Chiral Symmetry Breaking in Liquid Crystals: Appearance of Ferroelectricity and Antiferroelectricity

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Received: 30 September 2020; Accepted: 17 November 2020; Published: 19 November 2020

Abstract: The study of chiral symmetry breaking in liquid crystals and the consequent emergence of ferroelectric and antiferroelectric phases is described. Furthermore, we show that the frustration between two phases induces a variety of structural phases called subphases and that resonant X-ray scattering is a powerful tool for the structural analysis of these complicated subphases. Finally, we discuss the future prospects for clarifying the origin of such successive phase transition.

Keywords: chirality; symmetry breaking; ferroelectricity; antiferroelectricity; subphases; resonant X-ray scattering

1. Introduction: Liquid Crystals

Liquid Crystals (LCs) are stationary state meso-phases appearing between crystals and isotropic liquids, and have intermediate properties between them, i.e., fluidity and complete disorder as liquids and three-dimensional long-range anisotropic ordering as crystals. Spontaneous meso-scale organization is also characteristic of LCs, and comparatively easy fabrication of fine structures can be done. Usually rod-like or disk-like shaped molecules with a hard-core part at their center and flexible end chains tend to exhibit liquid crystal phases. Here, we mainly treat the LCs of rod-like molecules, in which the phase transition occurs by a thermal process (called “thermotropic liquid crystals”). By the degree of ordering, LCs are classified into many types. The most disordered type of LC is called the nematic phase, which has no positional order but the orientational order of a molecular long axis. The nematic phase appears just below the isotropic liquid phase, and, between the nematic phase and crystal phase, another LC phase frequently appears. This LC phase has a one-dimensional positional order (layer order) in addition to the molecular orientational order, called smectic phase. Smectic phases are additionally classified in many types by molecular orientation along the layer normal or in a layer. Two common smectic phases are SmA and SmC. In SmA, the molecular long axis is parallel to the layer normal, and, in SmC, it is tilted, as shown in Figure 1.
2. Introduction of Chiral Symmetry Breaking to Liquid Crystals and the Appearance of Ferroelectricity in Liquid Crystals

Chirality has an important factor for many scientific fields, such as biology, chemistry, and physics. For example, in drag development, one of the enantiomers is active and good for health but the other becomes poison. In physics, chirality strongly influences the optical properties, such as optical rotation and circular dichroism. Circular optical polarization properties are the signature of the sample dissymmetry leading to parity breaking; this is what is defined as chemical chirality. Parity breaking is a consequence of the absence of any Sn (improper rotation) symmetry element in the sample symmetry. The disappearance of inversion symmetry due to the chirality induces several physical properties such as pyroelectricity, piezoelectricity and ferroelectricity. Of the 32 different space groups, there are 21 that do not have inversion symmetry and they exhibit piezoelectricity. Among them, 10 space groups show pyroelectricity with spontaneous polarization. However not all materials exhibiting pyroelectricity exhibit ferroelectricity [1]. In the case that the spontaneous polarization can be reversed in the application of an external reverse electric field, it is called ferroelectricity. Even in LCs with fluidity, the ferroelectricity may appear. Most of rod-like molecules exhibiting LC phases have permanent electric dipole moments parallel and/or perpendicular to the molecular long axes. If their dipole moments are aligned properly, it is possible to accomplish the occurrence of ferroelectricity in liquid crystals. However, some factors prevent the occurrence of ferroelectricity: (1) thermal fluctuation is large, so that dipole-dipole interaction is weak because thermal kinetic energy is larger than dipole-dipole interaction energy. (2) Due to the high symmetry, free rotation around the molecular long axis and head and tail equivalence disturbs ferroelectric property. (3) In the case that the dipole moment is too strong, fluidity induces dimmer organization, and the antiparallel arrangement of the dipole moment occurs and total polarization is cancelled out.

