the terminal position of the alkyl chain, the bilayer structure is frequently formed, and its stability decreases with increasing alkyl chain length.

Among the molecules, it is found that 4-[4-(7-hydroxyheptyloxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (*I-7*) exhibits three smectic-*C* phases by polarizing microscope observations [9]. They were named Sm*C*, Sm*C'*, and Sm*C''* sequentially from the higher temperature. In the preliminary x-ray measurement, a monolayer diffraction peak was observed in Sm*C*, and in Sm*C'* and Sm*C''* additional bilayerlike diffraction peaks are

observed [9]. Although each phase is clearly distinguished from each other because of the different textures, it is still not clear, in particular, what is the difference between the Sm*C'* and Sm*C''* phases.

In this study we investigated details of the structures of these Sm*C* phases using high resolution x-ray diffraction in order to reveal the difference between the three Sm*C* phases. Furthermore, we are interested in the origin of the appearance of these phases. Hence, we also measured the infrared absorption maximum of the intermolecular hydrogen bond using Fourier transform infrared spectroscopy, and discussed the relation between the phase structure and the strength of the hydrogen bond between molecules in adjacent layers.

II. EXPERIMENT

Conventional x-ray experiments were carried out using a small angle x-ray diffraction system (MicroMax–007HF; Rigaku Corp., $\lambda = 1.54 \text{ \AA}$) equipped with a handmade hot stage on the ω rotating stage, whose rotation axis is normal to the incident x ray and parallel to the substrates. The temperature of the sample was controlled by a temperature controller (DB1230; CHINO), within an accuracy of $\pm 0.1^\circ\text{C}$. The sample was inserted into a 12- μm -thick homogeneously aligned cell composed of 80- μm -thick ITO glass substrates coated with rubbed polyimide (AL1254; JSR). X rays were generated at 40 kV and 20 mA and its resolution was $4.14 \times 10^{-3} \text{ \AA}^{-1}$ in the vertical direction. Each diffraction pattern was obtained using the two-dimensional detector which combines an image intensifier (Hamamatsu) and a cooled CCD camera (C9299-01; Hamamatsu).

In particular, for the investigation of the Sm*C'* phase's detailed structure, we conducted the microbeam small and wide angle x-ray scattering at Photon Factory BL-4A (KEK). Incident x-ray energy was 14 keV ($\lambda = 0.886 \text{ \AA}$). Each diffraction pattern was obtained using the two-dimensional detector. The incident beam was monochromated and focused using a double Si/W multilayer monochromator and a Kirkpatrick-Baez focusing system, respectively, with an angular divergence of 0.5 mrad and a spatial resolution of $3 \times 4 \mu\text{m}^2$. The detail of the optical geometry is shown in our previous papers [10]. In the present measurements, a CCD detector with an image intensifier (Hamamatsu) was used at a diffraction angle corresponding to the layer spacing $2\theta_B$. Since the layer

