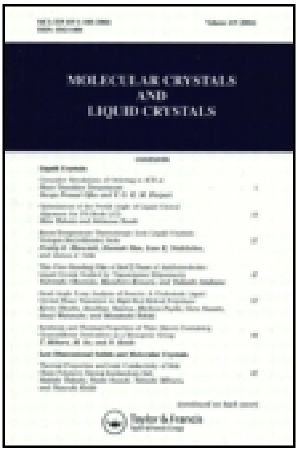

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Fin de Siècle Competition, Nematic Active or Smectic Passive, and Resulting Unimaginable Antiferroelectricity and Ferrielectricity —LCs in My Memory—

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Fin de Siècle Competition, Nematic Active or Smectic Passive, and Resulting Unimaginable Antiferroelectricity and Ferrielectricity —LCs in My Memory—

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Both ILCC and my research and educational career began in 1965, but I started to study LCs when smectic ferroelectric LCs were discovered in 1975. The 8th ILCC 1980 Kyoto gave rise to a belief that ferroelctricity must play an important role in the next generation LC displays such as wall-mountable color LC TVs, a big dream at that time. Unfortunately things didn't quite work out that way; now the market is full of TFT nematic color LC TVs. Scientifically, however, I have successfully clarified several unexpected LC aspects, some of which are so intriguing and reverberating even now. This is a 45-year story how I studied a cross section of LCs with my young capable colleagues in the most exciting historical background, woven by ILCCs as the warp and by the synclinic ferroelectric and anticlinic antiferroelectric orderings as the woof.

Keywords Antiferroelectricity; ferrielectricity; ferroelectricity; ILCC; ILCS; long-range interlayer interactions

1. A 'Groping-Blindly-in-the-Dark' Sort of Period

My research and educational activities started in 1965, when I finished my PhD graduate course and took the first step as a research associate. I was studying the optical properties of alkali halides, but not liquid crystals (LCs), at that time. In the same year, 1965, at Kent in Ohio, Glenn Brown organized the 1st International Liquid Crystal Conference (ILCC), and the 2nd one also at Kent in 1968. Since then, ILCCs have been regularly held in even-numbered years in various places across the globe; this one at Krakow is 23rd. These ILCCs are used as a chronological reference frame of 'LCs in My Memory' as illustrated in Figure 1. I didn't have a chance to talk with Glenn Brown during his lifetime. But in 1997 when I participated in the dedication of the new Building for Liquid Crystal Institute, I enjoyed the day's event

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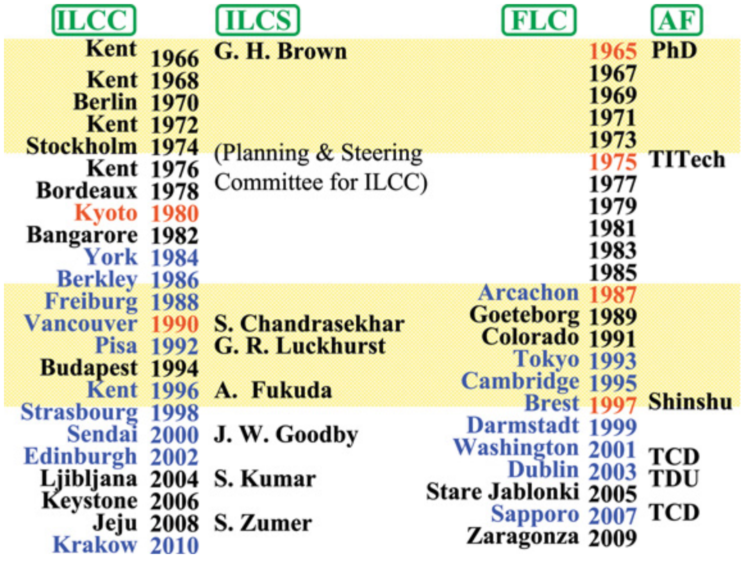