Since usually the symmetry of the SmC phase is C\textsubscript{2h}, it is impossible to possess spontaneous polarization because of the existence of inversion symmetry. However, by introducing the chirality in the system, its symmetry is broken to C\textsubscript{2} without inversion symmetry, so it is possible to produce the spontaneous polarization along the C\textsubscript{2} axis. In SmC\textsuperscript{(*)}, molecules still rotate around the molecular long axis, but the rotation is biased and then the biaxiality appears. Hence, if molecules have a transverse dipole moment, and the average biasing direction of the transverse dipole moment tends to align normal to the tiling plane, macroscopic polarization is able to appear in the smectic layer because the C\textsubscript{2} axis is normal to the molecular tilting plane. In such deep consideration for the symmetry of the LCs, Meyer et al. discovered ferroelectricity in LCs [2,3]. In the SmC\textsuperscript{*} phase,
Here, $n$ is the director (average direction of molecular long axes), and $z$ is a unit vector normal to the smectic layer. Tilt angle $\theta$, which is the angle between $z$ and $n$, is defined to zero when $z$ is coincident with $n$.

Strictly speaking, due to the chirality, molecular tilting direction (azimuthal angle in Figure 2) is slightly shifted from layer to layer, so that the helical structure whose axis is parallel to the layer normal is formed in the bulk state. Hence, net polarization of the thick sample may become zero, because the direction of the polarization in a smectic layer is normal to the tilting direction. The helical pitch is typically much longer than the smectic layer spacing, which has be of the order of thousands times of the layer spacing, and the deviation of azimuthal angle between molecules in neighboring layers is small (less than 1 deg.). Therefore, SmC* is not a real ferroelectric phase in the case of the bulk state. However, by confining this LC into thin sandwich cells, which are composed of two clean glass plates and have a gap less than the helical pitch, and aligning the helical axis parallel to the substrate surface (called “planar alignment”) as shown in Figure 3, helix is suppressed (unwound) by the surface effect. As a result, in such a condition, the molecular tilting plane is parallel to the surface, so that the spontaneous polarization exists along the surface normal direction. In such a thin cell whose substrate is coated with optically transparent electrodes such as ITO (Indium-Thin-Oxide), molecules are tilted in two states (A or B) by molecular tilt angle $\pm \theta$ with respect to the layer normal. If an electric field with proper magnitude whose direction is parallel to the smectic layer is applied to the ferroelectric SmC* phase in this condition, the polarization is forced to align along the field direction. Since the molecular tilting (and also director) is normal to the polarization, it is also normal to the field direction. Therefore, the director is tilted to the z-axis of Figure 3 and parallel to the substrate (xy) plane (A or B). If the sense of an applied field is inverted, polarization and its corresponding molecular tilting direction are also inverted correspondingly, so that the director is still parallel to the substrates but the tilting sense is opposite. As shown in Figure 4, apparent tilt angle and corresponding polarization shows a single hysteresis behavior with respect to the applied field, which is characteristic for the ferroelectric property. Hence, the indirect ferroelectricity appears due to the surface effect, and this state is called surface-stabilized ferroelectric liquid crystals (SSFLCs) [4].

Figure 2. Bulk structure of the SmC* phase. C-director (blue arrow) means the projection of directors (molecular long axis) on the smectic layer plane, and the polarization (red arrow) is parallel to the smectic plane but normal to the C-director.
Figure 3. Molecular arrangement of SmC* in the thin planar alignment. Due to the surface effect, molecules are located at A or B states, and the corresponding polarization is oriented up or down to the substrate normal. By applying the electric field normal to the substrates, molecules switch to A and B states as the sign of transverse polarization is consistent with the sign of electric field.

Figure 4. Apparent tilt angle of SmC* as a function of the electric field, and the corresponding molecular arrangement under the electric field.