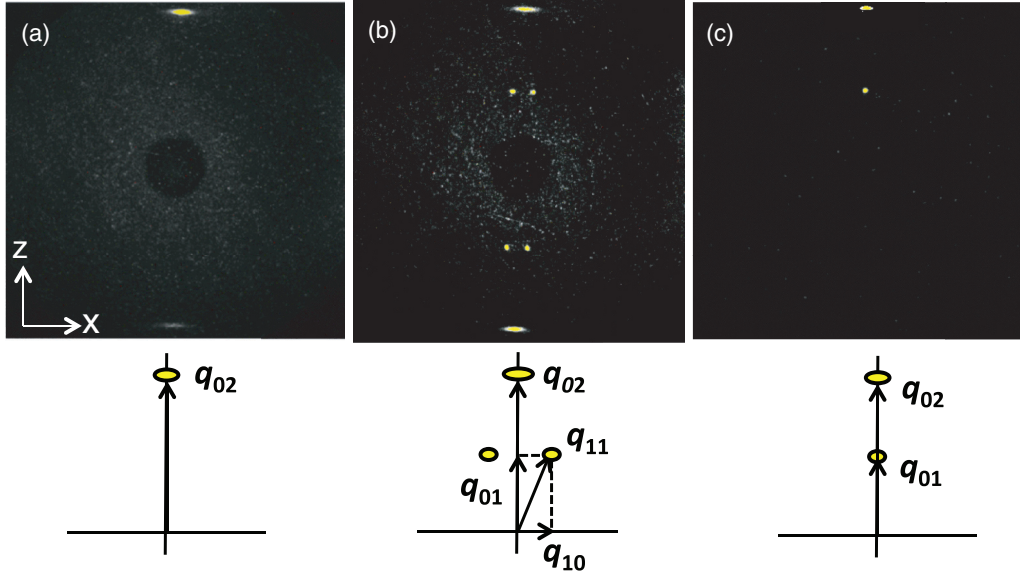


FIG. 1. (Color online) Two-dimensional small angle x-ray diffraction pattern of three SmC phases: (a) SmC (monolayer SmC₁) at 106 °C, (b) SmC' (modulated SmC) at 103 °C, and (c) SmC'' (bilayer SmC₂) at 96 °C. Rubbing direction is parallel to z, and the sample rotates around the axis to obtain the Bragg condition. Bottom figures are schematic images of the diffraction pattern.

diffraction intensity is about 1000 times stronger than the intensity of wide angle diffuse scattering reflecting liquidlike in-plane order, the 2.6-mm-thick aluminum plate was set in the small angle region to reduce the diffraction intensity [11]. For the small angle microbeam x-ray measurement, BL03XU of SPring-8 (JASRI, Hyogo) was also used. The incident beam was monochromated to 12.4 keV ($\lambda = 1 \text{ \AA}$) using a double crystal monochromator. Using a pinhole geometry system, the beam size was vertically $6 \mu\text{m}$ and horizontally $8 \mu\text{m}$, and the angular divergence was vertically $6 \mu\text{rad}$ and horizontally $12 \mu\text{rad}$. We used an imaging plate (RIGAKU, R-AXIS VII) as a two-dimensional x-ray detector, and the camera lengths are set to 2.2 m. Exposure time was 60–180 s, depending on the scattering intensity from samples. Textures at the irradiated position were simultaneously observed using the handmade polarized microscope. The temperature of the samples was controlled by a temperature control unit (Chino, DB1230).

Using a Fourier transform infrared spectrometer (FT/IR-6100; JASCO Corp.) we measured the absorption spectra corresponding to O-H group vibration influenced by the intermolecular hydrogen bonding around 3400 cm^{-1} [12]. Wave number resolution was 1 cm^{-1} , and the integration time was 30 s. To exclude water vapor in the sample room as much as possible, the sample room was purged in dry air. Homogeneously aligned samples were prepared using $80\text{-}\mu\text{m}$ -thick glass substrates coated with rubbed polyimide. Cell thickness was $25 \mu\text{m}$. For the comparison, a homologous series of I-7, 4-[4-(7-hydroxyhexyloxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (I-6: Iso 151.8 °C N 124.4 °C SmA₂ 122.2 °C SmC₂ 98.0 °C Cryst) and 4-[4-(7-hydroxyhexyloxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (I-8: Iso 144.4 °C N 128.3 °C SmA 116.0 °C SmC 98.0 °C Cr) were also measured. The absorption peak was fitted by the Lorentzian function.

III. RESULTS AND DISCUSSION

Figure 1 shows the two-dimensional x-ray diffraction pattern of three SmC phases. In the SmC phase [Fig. 1(a)], one sharp peak was observed at $q_{02} = 2\pi/d_{02}$ ($d_{02} = 28 \text{ \AA}$), which is close to the molecular length in case of all trans conformation (31 \AA). Hence, it is found that the highest temperature SmC forms the monolayer structure (SmC₁). On the other hand, in the lowest temperature SmC phase (SmC'' phase), two sharp peaks were observed at $q_{02} = 2\pi/d_{02}$ ($d_{02} = 26.2 \text{ \AA}$) and $q_{01} = 2\pi/d_{01}$ ($d_{01} = 53 \text{ \AA}$), indicating that SmC'' forms the bilayer structure, assigned as SmC₂ [Fig. 1(c)].