ILCC		ILCS	FLC		AF
Kent	1966	G. H. Brown		1965	PhD
Kent	1968			1967	
Berlin	1970			1969	
Kent	1972			1971	
Stockholm	1974	(Planning & Steering Committee for ILCC)		1973	
Kent	1976			1975	TITech
Bordeaux	1978			1977	
Kyoto	1980			1979	
Bangarore	1982			1981	
York	1984			1983	
Berkley	1986			1985	
Freiburg	1988		Arcachon	1987	
Vancouver	1990	S. Chandrasekhar	Goeteborg	1989	
Pisa	1992	G. R. Luckhurst	Colorado	1991	
Budapest	1994		Tokyo	1993	
Kent	1996	A. Fukuda	Cambridge	1995	
Strasbourg	1998		Brest	1997	Shinshu
Sendai	2000	J. W. Goodby	Darmstadt	1999	
Edinburgh	2002		Washington	2001	TCD
Ljibljana	2004	S. Kumar	Dublin	2003	TDU
Keystone	2006		Stare Jablonki	2005	
Jeju	2008	S. Zumer	Sapporo	2007	TCD
Krakow	2010		Zaragonza	2009	

Figure 1. Chronological reference frame of 'LCs in my memory'. Abbreviations used are: ILCC (International Liquid Crystal Conference), ILCS (International Liquid Crystal Society), FLC (International Conference on Ferroelectric Liquid Crystals), TITech (Tokyo Institute of Technology), Shinshu (Shinshu University), TCD (Trinity College Dublin), and TDU (Tokyo Denki University). (Figure appears in color online.)

and was able to see his family, Mrs. Brown, Jessie and daughter, Barbara. Some snapshots are given in Figure 2.

It was 1975 that I started to study LCs, when I found a position at Department of Organic and Polymeric Materials, Tokyo Institute of Technology (TITech). I was working there until my compulsory retirement at the age of 60 in 1997. The first half of my TITech 22 years was a 'groping-blindly-in-the-dark' sort of period, as I changed my research field from alkali halides to LCs. After 10 years or so, I was really enjoying LC research in the 2nd half. In TITech there was Eiichi Kuze as a Full Professor. He invited me as an Associate Professor, and allowed me to choose a topic of my research as well as a Research Associate I would collaborate with. I chose LCs as one of the main organic materials to be studied, and invited Hideo Takezoe as a Research Associate. Figure 3 is a photo taken at that time: In addition to the three of us, we can see Katsumi Kondo, our PhD graduate student, who entered Hitachi after graduation and developed super-TFT nematic LCDs using in-plane switching mode [1,2].

When I moved to TITech, just then, ferroelectricity in the chiral tilted smectic LC phase, designated as SmC^*, was discovered by Bob Meyer *et al.* [3] At that time, segment-driven twisted nematic displays were already used in wristwatches and calculators, but a large majority in the LCD community felt it difficult to develop matrix-driven twisted nematic LCDs of good performance. Under these circumstances, Bob Meyer presented a plenary lecture at the 6th ILCC 1976 Kent and wrote in the proceedings [4]: 'Especially interesting are the possible switching effects in very thin layers between conducting glass plates, in which surface pinning effects may be utilized to achieve an electro-optical memory.' Since the optical bistability was

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MATERIALS SCIENCE BUILDING

Friday, June 6, 1997
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Figure 2. Glenn Brown and Horst Sackmann at the 1st ILCC 1965 Kent [H. Stegemeyer, Liq. Cryst. Today, **4** (No. 1), 1 (1994)]. Two snapshots at the dedication of the new building for Liquid Crystal Institute. From right to left in the middle photo: George Gray, Bill Doane, Alfred Saupe, and Atsuo Fukuda. (Figure appears in color online.)

