Distinct layered structure with density modulation in solid phase formed from B_2 phase of banana molecules

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A unique two-dimensional (2D) long-range structure has been observed in a low-temperature phase X_1 for a banana molecule having bromine atom substituted on the central core using synchrotron radiation (SR) x-ray scattering measurements. The X_1 phase is formed from the B_2 phase with the SmC_AP_A structure upon cooling and then shows multiple reflections around the first layer line, which are interpreted as a peculiar frustrated structure with long-range layer modulation order. Furthermore, the observation of a well-defined (100) reflection with a spacing of 171Å means that there is the electron density modulation along the layers. By coupling these reflections, a 2D lattice with a=173 Å, c=53.4 Å, and β=81.1° is determined where the a axis is parallel to the original layer of the B_2 phase. This unique structure with modulation can be interpreted as an undulated layer structure and suggested to be the result from deformation with polarization splay defects periodically occurring along the layer. The angle, β=81.1°, between a and c axes indicates that the position of splay defects in one layer is staggered from that in the neighboring layer. In other words, the splay defect lines run in a direction tilted by roughly 80° with respect to the a axis.

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I. INTRODUCTION

The discovery of banana-shaped mesogens [1], as recognized by exhibiting the so-called banana phases, has opened a field of research in liquid crystals for chirality and ferroelectricity in achiral systems. As contended by Watanabe and co-workers [1,2], the molecules cannot rotate freely around their long axes due to their bent shape, which consequently results in a polar mesophase. By confirming ferro- or antiferroelectricity in the fluid B_2 phase [1,2], the main issue is to comprehend a unique phase structure dominated by the formation of macroscopic polar order [3]. In addition to the most-studied B_2 phase, the B_1 phase [4–6] and B_7 phase [7–13] were reported as density modulated structures, which macroscopically cancel out polarization by organizing a frustrated antidomain structure [14–16] and by adopting a molecular splay deformation in a single layer [12], respectively. The amplitude of density modulation in the frustrated structure is different in the B_1 and B_7 phases. The periodicity of the modulation, which is thought to be formed by breaking layers, in the B_1 phase was reported as ranging from 40 Å [4,5] to over 100 Å [6]. In contrast, the modulated wavelength was detected to be around 100–300 Å in the B_7 phase [12,13]. In all these phases, the resulting two-dimensional lattices are rectangular, but more recently, a notable switchable phase with the two-dimensional oblique lattice was reported [17].

On the other hand, relatively few studies for frustrated solid phases appearing in the lowest temperature region have been published since they usually show high orders and low mobilities, which cannot be understood with useful techniques such as an electro-optic measurement. One interesting phase is the B_4 phase [2,18], which often appears in the lowest temperature region of commonly studied banana-shaped homologs, the 1,3-benzene bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoate] (P-*n*-O-PIMB) [1]. It has been considered to possess a helical structure along the layer direction, such as a twisted grain boundary (TGB)-like structure. Such a helical frustration is also considered to escape from the spontaneous formation of a macroscopic polar structure [18]. In this paper, we report another type of frustrated structure in the solid phase. It is called the X_1 phase, and it appeared from the well-known B_2 phase of 4-Br-P-14-O-PIMB [19] upon cooling. We performed a SR x-ray measurement on the solid X_1 phase and found that the X_1 phase preserves a long range two-dimensional lattice, possibly arising as a result of a dissipation from the polar structure.

II. EXPERIMENT

The optical microscopic textures of the materials were examined using an Olympus BX50 polarizing microscope connected to a temperature-controlled Mettler Toledo FP82 hot stage. The transition temperature and corresponding enthalpies were determined using a differential scanning calorimeter (Perkin Elmer, Pyris1 DSC).