In the SmC' phase [Fig. 1(b)], two diffraction spots at a smaller angle appear symmetrically with respect to the diffraction spot corresponding to the monolayer structure. Such a pattern is observed in the modulated smectic phase such as the smectic antiphase named Sm \bar{A} [3,4]. Each peak was observed at $q_{02} = (0, 0.23)$ corresponding to monolayer periodicity $d_{02} = 27.3 \text{ \AA}$ and $q_{\pm 11} = (\pm 0.020, 0.115)$ corresponding to bilayer length $d_{01} = 53.8 \text{ \AA}$ and in-plane modulated length $d_{10} = 310 \text{ \AA}$ at 105 °C, just below the phase transition from SmC (SmC₁) to SmC'. The fact that q_{11} and q_{-11} is symmetric along the layer normal, and that the relation $|q_{02}| \approx 2|q_{01}|$, clearly indicates that the modulation is parallel to the layer [7], but not tilted as the Col_{ob} model shown in Ref. [14]. Figure 2 shows temperature dependence of the monolayer and bilayer spacings of SmA, SmC, SmC', and SmC'' phases. In three SmC phases (SmC, SmC', and SmC''), the layer periodicity decreases continuously due to the molecular tilting with decreasing temperature. Furthermore, we have observed surface stabilized bistable texture in the thin cell, as reported in the previous study [9]. Hence we can conclude that the three SmC phases are tilted synclonic phases. Tilt angle $\theta_{\text{x ray}}$ was 15.5° at 110 °C (SmC), 22.5° at 100 °C (SmC'), and 24.3° at 96 °C (SmC''). This is calculated from the following equation:

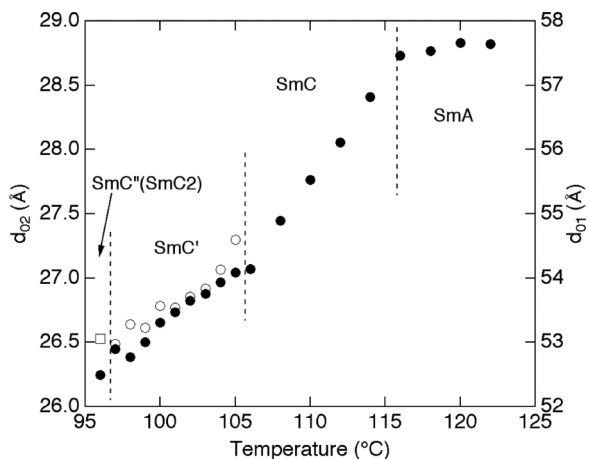


FIG. 2. Temperature dependence of the monolayer (d_{02} , closed symbol) and bilayer spacing (d_{01} , open symbol) in the SmA, SmC, SmC', and SmC'' phases.

$\theta = \cos^{-1}[d_C(T)/d_A]$ [13], where d_A is the layer spacing in SmA ($=28.8 \text{ \AA}$), and $d_C(T)$ is the layer spacing in SmC at $T \text{ }^\circ\text{C}$.

For the structure of SmC', three models are considered, as shown in Fig. 3. Figure 3(a) shows the chemical structure of I-7. Note that the arrow indicates molecules in order to distinguish heads from tails of molecules, but does not mean the dipole moment. In Figs. 3(b) and 3(c) the layer modulation occurs only normal and parallel to the tilting plane, respectively. On the other hand, in the last model shown in Fig. 3(d), the layer modulation occurs two dimensionally. In order to clarify which is the most suitable structure,

we measured two-dimensional small and wide angle x-ray diffraction simultaneously.

Figure 4(a) presents a two-dimensional small and wide angle microbeam x-ray diffraction pattern obtained from the planar cell without an applied field in the SmC' phase. In the small angle region we obtained the same diffraction pattern as Fig. 1(b), and this result suggests that the layer modulation appears parallel to the glass substrates, as shown in the right bottom side of Fig. 4(a). In the wide angle region we obtained oriented broad scattering peaks corresponding to the average intralayer molecular distance. Two wide angle diffuse peaks are almost symmetric with respect to the small angle monolayer diffraction peak spots [the tilt angle with respect to the layer normal (the direction of q_{02}) was less than 1.5°]. This is consistent with the texture observation, and the extinction direction in this sample is almost normal to the layer. Furthermore, Fig. 4(b) shows the two-dimensional small and wide angle microbeam x-ray diffraction pattern obtained from the planar cell in the SmC' phase when a square wave electric field (10 kHz, $\pm 20 \text{ V}$) is applied. As shown in the microphotograph at the irradiated position, the so called bistable state, in which the molecular tilting plane is parallel to the substrate, is observed due to the dielectric response to the applied field as shown in the right bottom side of Fig. 4(b). This state was held after turning off the electric field. In this state, two wide angle diffuse peaks are almost tilted with respect to the small angle monolayer diffraction peak spots. The tilt angle determined by x ray is about 15° , which is almost consistent with the apparent optical tilt angle. On the other hand, layer modulated peaks ($q_{\pm 11}$) are not observed, because the Bragg condition is not matched. By rotating the sample a few degrees around the axis normal to the layer normal and