Figure 3. Members of Kuze Lab at TITech in 1978. From right to left in the front line: Katsumi Kondo, Hideo Takezoe, Atsuo Fukuda, and Eiichi Kuze.

considered to be useful for the realization of large-scale high-quality LCDs, such as wall-mountable color LC TVs, a big dream at that time, some groups in Japanese academic institutions, including mine at TITech, began to study the structures and properties of smectic Ferroelectric LCs (FLCs). Thus I entered into the LC wonderland with several textbooks under my arm. This is a story how I studied a cross section of LCs with my young capable colleagues in the most exciting historical background.

The 8th ILCC 1980 Kyoto was organized by Seimin Takeda. There were two impressive lectures: One was made by Tadashi Sasaki (Sharp Corporation), who clearly showed the right direction in which the R & D of LCDs should be performed and told LCD's future confidently [5]. And the other was made by Noel Clark and Sven Lagerwall [6]. These lectures produced a major shock wave that extended beyond the academic community, and many industrial people came to believe that smectic FLCs must be the materials of the next generation LCDs. An unbelievably large number of chemistry-related companies synthesized tens of thousands of related compounds. Utilizing these abundant materials, various manufacturers in the electrical, optical, and machinery industries prototyped smectic LCDs. Such R & D trends gave me an entirely favorable research environment; my Lab at Faculty of Engineering, but not at Faculty of Science, in TITech was full of capable, well-motivated graduate students and researchers who were allowed access to those newly synthesized precious smectic LCs. What did that enthusiasm bring about? Now the market is full of large-sized flat-screen color LC TVs, which utilize nematic LCs and TFT active-matrix electrodes in masterly ways. Bang went the realization of that dream using smectic LCs and passive-matrix electrodes. My involvement in this matter cannot be considered fruitful from a technological point of view. Scientifically, however, Fortune smiled on us; my colleagues and I have successfully clarified several unexpected structures and properties.

2. My Happy TITech Second Half Period

Among newly synthesized smectic LCs, a group of interesting materials were included, and became a main topic of my 2nd period in TITech. It was started from the 1st International Conference on FLCs held at Bordeaux-Arcachon in 1987 (1st FLC 1987 Arcachon), which was organized by Sven Lagerwall. There was an interesting report by Kenji Furukawa *et al.* (Chisso Corporation) that one of their newly synthesized compounds, later nicknamed MHPOBC, showed a characteristic switching with conspicuous DC threshold. They considered that the switching was observed in a novel phase other than the ordinary ferroelectric SmC^* phase [7]. After some struggles, we clarified the novel phase is antiferroelectric tilted smectic. The directors in adjacent layers are almost anticlinic, aside from a slight precession from layer to layer; hence the director forms macroscopic helical structure. We designated the phase as SmC_A^*. The antiferroelectricity and the anticlinic structure were confirmed by observing the polarization reversal current and the disappearance of the full-pitch Bragg reflection band, respectively [8,9].

MHPOBC gave us another fruit, a novel *ferrielectric* phase. It emerges in a narrow temperature range between anticlinic antiferroelectric SmC_A^* and synclinic ferroelectric SmC^* [10]. After studying several properties, we proposed the three-layer ferrielectric model, one synclinic ferroelectric and two anticlinic antiferroelectric orderings in a 3-layer unit cell, as shown in Figure 4(a) [11]. Since the emergence