For the detailed x-ray analysis, the homeotropically aligned sample was first prepared by slowly cooling (1 °C min^{-1}) a droplet of the sample on a glass plate treated with organosilane. The x-ray beam was irradiated parallel to the face of the glass substrate (see Fig. 1). Both the SR wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS) patterns were recorded at a scanning rate of 1 °C min^{-1} through the transformation from the B_2 phase to the X_1 phase at the 4C2 beamline of the Pohang Light Source

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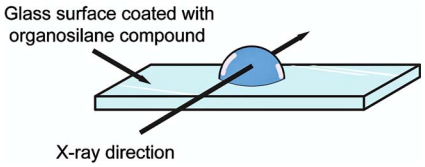
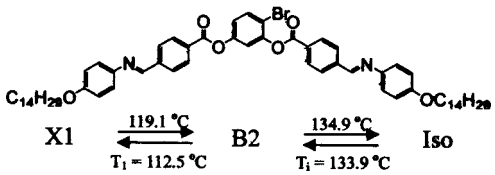


FIG. 1. (Color online) Experimental geometry of x-ray diffraction for obtaining a homeotropically aligned sample profile.

(PLS), Korea. The camera length was calibrated using reflections of the lamellar phase of styrene-ethylene-butadiene (SEB) having a first order reflection at $q=0.019\,075$ Å^{-1} for the SAXS measurement and a first order (00l) reflection ($q=0.107\,626$ Å^{-1}) of silver behenate for WAXS measurement. The detector is a Princeton two-dimensional charge-coupled device (CCD) with 2084×2084 pixels. The pixel size is 57.6×57.6 μm^2.

III. RESULTS AND DISCUSSION

Among the materials exhibiting the X_1 phase, we have selected the 4-Br-P-14-O-PIMB with the following chemical structure.



Its phase sequence and transition temperatures, T_1 and T_i were determined from the differential scanning calorimetry (DSC) thermograms shown in Fig. 2. T_i corresponds to the transition from the isotopic melt to the B_2 phase, and T_1 to the transition from the B_2 phase to the X_1 phase. When we compare this phase behavior with that of P-14-O-PIMB, we know that the B_4 phase is altered to the X_1 phase by the attachment of the Br group to the bent core.

As previously reported [19], the B_2 phase appears from the isotropic melt as many germlike domains, which finally coalesce to form fine fan textures. The majority of the fan textures exhibit no stripe, which is a characteristic of the homochiral phase that has been observed in the B_2 phase of the parent P-*n*-O-PIMB homologs without Br substitution

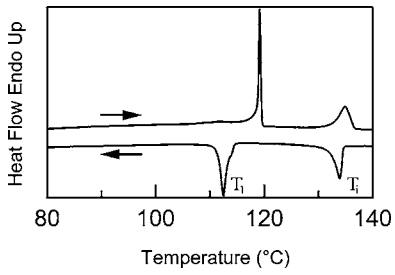


FIG. 2. DSC thermogram of 4-Br-P-14-O-PIMB measured at a scanning rate of 1 °C min^{-1}.

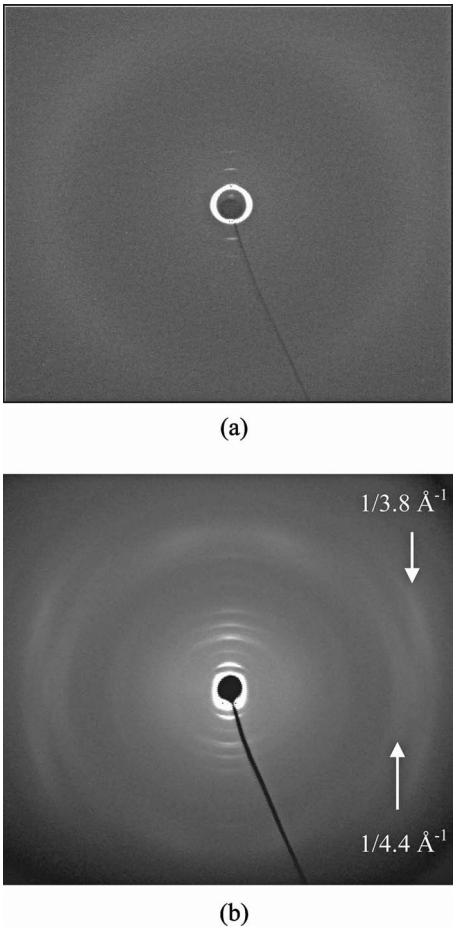


FIG. 3. Typical WAXS patterns of (a) B_2 (at 120 °C) and (b) X_1 phases (at 25 °C).