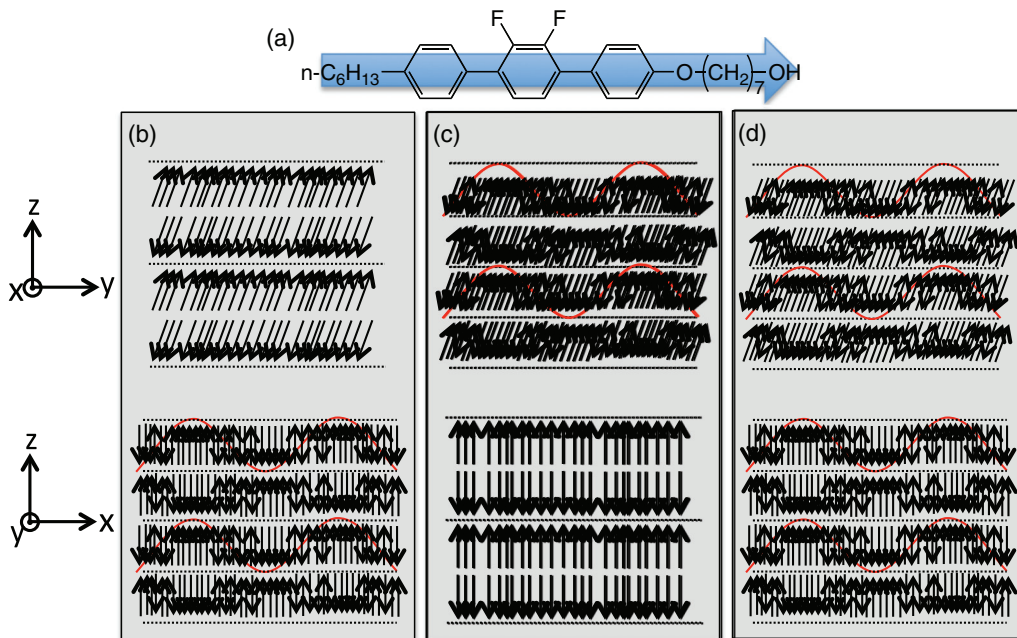


FIG. 3. (Color online) Chemical structure of I-7 (a) and three structural models in the modulated SmC phase (b)–(d). Arrows indicate molecules in order to distinguish the head and tail of molecules. Its head shows the terminal hydroxy group side, and note that it does not mean the direction of the dipole moment. The red line is the layer modulation (distribution of head or tail part of the molecules). (b) Layer modulation occurs normal to the molecular tilt plane (x - z plane). (c) Layer modulation occurs parallel to the molecular tilt plane (y - z plane). (d) Layer modulation occurs both parallel and normal to the molecular tilt plane.