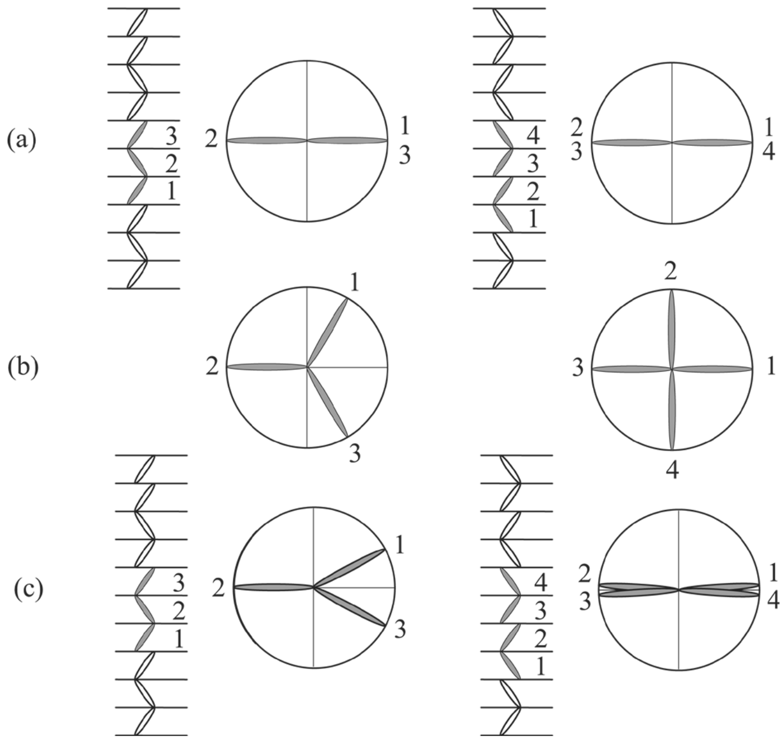

Figure 4. (a) Ising, (b) clock, and (c) modified models for 3- and 4-layer superstructures.

of the ferrielectric phase results from the frustration between SmC_A^* and SmC^*, and since the ratio of the synclinic ferroelectric odering in the unit cell,

$$q_T = \frac{[F]}{[A] + [F]}, \tag{1}$$

is equal to 1/3, we will designate the ferrielectric phase as SmC_A^* ($q_T = 1/3$) or Sm$C_A^*(1/3)$. Here [F] and [A] are the numbers of the synclinic ferroelectric and anticlinic antiferroelectric orderings in the unit cell, respectively. The q_T number plays an important role. In fact, the average tilt angle and the spontaneous polarization are about 1/3 of those in SmC^*. Moreover, the macroscopic helical pitch, $p(\mathrm{Sm}C_A^*(q_T))$, can be approximately given by

$$\frac{1}{p(\mathrm{Sm}C_A^*(q_T))} = \frac{q_T}{p(\mathrm{Sm}C^*)} + \frac{1 - q_T}{p(\mathrm{Sm}C_A^*)}, \tag{2}$$

where the macroscopic helical pitches of SmC_A^* and SmC^*, $p(\mathrm{Sm}C_A^*)$ and $p(\mathrm{Sm}C^*)$, have the opposite signs [12,13]. Now let me introduce the first authors of my favorite JJAP papers [9,10]. Dr Anti and Dr Ferri, Chandani-Perera and Ewa Gorecka, are snapshotted in Figure 5. E. Gorecka has a plenary lecture (P4) on Thursday and A. D. L. Chandani-Perera is a coauthor of an invited talk (I5) given by Ken Ishikawa on Monday in this Conference.

Figure 5. Dr Anti and Dr Ferri. A. D. L. Chandani-Perera (right) and Ewa Gorecka (left) on New Year's Day in 1990 at my flat in Tama Plaza, Yokohama. (Figure appears in color online.)

Meanwhile Tadaaki Isozaki, who was staying in my Lab for studying the structures and properties of smectic LCD materials on assignment from Showa Shell Sekiyu K. K. and later moved to Sony to develop LCoS-projection-type displays [14], systematically drew Electric-field–Temperature ($E-T$) phase diagrams in several binary mixtures; he concluded that several biaxial subphases emerge on the high temperature side of SmC_A^* as a result of the competition between the anticlinic antiferroelectric SmC_A^* and the synclinic ferroelectric SmC^* main phases [15,16]. So we decided to keep using q_T, the ratio of the ferroelectric ordering in the unit cell, to specify the observed biaxial subphases, proposing a 4-layer Ising model with $q_T = 1/2$ for the novel antiferroelectric subphases nicknamed as AF as shown in Figure 4 (a). The main phase SmC_A^* has $q_T = 0$, and it increases monotonically with temperature, becoming $q_T = 1$ in the other main phase SmC^*. In-between two prototype subphases with $q_T = 1/3$ and $1/2$ may emerge, and in addition, there may appear some additional subphases with such q_T's as located in the three possible regions, $0 < q_T < 1/3$, $1/3 < q_T < 1/2$, and $1/2 < q_T < 1$. Puzzling facts were the emergence of the uniaxial subphase designated as SmC_α^* and the phase emerging sequences which change apparently with decreasing the strength of antiferroelectricity as shown in Table 1. Cepic and Zeks [17] were the first to suggest the SmC_α^* short-pitch helical structure, but I could not believe their prediction. How on earth could the next nearest neighbor smectic layers interact? Moreover, all of our experimental data at that time indicated the staircase characters of SmC_α^* [18–21]. Consequently I thought some fluctuational effects must be responsible for the emergence of