3. Discovery of Antiferroelectricity in Liquid Crystals

As mentioned later, the ferroelectric SmC* phase shows a fast electro-optic response, whose speed is in the order of microseconds, much faster than that in the nematic phase using flat panel displays (msec order). This is because of the direct coupling between the applied electric field and the spontaneous polarization, which is different from the dielectric coupling in the nematic phase. Hence, FLC has been expected to utilize next-generation fast flat panel displays, and more than thousands of FLC compounds were synthesized and extensively studied in order to commercialize it as a new fast response display [5]. In this situation for the study on ferroelectric liquid crystals, an antiferroelectric phase was discovered in 1989 [6]. A first compound in which antiferroelectric liquid crystal (AFLC) was confirmed was 4-(1-methylheptyloxy carbonyl) phenyl 4'-octyloxy biphenyl-4-carboxylate (MHPOBC), whose chemical structure is shown in Figure 5. At first, it was reported that this compound shows so-called tristable switching in the lower-temperature smectic phase by the Tokyo Tech group [7,8]; the switching shows two states, which is the same as ferroelectric bistable states mentioned above and another state without any electric field, but was not clarified why such a switching occurs. Later, considering previous results and the result of obliquely incident transmission spectra, Chandani et al. concluded that molecules are
tilted in the opposite sense in neighboring layers and the corresponding polarization was cancelled out in two layers without any electric field, as shown in Figure 6b [6]. When the proper electric field is applied, electric-field induced phase transition to ferroelectric states occurs. Apparent tilt angle and corresponding polarization shows a double hysteresis behavior with respect to the applied field, which is characteristic for antiferroelectric property, as shown in Figure 6a. In the bulk state, a helical structure was also formed like SmC* due to the chirality, in such a molecular arrangement with helix, obliquely incident transmitted spectra are clearly different from that in the ferroelectric SmC* phase. Details are explained as follows.

Figure 5. Chemical structure of MHPOBC, in which antiferroelectric SmCA* was discovered.

Figure 6. Apparent tilt angle of SmCA* as a function of the electric field (a), and the corresponding molecular arrangement under the electric field (b).

The important difference between ferroelectric SmC* and antiferroelectric SmCA* is symmetry; SmC* and SmCA* have C₂ and D₂ symmetries, respectively. Reflecting this symmetry difference, the physical properties between them are distinguished. The most remarkable difference of the optical transmission spectra is as mentioned previously [6]. Bulk states in both phases have helical structures induced by twisting power due to the chirality. If the helical pitch (strictly speaking, optical pitch, which is physical pitch multiplied by refractive index) is consistent with the visible wavelength, the circular polarized light with the same wavelength and the same handedness is selectively reflected, called selective reflection. Hence, when the transmission spectrum is measured, a clear dip is observed at this wavelength [6]. When the incident light is parallel to the helical axis, the periodicity of the optical birefringence corresponds to half the pitch in both SmC* and SmCA*. However, when the incident light is oblique to the helical axis, the situation changes; in antiferroelectric SmCA*, the periodicity of the optical birefringence corresponds to half the pitch, but in ferroelectric SmC*, it corresponds to the full pitch. Hence, from the oblique incident transmission spectra, both phases are clearly distinguished as shown in Figure 7 [6], which comes from the difference from the molecular arrangement.
Figure 7. Transmitted spectra at obliquely incident light in SmC* and SmCA*. In SmCA*, the periodicity of optical birefringence is half the helical pitch, so that the dip of transmission due to the selective reflection of the full pitch band is not observed (at the red arrow position) [6].