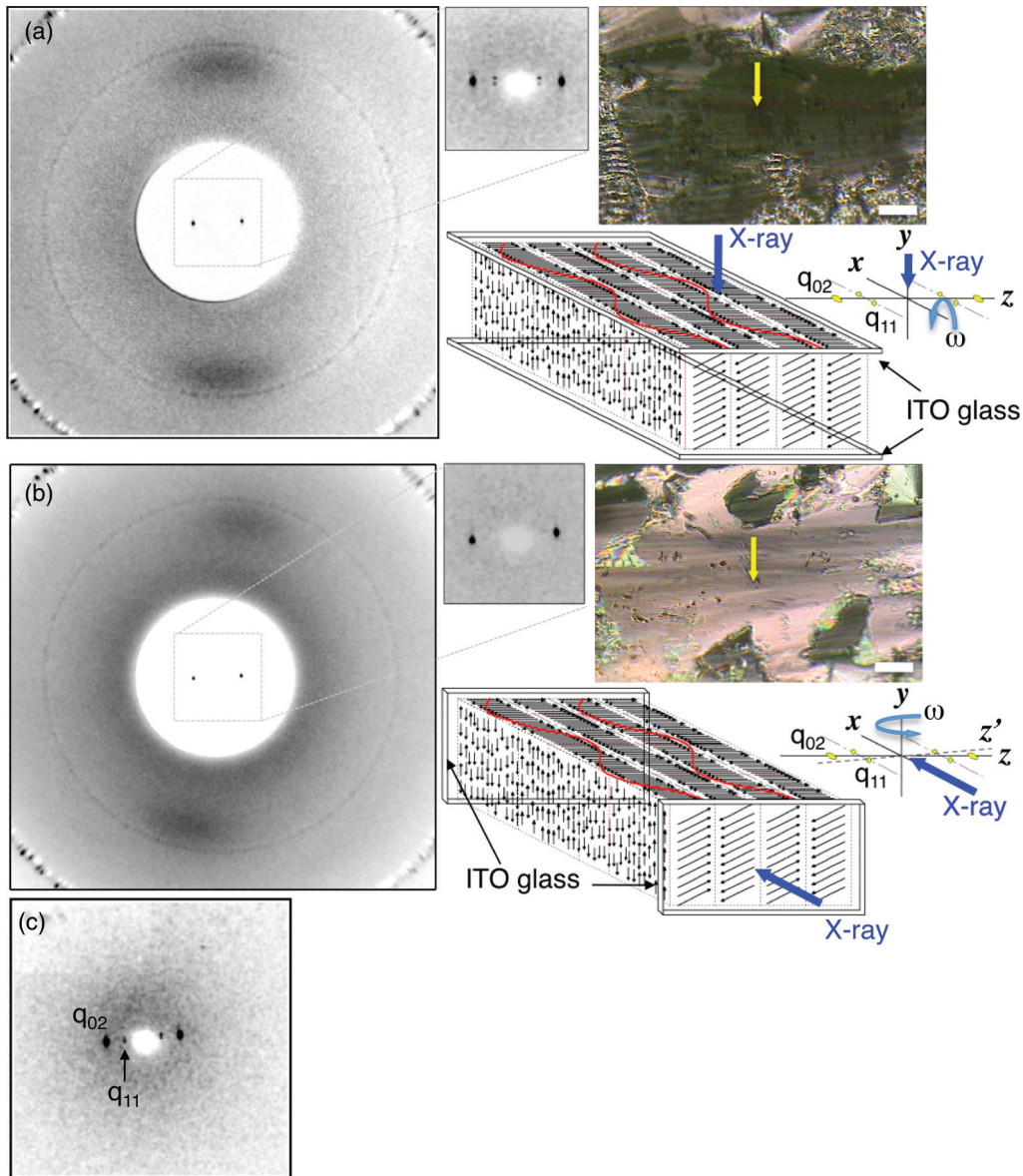


FIG. 4. (Color online) Two-dimensional small (center top side) and wide (left side) angle microbeam x-ray diffraction pattern in the SmC' phase obtained from the 25- μm -thick planar cell without an applied electric field (a) and under the application of a square wave electric field (10 kHz, ± 20 V) (b). Right top figures of (a) and (b) are microphotographs of irradiated position (indicated by arrows). The white scale bar in the photographs indicates 50 μm . Right bottom figures of (a) and (b) show the 3D structure of the planar cells and the relation between incident x ray, rotation axis ω , and molecular coordinates; z is the layer normal and the y - z plane is a tilting plane. (c) Two-dimensional small x-ray diffraction pattern by rotating the sample cell from the geometry of (b) a few degrees of ω as z' normal to the incident x ray.

parallel to the substrate (ω), $q_{\pm 11}$ appears, which indicates that the modulated structure remains even in the electric field application, as shown in Fig. 4(c). These results suggest that the layer modulated plane is vertical to the c director and layer normal direction in SmC' , as depicted in Fig. 3(b) and the right bottom side of Fig. 4(b).

So far the antiphase SmC phase observed in the rodlike molecules was reported in a few papers [7], but the relation between layer modulation and molecular orientation was not clear. It is concluded that the relation between the layer modulated direction and molecular tilt direction in the layer-modulated SmC phase considerably becomes clear this time. Figure 5 shows the temperature dependence of the

in-plane modulated periodic length. On cooling, this modulation appears just below the SmC - SmC' transition, and modulation length diverges up to the SmC' - SmC'' (SmC_2) transition.