Table 1. Phase emerging sequences. With decreasing the strength of antiferroelectricity, the sequence seems to vary from Type [i] to [vi]

Type	Phase emerging sequence
[i]	SmC_A^*–SmC_α^*–SmA
[ii]	SmC_A^*–SmC_A^*(1/3)–SmC_α^*–SmA
[iii]	SmC_A^*–SmC_A^*(1/3)–SmC_A^*(1/2)–SmC_α^*–SmA
[iv]	SmC_A^*–SmC_A^*(1/3)–SmC_A^*(1/2)–SmC^*–SmC_α^*–SmA
[v]	SmC_A^*–SmC_A^*(1/3)–SmC^*–SmC_α^*–SmA
[vi]	SmC_A^*–SmC^*–SmC_α^*–SmA

uniaxial SmC_α^*. This was my fault anyway, although my young colleagues in TITech were so reliable that their data are correct even now; the staircase characters have been recently ascribed to the electric-field-induced deformation of the short-pitch helical structure [22–25].

In this way, the good old days in TITech was going by in a flash. Two memorable events regarding ILCCs and FLCs. One is the establishment of the International Liquid Crystal Society (ILCS) at the 13th ILCC 1990 Vancouver on the basis of the Planning and Steering Committee of ILCC. The Founder President was S. Chandrasekhar, who wrote a message in the first issue of ‘Liquid Crystals Today’, News Letter of ILCS [26]. It had been published as the printed edition until Volume 9 (1999); ‘Liquid Crystals Today’ was relaunched in April 2000 as the on-line edition, to which all ILCS members are given free access by visiting its website. Results of the first elections held by ILCS were announced by S. Chandrasekhar at the 14th ILCC 1992 Pisa, Italy: President Geoffrey Luckhurst and Vice-President Shunsuke Kobayashi. In accordance with the ILCS bylaws, the term of office of all the officers of the Society is two years, and the President and Vice-President who are elected by the membership can serve for consecutive terms. Successive Presidents are listed in Figure 1. Vice-President John Goodby and I were elected at the 16th ILCC 1996 held in its birth place, Kent State University [27], and our appointments were also confirmed at the 17th ILCC 1998 Strasbourg [28].

The other is the 4th FLC 1993 Tokyo I hosted. There I learned from Jacques Prost how to understand Isozaki’s data in terms of ‘the degeneracy lifting at the frustration point’ [29,30]. The phase transition between anticlinic antiferroelectric SmC_A^* and synclinic ferroelectric SmC^* is usually treated by simply considering such a free energy,

$$const - \alpha(T - \mathrm{T_c})cos\phi - Q\ cos2\phi. \tag{3}$$

Here ϕ is the azimuthal angle difference of the director between adjacent layers [31–33]. At lower temperatures SmC_A^* is stable and the minimum at $\phi = \pi$ is lower than that at $\phi = 0$, whereas SmC^* becomes stable at higher temperatures and the minimum at $\phi = 0$ becomes lower. At the phase transition temperature $\mathrm{T_c}$, a large number of superstructures characterized by the mixture of the synclinic ferroelectric and anticlinic antiferroelectric orderings must have the same free energy. When the short-range interlayer interactions (SRILIs) alone are operative, these superstructures are degenerate. Any long-range interlayer interactions (LRILIs) lift the degeneracy and stabilize some of the superstructures to exist as intermediate subphases in finite temperature ranges between the main phases, SmC_A^* and SmC^*.