The structure in SmC* showing the ferroelectric property and that in SmCA* showing the antiferroelectric property are very similar. However, due to the difference of system symmetry, a defect structure is also drastically different, and this difference can judge the anticlinic structure in SmCA*. Now we consider the helical pitch in SmC* and SmCA* to be very long or infinite. When we make homeotropic alignment (in which the layer plane is parallel to the substrate), typical defect texture called “Schlieren” is frequently observed. In the nematic phase, similar schlieren textures are also observed in the planar alignment, and it is caused by the spatially deviation of director $n$ orientation, which is the average direction of molecular long axis around the visible wavelength region. Schlieren texture in the homeotropic alignment of tilted smectic phase, on the other hand, is caused by the deviation of the direction of the projection of the director to the smectic layer ($c$-director). Due to the symmetry, $n$ and $-n$ are equivalent, but $c$ and $-c$ are not, because they indicate alternately anticlinic tilting orientation of director. Hence, only four blush schlieren texture, indicating disclination defect with the strength $s = \pm 1$, is observed in the ferroelectric SmC* as shown in Figure 8a. However, in antiferroelectric SmCA*, two blush schlieren texture, indicating disclination defect with the strength $s = \pm 1/2$, is also observed in addition to the four-blush one [9,10]. Considering $c$ is not equal to $-c$ like SmC*, it is difficult to attain this defect structure, because it is necessary to provide discontinuous plane along the solid line as shown in Figure 8b for the appearance of the $s = \pm 1/2$ defects and the defect energy becomes extremely high. However, in the SmCA*, it has an anticlinic structure, so that $c$-director in adjacent layers are antiparallel. Therefore, by introducing a screw dislocation with a Burgers vector of the same magnitude as the single layer thickness together with wedge disclination with $s = \pm 1/2$ at the same position, discontinuous boundary plane can disappear. This defect is called dispiration [10], which is a combined defect of dislocation and disclination. As far as I know, this is the first obvious experimental proof of the existence of a dispiration. Additionally, conversely speaking, the appearance of dispirations provides experimental evidence of the anticlinic structure in the antiferroelectric liquid crystalline phase [11]. Results of the transmission spectra measurement and texture observation seem to be indirect experimental proofs of the structure of AFLCs. However, this is enough to explain the anticlinic structure in AFLCs and electro-optic property. The final direct decision of the structure of AFLCs was performed by the resonant X-ray scattering technique; the results are shown in Section 5.
Figure 8. Texture under the crossed polarized observation in the homeotropic alignment in SmC* (a) and SmCA* (b). In SmCA*, two brushed texture by wedge disclination with $s = \pm 1/2$ was observed, which proves the existence of wedge-screw dispiration. (c) The structure of wedge-screw dispiration in SmCA*. The small arrows indicate c-directors, which is the projection of directors on the smectic layer plane. Wedge disclination lines with Frank vector (0, 0, $\pi$) as well as the screw dislocation lines with Burgers vector (0, 0, $d$) are indicated by bold arrows, which parallel the layer normal (z axis). Here, $d$ is the layer thickness. This defect can appear by the anticlinic structure in SmCA* [11].

4. Frustration of Ferroelectric and Antiferroelectric Phases; Successive Phase Transition to Several Subphases between Two Phases

When the antiferroelectric SmCA* phase was discovered in 4-(1-methylheptyloxy carbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC), three phases with a narrow temperature range called “subphases” or “SmC* variants” were already observed between SmA and SmCA*. Fukui et al. first noticed the existence of subphases by differential scanning calorimetry (DSC) [12]. At almost the
same time, Takezoe et al. [13] and Chandani et al. [14] reported three subphases between SmA and SmCA* in MHPOBC, and these subphases were tentatively designated as SmCα*, SmCβ* and SmCγ* in order of temperature at the beginning, and later found that SmCβ* was normal ferroelectric SmC*. The SmCγ* phase shows four-state switching in the planar cells [15], and, by conoscope observation [16], this phase shows an averagely three-layer periodic structure in which two molecules are tilted to the one side and one molecule is tilted to another side with respect to the layer normal, as shown in Figure 9b. After further study, some other phases are frequently observed between ferroelectric SmC* and antiferroelectric SmCA* phases. These phases exist in a very narrow temperature range (several K to 0.2 K) but are clearly distinguished by texture observation [17], conoscope observation [18–20], dielectric [21,22] and thermal measurements [23,24], etc. Later complicated successive phase transition to many subphases is extensively being studied. In particular, subphases are frequently observed in the binary mixture of FLCs and AFLCs [18–20,25].