From the microbeam x-ray results, it is found that the SmC' phase is a layer-modulated smectic phase. Considering the modulated structure, the origin is from the frustration of the monolayer and bilayer structures. It is reasonable to consider that the bilayer structure in SmC_2 was stabilized by the hydrogen bond between the terminal hydroxy groups of molecules in adjacent layers [8]. Therefore, it is important to the strength of the hydrogen bond between interlayer hydroxy groups. The effect of the intermolecular hydrogen bond on the formation of the modulated layer structure was investigated

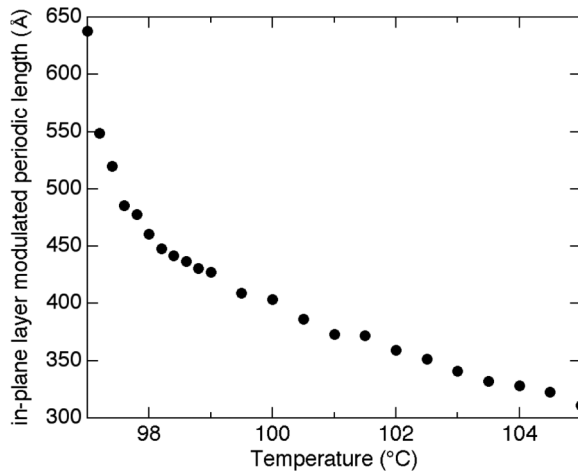


FIG. 5. Temperature dependence of the in-plane layer modulated periodic length obtained from q_{10} in Fig. 1. In this cell the phase transition temperatures from SmC to SmC' and from SmC' to SmC'' are 105.5 and 96.9 °C, respectively.

by Fourier transform infrared (FTIR) spectroscopy. Figure 6 presents temperature dependence of a wave number of an absorption peak corresponding to O-H vibration influenced by the intermolecular hydrogen bond of I-7. An absorption peak around 3400 cm^{-1} shifts to a lower wave number with decreasing temperature. This lower shift indicates that the intermolecular hydrogen bond becomes stronger [15,16]. Temperature dependence of the wave number of an absorption peak corresponding to intermolecular hydrogen bonds of I-6, which exhibits a bilayer SmC (SmC₂), and I-8, which exhibits a monolayer SmC (SmC₁), are also shown in Fig. 6. Remarkably, the wave number of the absorption peak in the SmC' phase of I-7 gradually shifts from that of I-8 with the monolayer structure to that of I-6 with the bilayer structure. This result suggests that a kind of dimerization due to the intermolecular hydrogen bond induces the bilayer structure of SmC'' (SmC₂) passing through the modulated structure in the SmC' caused by the frustration between the monolayer and bilayer structures.

In summary, we investigated the phase structures and hydrogen-bond behavior of three SmC phases (SmC, SmC', and SmC'') of I-7. It was revealed that the SmC' phase exhibits novel smectic-C antiphase possessing the in-plane

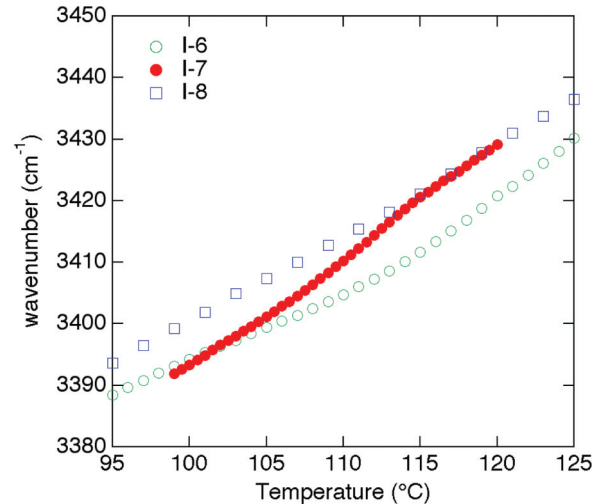


FIG. 6. (Color online) Temperature dependence of the wave number of an absorption peak around 3400 cm^{-1} corresponding to O-H vibration influenced by intermolecular hydrogen bonds of I-6 (open circle), I-7 (closed circle), and I-8 (open square).

modulation of the molecular arrangement, and the SmC'' phase is a uniformly bilayer SmC₂ phase. In the SmC' and SmC'' phases we concluded that modulated and bilayer structures are induced by an intermolecular hydrogen bond between neighboring molecules in adjacent layers.

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