The subphases can be specified by q_T given in Eq. (1), and a lower-temperature subphase is expected to have a smaller q_T than a higher temperature one, as the LRILIs must be weak. In solid state layered crystals, LRILIs appear easy to find, but in smectic liquid crystals, where positional correlations between molecules in layers which are not adjacent are completely negligible, it is hard to consider any interactions even between next nearest neighbor layers. After having examined some obvious candidates of LRILIs in vain, they demonstrated that thermally excited polarization fluctuations must play an important role. The LRILI due to the polarization fluctuations explain the staircase characters to some extent, but not the emergence of both biaxial and uniaxial subphases, in particular, Sm$C_A^*(1/3)$ which is the most stable and hence the most frequently observed biaxial subphase.

3. Compulsory Retirement from TITech

Thus my retirement from TITech started with a fundamental question: What LRILIs are conceivable? I studied this matter in several institutions, Shinshu University, Trinity College Dublin (TCD), Tokyo Denki University (TDU), and TCD again, as indicated in Figure 1. In the first resonant X-ray scattering paper in 1998 [34,35], Mach *et al.* concluded that the 3- and 4-layer subphases, Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$, should have such clock model structures, contrary to our original Ising model structures, as illustrated in Figure 4(b). But these clock models contradicted the experimentally confirmed macroscopic helical structures, and such modified models as shown in Figure 4(c) were proposed subsequently [36,37]. The modified models are much closer to the Ising models, so we can still unambiguously define the q_T number, if we re-interpret [F] and [A] as the numbers of *quasi*-synclinc ferroelectric and *quasi*-anticlinic antiferroelectric orderings in a unit cell, respectively. The modified models puzzled me a lot !!! The ordinary chiral interaction produces the macroscopic long-pitch helical structure. Almost all other intermolecuar interactions favor their parallel alignment; why the additional microscopic short-pitch distorted helical structure emerges?

Emelyanenko and Osipov [38] resolved the puzzle quite intuitively. At the same time, they naturally explained the staircase character of the subphase emergence, which I kept insisting on as the experimentally observed fact [21]. They put aside the flat Ising model and took a more realistic planar rotator model to account for the appearance of the microscopic short-pitch distorted helical structure. Their total free energy consists of two parts, polarization-independent part and polarization-dependent part,

$$F = \sum_{i=1}^{N} (F_i + \Delta F_i), \tag{4}$$

where N is the total number of smectic layers and the free energy F_i does not depend on the polarization. Assuming that the tilt angle θ is constant, they wrote the free energy F_i as

$$F_i = F_0(\theta) - a(\theta)\frac{\Delta T}{T^*}(cos\,\varphi_{i-1,i} + \cos\varphi_{i,i+1}) - b(\theta)(cos^2\,\varphi_{i-1,i} + cos^2\,\varphi_{i,i+1}). \tag{5}$$

The first term $F_0(\theta)$ is the same for all the layers and depends on the tilt angle θ, and the second and third terms depend not only on θ but also on the relative orientation of the director $\mathbf{n}_i$ specified by the azimuthal angle φ_i, where $\Delta T \equiv T - T^*$, and T^* is the transition temperature between synclinic SmC^* and anticlinic Sm$C_A{}^*$ in the absence of any subphases. All the polarization dependent terms are included in ΔF_i which is written as

$$\Delta F_i = \frac{1}{2\chi}\{\mathbf{P}_i^2 + g(\mathbf{P}_i \cdot \mathbf{P}_{i+1} + \mathbf{P}_i \cdot \mathbf{P}_{i-1})\} + c_\mathrm{p}(\mathbf{P}_i \cdot \xi_i) + c_\mathrm{f}\cos\theta(\mathbf{P}_i \cdot \Delta\mathbf{n}_{i\pm1}). \quad (6)$$

The polarization-dependent part consists of the piezoelectric and flexoelectric polarization effects as well as the polarization-polarization interactions. As you see, they considered the interactions between adjacent layers only, and took account of g, the molecular positional correlation in adjacent layers, which must be small [29,30].