![Figure 9. Molecular arrangement of subphase between SmC* and SmCA*, and the corresponding qT number. (a) antiferroelectric SmCA*, (b) corresponds to SmCγ* phase, (c) is the subphase with four-layer periodicity, and (d) ferroelectric SmC*.](image)

First, discovered subphase (SmCγ*) forms a three-layered periodic structure mentioned above, and four-layered periodic subphases were next discovered in 4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl- 4-carboxylate (MHPOBC) [26]. Typical molecular arrangements are shown in Figure 9c. In the four-layer periodic phase, two molecules in the nearest layer tilt with the same sense, but the molecules in the next two layers tilt with opposite sense, and such a molecular arrangement is formed repeatedly. Here, molecular ordering in adjacent layers is defined as follows: when the molecules in adjacent layers tilt with opposite sense, the molecular ordering is “A”, which means antiferroelectric (or anticlinic) ordering. Additionally, when they tilt with the same sense, the molecular ordering is “F”, which means ferroelectric (or synclinic) ordering. Here, any subphase expected to appear is specified by an irreducible rational number, qT [25],

\[
q_T = \frac{[F]}{([A] + [F])}
\]
where [F] and [A] are the number of synclinic ferroelectric and anticlinic antiferroelectric orderings, respectively. In the three-layered periodic subphase (SmC*), \( q_T = 1/3 \), while \( q_T = 1/2 \) in the four-layered periodic subphase. In antiferroelectric SmCA* and ferroelectric SmC*, \( q_T = 0 \) and 1, respectively, so that the \( q_T \) number of the subphase step by step and gradually increases on heating.

At first, at least five subphases are proposed in the electro-optic and conoscope measurements [25], but because of the experimental difficulty such as the temperature accuracy being less than \( \pm 0.1 \) °C due to the narrow temperature range of each subphase and indirect information about the structure obtained by such an experiment, only two subphases got the public’s attention. For \( \text{SmCA}^*(q_T = 1/3) \) and \( \text{SmCA}^*(q_T = 1/2) \), the structures are relatively recognized because these subphases are observed more frequently in many liquid crystal compounds and mixtures, and there are many experimental data. Finally, the three-layer or four-layer periodic structures have been decisively recognized world wide by the resonant X-ray scattering technique about 15 years ago [27].

5. Resonant X-ray Scattering and the Determination of Molecular Arrangement of Subphases

The conventional X-ray scattering comes from the electron density distribution of the materials. Because the spherical symmetry of electron density was supposed in each atom, the X-ray susceptibility of the system is usually regarded as a scholar. In this technique, density periodicity can be detected by the Bragg condition. The smectic phase has a one-dimensional positional order with a two-dimensional liquid order, and the density has a periodicity along the layer normal. Since the X-ray susceptibility is treated as a scholar, the densities of the smectic layer in which tilt of the molecule is left and right are not distinguished. Hence, in synclinic SmC* and anticlinic SmCA* (and other suphases), X-ray diffraction profiles reflecting the density distribution along the layer normal are the same.

On the other hand, the resonant X-ray scattering (RXS) technique treats the X-ray susceptibility as a tensor but not a scholar at the absorption edge energy of a specific element as surfact, selenium and bromine, etc. Thus, RXS intensity reflects the system symmetry, and, as a result, the prohibited Bragg diffraction in the conventional method can appear as satellite peaks, which reflects the corresponding system symmetry. Hence, the orientational order (local layer structure) of different subphases can be clarified by measuring and analyzing resonant scattering satellite peaks. Using this technique, Mach et al. firstly directly clarified the two-, three-, and four-layer periodic structures in \( \text{SmCA}^*(q_T = 0) \), \( q_T = 1/3 \) and \( q_T = 1/2 \) [27]. RXS satellite peaks obtained from the subphase at the resonant condition appear at

\[
\frac{Q}{Q_0} = l + m/\nu \pm \epsilon
\]