[2]. The type of layer structure was identified from electro-optic measurement. The extinction brushes rotated and birefringent color changed upon application of the dc voltage; these are distinct characteristics of the homochiral domain. The reversal of the current upon applying a triangular wave form appeared as two peaks, showing the antiferroelectricity of the B_2 phase with a spontaneous polarization of 600 nC cm^{-2}. Thus, we conclude that the layer structure of the B_2 phase is SmC_AP_A [3,19].

Figure 3(a) shows the WAXS patterns of the oriented B_2 phase. It includes the inner sharp layer reflections and outer broad reflections, which are attributable to the fluid smectic phase with a liquidlike packing of molecules within a layer. The splitting of the outer reflections above and below the equator is characteristic of the banana smectic phase. The layer spacing is 45.2 Å. This spacing is relatively smaller than the extended molecular length (58.8 Å) and very similar to that (~45.4 Å) in the B_2 phase of the parent P-14-O-PIMB molecule with the same terminal chain length. The tilt angle elucidated from the electro-optical microscopy is 35°, which is similar to that in the B_2 phase of P-*n*-O-PIMB homologs.

The lowest-temperature X_1 phase shows birefringence weaker than the high-temperature B_2 phase under the polarized optical microscopic observation. It is a solid as ex-

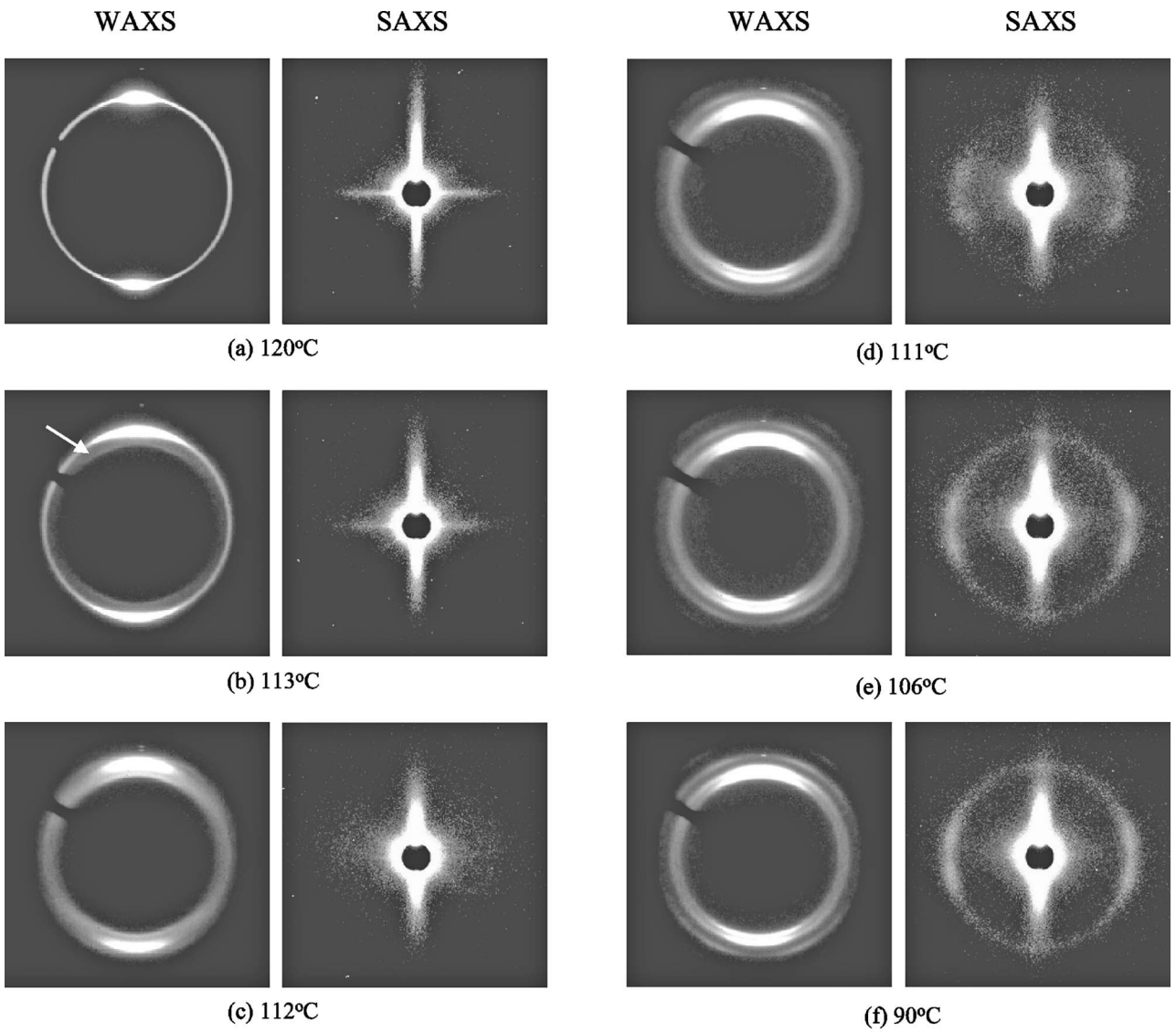


FIG. 4. X-ray patterns observed upon cooling process from 125 °C to 80 °C at a scanning rate of 1 °C min^{-1}. WAXS patterns on the right cover the spacing range around the first layer reflection of the smectic layer phase, while SAXS patterns on the left cover the spacing range from 100 to 300 Å (the arrows in b indicates the streak).

pected, since it does not carry any mobility at all. However, it shows a completely different x-ray pattern [see Fig. 3(b)] from that of a crystalline phase. Along the meridian direction a series of the (00*l*) reflections can be seen which are indicative of an existence of the layered structure while only the diffuse streaks are observed in the outer region. The outer streaks show their maxima at 1/4.4 $Å^{-1}$ and 1/3.8 $Å^{-1}$ on and out of the equatorial line, respectively, as given by the arrows in Fig. 3(b) and are thought to be attributed to the lateral molecular packing. The overall feature of the diffraction pattern is far from the crystalline pattern. The structure is considered to be a frustrated one like the solid B_4 phase [18].