Let's take such a flat 4-layer superstructure given in Figure 4(a) as a starting arrangement, for example. The piezoelectric polarization emerges perpendicularly, whereas the flexoelectirc polarization is parallel to the tilt plane. The point is that the total polarization in layer i is not necessarily parallel to that in layer $i \pm 1$. So minimizing the total free energy rearranges polarization to form a new non-flat superstructure with the 4-layer periodicity. In other words, we can say that effective LRILIs result from the polarization-dependent part, although we are considering the interactions between adjacent layers only. Such minimization was actually done by considering unit cells consisting of up to 9 smectic layers. Several subphases emerge between the main phases, SmC_A^* and SmC^*, as temperature increases, and their stability range depends on g and $c_\mathrm{f}/c_\mathrm{p}$ as illustrated in Figure 6. The details of the unit

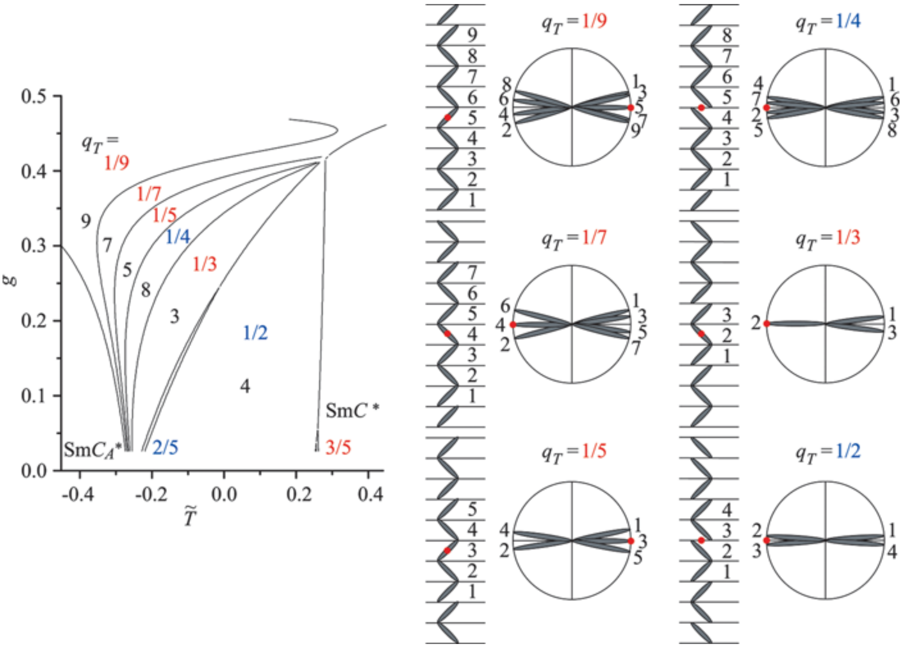

Figure 6. Emelyanenko-Osipov model. The $g - \widetilde{T}$ phase diagram indicates the staircase character of the subphase emergence. Ferrielectric subphases are specified with red q_T's, whereas antiferroelectric ones with blue q_T's. The unit cells are also given. See text for details. (Figure appears in color online.)