where \( Q \) is the scattering vector and \( Q_0 = 2\pi/d \) is the smectic layer spacing, \( l = 1, 2, 3 \ldots \) is the diffraction order due to the smectic layer spacing, \( \nu \) is the number of layers in the unit cell of a subphase, \( m = \pm 1, \pm 2, \ldots, \pm (\nu - 1) \) defines RXS peak positions due to the super-lattice periodicity. \( \epsilon = dP \), and \( P \) is the pitch of the macroscopic helix. Later, using this technique, some groups have extensively studied subphases with 3- and 4-layer periodic structures [28–31]. Related to the RXS experiment, Levelut and Pansu calculated the tensorial X-ray structure factor in the smectic phase with the various structure models [32].

The author and his coworkers also performed a new experiment using microbeam resonant X-ray scattering to determine the structure of the novel subphase except \( q_T = 1/3 \) and \( q_T = 1/2 \). Here, we synthesized Br-containing chiral molecule, \((S,S)\)-bis-[4′-[-(1-methylheptyloxy)carbonyl]-4-biphenyl] 2-bromo-terephthalate (compound 1) [33], and measured RXS in the mixture of compound 1 and \((S,S)\)-\( \alpha \) -bis (4-[4′-[-(1-methylheptyloxy)carbonyl]biphenyl-4-yl] oxycarbonyl)phenoxy)hexane [34]. The results are shown in Figure 10. The most notable result was Figure 10d; \( \pm 0.17 \) satellite peaks are observed, which clearly indicates a six-layer periodic superstructure just above the \( \text{SmCA}^*(q_T = 1/2) \) phase. Based on the paper written by Osipov and Gorkunov [35], we calculated the satellite peak intensity of six-layered structures. Considering the calculated results and finite dielectric constants caused by a non-zero net spontaneous polarization are observed for the observed six-layer subphase.
(qT = 2/3), we conclude that the ferrielectric structure of Figure 10e is considered to be more suitable to explain our experimental results. This structure was theoretically predicted by Emelyanenko and Ishikawa [36]. The smectic phase with six-layer periodicity has been already found between the SmC* and SmCα* phases by Wang et al. [37], but this is the first evidence of the subphase except qT = 1/3 and 1/2 between SmC* and SmCα*.

![Figure 10. Two-dimensional microbeam resonant X-ray scattering profiles at various temperatures: (a) SmCα*(qT = 0), (b) qT = 1/3, (c) qT = 1/2, (d) qT = 2/3, and (e) SmC*(qT = 1) [34]. The red arrows indicate the satellite peak positions.](image)

Further experiments were conducted and three new subphases were found by Feng et al. [38]. The results are shown in Figure 11, obtained from the mixture of Se-containing chiral liquid crystalline molecules. Between SmCα*(qT = 0) and SmCα*(qT = 1/3), subphases showing 3/8 and 5/8 resonant scattering are observed. Phase transition to this subphase was also observed by in situ texture observation by the polarized microscope equipped in the RXS system. From the calculation of relative intensities of RXS peaks based on Osipov and Gorkunov’s paper [35], we could conclude that this subphase is SmCα*(qT = 1/4) with an eight-layer periodic structure, as shown in Figure 11d. This summary is also consistent with to the simplest Farey sequence number, and the results of electric-field induced optical birefringence measurement. Furthermore, this subphase was universally observed in the different mixture of two Se-containing chiral molecules.
Figure 11. Microbeam resonant X-ray scattering intensity profiles in a binary mixture including a Se-containing chiral molecule for two-layer SmCA$^*$ (a), eight-layer $qT = 1/4$ (b), and three-layer $qT = 1/3$ (c) [38]. (d) Molecular arrangement of $qT = 1/4$ with an eight-layer periodic structure obtained from the calculation using the Osipov–Gorkunov formula [35].