The structural transformation between the B_2 and X_1 phases was examined here by the SR x-ray scattering measurements upon cooling homeotropically oriented B_2 phase. The temperature was scanned from 120 °C to 80 °C at a rate of 1 °C min^{-1}. The selected x-ray patterns taken at temperatures near T_1 are shown in Fig. 4.

The series of photographs on the left and right in Fig. 4 show the WAXS and SAXS patterns which cover spacing range of the first smectic layer reflection and reflections with spacing from 100 to 300Å, respectively. For the B_2 phase at 120 °C, the WAXS reflections attributable to the smectic layer are observed on the meridional line [see Fig. 4(a)]. Upon cooling to 113 °C near T_1, a change takes place such that streaks appear just in the inner region of the first layer reflection of the B_2 phase. The streaks are slightly inclined toward the meridional line by roughly 70–80 ° [Fig. 4(b)]. Upon further cooling, the streak is gradually replaced by the reflections and simultaneously a broad reflection appears in a direction of the equator in the SAXS pattern at 111 °C [Fig. 4(d)]. At 105 °C where the transition to the X_1 phase surely takes over as shown in the DSC thermogram (refer to Fig. 2), the reflection with a spacing of 171 Å in the SAXS region becomes clearer, and then several reflections can be detected in the WAXS region [see Figs. 4(e) and 4(f)]. The reflections in the SAXS pattern are split above and below the equatorial

TABLE I. X-ray diffraction data for 4Br-P-14-O-PIMB in the X_1 phase at 90 °C.

	d_{obs}/Å	$h\,0\,l$[a]	d_{calc}/Å[a]
$l=0$	171	100	171
$l=1$	52.5	001	52.8
	48.6	101	48.4
	42.6	201	42.1
	36.6	301	36.1
	31.1	401	31.0
$l=2$	26.4	002	26.4
	25.4	102	25.5

[a]Based on the lattice with $a=173$ Å, $c=53.4$ Å, and $\beta=81.1°$.

line, so that the large-scale repetition arises in a tilted direction from the glass surface, i.e., the initial layer plane of the B_2 phase. The tilt angle is roughly 10°. In the temperature region lower than 105 °C, no essential change was observed.

The spacings of the SAXS and WAXS reflections observed at 90 °C are listed in Table I. All reflections observed for the X_1 phase can be interpreted by a two-dimensional lattice with $a=173$ Å, $c=53.4$ Å, and $\beta=81.1°$. The a axis is parallel to the originally aligned layer of the B_2 phase, and the c axis is tilted by roughly 10° from the normal of the original B_2 layer. rrespective of the simple lattice, the x-ray pattern in Fig. 4(f) seems to be complex. The complexity arises due to rotational freedom. The crystallographic (001) plane of the lattice is parallel to the glass substrate; thus, the sample is rotationally disordered about the normal to this plane (refer to Fig. 1). Figure 5 shows the orientations of the reciprocal lattice that give rise to the diffraction pattern, which corresponds to the observed pattern.

Why does such a specific two-dimensional structure appear in the X_1 phase? On the basis of the following points, we believe that it is a frustrated structure. At first, we refer to

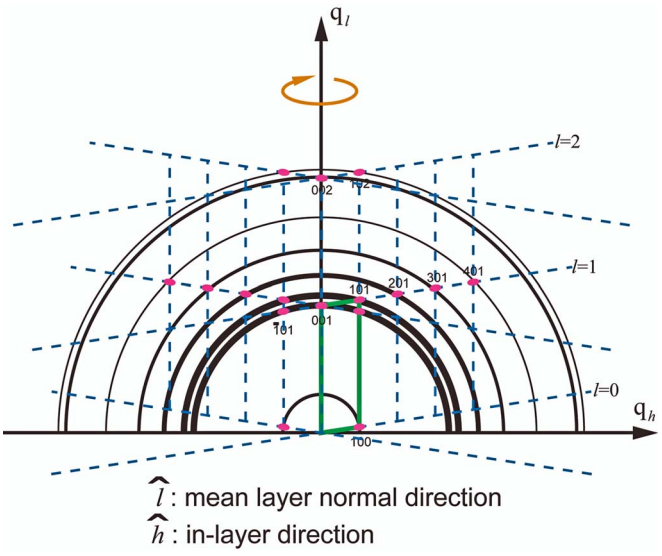


FIG. 5. (Color online) Schematic drawing of x-ray diffraction pattern of X_1 phase and reciprocal lattices in two orientations.

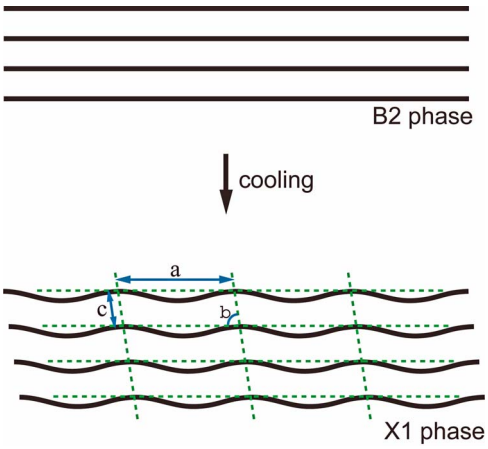


FIG. 6. (Color online) Illustration of structural model with two-dimensional lattice proposed for the X_1 phase which forms from the B_2 phase. The lattice parameters are $a=173$ Å, $c=53.4$ Å, and $\beta=81.1°$.

the streak appearing just when the transition starts [see the WAXS patterns of Figs. 4(b) and 4(c)]. The streak shows that some one-dimensional repeating structure arises along the direction normal to the streak, but that the repeating structure formed at one place does not have a positional correlation to that formed at another part [20]. The spacing of the repeating structure is about 53Å, which is slightly larger than the smectic layer thickness of the B_2 phase. We thus speculate that the smectic layers start to undulate at this temperature, but the correlation length of the undulation is markedly small. Upon cooling to 111 °C, at which temperature the B_2-X_1 transition is completed, the streak is replaced by (h01) reflections arising on the line of the streak, and simultaneously, the (100) reflection appears in the SAXS pattern. This means that the undulation occurs with a larger correlation length, giving a well-defined two-dimensional lattice as illustrated in Fig. 6.

Here, two peculiar features in the x-ray pattern of the X_1 phase must be noted. The first feature is that the (100) reflection can be clearly detected. If a simple undulation of a layer is formed, i.e., if the molecules are equally spaced within a layer, the intensity of (h00) reflections should be zero since no significant density modulation arises along the a axis. In fact, such a feature has been observed in the B_1 phase [4]. The observed (100) reflection must originate from the electron density modulation along the layers. It has also been reported that such an electron density modulation could stem from the deformation when the polarization splay defects took place periodically along the layer [12,13]. As a second feature, the angle between the a and c axes is not 90°, but 81.1°. This indicates that the position of splay defects in one layer is staggered from that in the neighboring layer. In other words, the splay defect lines are tilted by roughly 80° with respect to the a axis. Such staggering is potential but a specific model which cannot be explained now [21].