Between SmCA$^*(qT = 1/3)$ and SmCA$^*(qT = 1/2)$, other different subphases are confirmed [38]. Figure 12 shows one-dimensional RXS intensity profiles along the layer normal of two Se-containing chiral molecules at various temperatures. Just above SmCA$^*(qT = 1/3)$, RXS satellite peaks were observed at $Q/Q_0 = 0.3$ and 0.7, which suggest that the subphase has a ten-layer periodic structure. Calculating RXS relative peak intensities for the respect to ten-layer periodic structures using the Osipov–Gorkunov formula and comparing electric-field induced optical birefringence measurement, we could summarize this subphase is SmCA$^*(qT = 2/5)$ and its molecular arrangement in the ten-layer periodic structure shown in Figure 12b. Furthermore, another RXS satellite peak at about $Q/Q_0 = 0.286$ ($-2/7$) was observed at the temperature between SmCA$^*(qT = 2/5)$ and SmCA$^*(qT = 1/2)$, suggesting the subphase SmCA$^*(qT = 3/7)$ with ferrielectric structure detecting by electric-field induced optical birefringence measurement. However, this satellite peak sometimes overlaps the RXS satellite peak at $Q/Q_0 = 0.3$ due to the coexistence of two subphases, and it is difficult to determine the structure decisively. We would like to perform more delicate measurements in the future.

In this way, the existence of suphases, which have not been recognized before, was clarified in addition to the three- and four-layered structures (SmCA$^*(qT = 1/3)$ and SmCA$^*(qT = 1/2)$). Similar subphases are theoretically predicted by Emelynaneko and Osipov [39]; they considered the frustration between ferroelectric SmC$^*$ and antiferroelectric SmCA$^*$ and resulting degeneracy lifting by long-range interlayer interaction due to the discrete flexoelectric effect, they predicted subphases that could emerge, and, in these subphases, $qT = 1/4$ is contained between SmCA$^*(qT = 0)$ and SmCA$^*(qT = 1/3)$. They also predicted the emergence of $qT = 3/7$ (seven-layer periodic structure) but not the emergence of $qT = 2/5$ (ten-layer periodic structure), because their numerical calculations were limited to nine smectic layers in the unit cell. When the calculations are expanded to ten layers, $qT = 2/5$ with ten-layer periodicity appears [40].
Figure 12. (a) Microbeam resonant X-ray scattering intensity profiles along the layer normal as a function of the normalized scattering vector ($Q/Q_0$, where $Q_0 = 2\pi/d$ and $d$ is a layer spacing) in of the mixture of AS657 (80 wt. %) and AS620 (20 wt. %). Between three-layer ($qT = 1/3$) and four-layer ($qT = 1/2$) subphases, ten-layer ($qT = 2/5$) and seven-layer ($qT = 3/7$) subphases are observed [38].

(b) Molecular arrangement of $qT = 2/5$ with a ten-layer periodic structure obtained from the calculation using the Osipov–Gorkunov formula [35].

6. Brief Summary: My Future Plan and Expectations for Applications

Finally, in the future, it is necessary to find additional subphases in different compounds to demonstrate their universality. For this purpose, not only resonant hard X-ray scattering, which requires specific elements, but also resonant soft X-ray scattering (RSoXS) using the absorption K-edge of carbon atom would be a powerful tool [41–43], and we have just started the study using RSoXS. As for applications, large flat panels may be difficult, but applications to small, high-definition display devices [44], optical modulators [45], and microwave and millimeter-wave control devices [46] can still be expected with the advantage of a fast response time (μsec order).

Funding: This research received no external funding.

Acknowledgments: This work is strongly supported by many collaborators outside, our staff and former and students. I acknowledge all these collaborators. In particular, special thanks are due to A. Fukuda, H. Takezoe, A. Iida, and J. K. Vij who led me to the interesting field and experiments, and made significant discussion. Some of the works was carried out under the approval of the Photon Factory Advisory committee (Proposal No. 2009G586, 2011G581, 2012G105 and No. 2014G154), and the second hutch of SPring-8 BL03XU constructed by the Consortium of Advanced Softmaterial Beamline (FSBL), with Proposal No. 2015A7255.

Conflicts of Interest: The author declares no conflict of interest.
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