It is realistic to consider that the X_1 phase could be a crystal at least in the limited small domain. However, this is not likely because the size of the two-dimensional lattice depends remarkably on temperature, even at temperatures

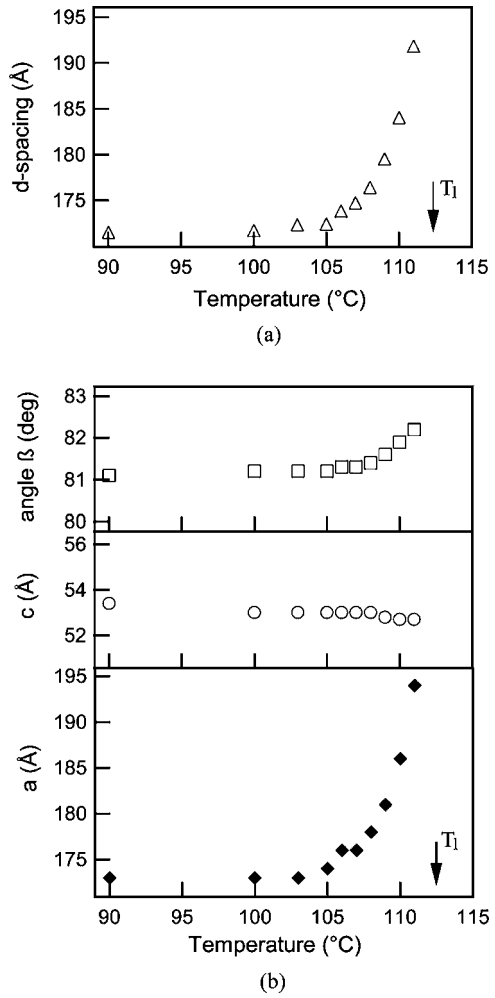


FIG. 7. Temperature dependences of (a) the spacing of a (100) reflection and (b) lattice parameters a, c, and β of a two-dimensional lattice.

below T_1 (112.5 °C). The spacings of (100) reflections are plotted against temperature in Fig. 7(a). As the temperature decreases from 111 to 105 °C, the spacing changes from 195 Å to 174 Å, and becomes almost constant at temperatures below 105 °C. The lattice parameter a also depends strongly on temperature, as shown in Fig. 7(b), although c and β are almost constant. It is thus obvious that the molecules are seeking a thermally stable position respect to the splay defects at respective temperatures, at least in the temperature region from T_1 to 105 °C. This suggests that the X_1 phase may be a kind of mesophase in which some molecular motion is allowed in the higher temperature region while it may be frozen in the lower temperature region below 105 °C.

IV. CONCLUSION

The low-temperature phase, X_1 of the banana shaped molecule, 4Br-P-14-O-PIMB, was examined by SR-WAXS and -SAXS measurements. In the X_1 phase, upon cooling from the B_2 phase with SmC_AP_A structure, the multiple satellite reflections have been observed around the first layer reflection line, which are indicative of the peculiar frustrated structure with a long-range layer modulation order along the layer. The two-dimensional lattice with $a=173$ Å, $c=53.4$ Å, and $\beta=81.1°$ is well determined by a coupling of the reflections. Also, the clear observation of small angle reflection with a spacing of 171 Å is indicative of the electron density modulation within the layers. This has been interpreted to arise from the deformation with splay defects periodically occurring. The a axis is parallel to the original layer plane of the B_2 phase, and the c axis makes an angle of 81.1° with the a axis, which is tilted by roughly 10° from the normal of the original B_2 layer. This indicates that the position of splay defects in one layer is staggered from that in the neighboring layer. In other words, the splay defect lines are tilted by 80° with respect to the a axis, resulting in the undulated layer structure. This is the second type of frustrated solid phase, which results from the escape from the polarization, but essentially differs from the first type of frustrated solid B_4 phase.

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