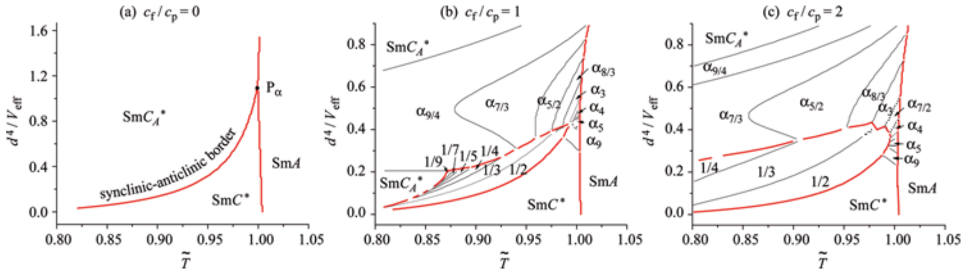

Figure 7. Extended Emelyanenko-Osipov model. Phase diagrams can naturally, though roughly, explain the emergence of uniaxial SmC_α^* and varieties of phase emerging sequences. See text for details. (Figure appears in color online.)

cells are also given in the figure. Their unit cells are 9, 7, 5, 8, 3, and 4 smectic layers in the oder of increasing temperature; the emergence of some additional subphases in the narrow areas were also suggested. The number of smectic layers doesn't change monotonically. But if we use q_T, it increases monotonically with temperature, as the LRILIs must be weak. Moreover, the tilt directions in different layers are antisymmetric with respect to the middle of the period, indicated by the closed (red) circles. So each subphase has a microscopic distorted helical structure, and its short-pitch is uniquely determined by q_T as

$$|p_{qT}| = \frac{2}{1 - q_T}. \tag{7}$$

When either of the denominator or numerator of q_T (an irreducible fractional number) is even, the number of smectic layers contained in the unit cell is equal to twice the denominator and the subphase may be antiferrolectric; otherwise, the denominator directly indicates the size of the unit cell and the subphase must be ferrielectric. Needless to say, neither q_T nor the number of smectic layers in the unit cell can uniquely determine the subphase superstructure even qualitatively; we generally need to find out the superstructure with the minimum free energy. In this original treatment, the macroscopic long-pitch helical structure of subphases is not taken into account and hence the superstructures are considered commensurate.

The LRILIs now become understandable intuitively; in particular, two questions below are answered appropriately, (1) why superstructures with unit cells consisting of three or more smectic layers are formed, although no direct interlayer interactions are operative between smectic layers that are not adjacent? and (2) why the director twists largely from layer to layer to form microscopic short-pitch distorted helical structures, although almost all the intermolecular interactions force molecules to become parallel one another? To make more detailed comparison between calculated and experimental results, we need to specify the SRILIs more clearly. We did this by considering that the anticlinic ordering is stabilized by transverse dipole-dipole correlation in adjacent layers, whereas the synclinic ordering is treated phenomenologically in terms of the spherical expansion. Thus we obtained the phase diagram shown in Figure 7(a) [33]. Here d is the normalized transverse dipole moment, V_{eff} is the normalized effective parameter in the spherical expansion, and hence the ordinate d^4/V_{eff} represents the ratio in strength between antiferroelectricity and ferroelectricity. When this ratio is large, say 1.5, the direct transition from SmC_A^* to SmA occurs. For its small value, say 0.5, the SmC_A^*–SmC^* transition is observed when crossing the synclinic and anticlinic border. In this phase diagram, SmC_A^* is always stabilized at lower temperatures.

By combining these SRILIs and LRILIs, we obtain the phase diagrams, which critically depend on another parameter c_f/c_p, the ratio between flexoelectric and piezoelectric coefficients, as illustrated in Figure 7 (b) and (c) [39]. Now the emergence of uniaxial SmC_α^* is naturally understood by the degeneracy lifting at the frustration point of three main phases, SmC_A^*, SmC^*, and SmA. In fact, SmC_α^* emerges around that point, and has the microscopic helical structure with commensurate short pitches with periodicities up to 9 smectic layers. Both commensurate character and discrete stepwise temperature variation result from their limited numerical calculations performed by considering subphase superstructures with unit cells consisting of up to 9 smectic layers. If an infinite number of smectic layers could be taken account of, we would naturally foresee the incommensurate short-pitch helical structure and its continuous change with temperature, which are experimentally well established [34,35,40–50]. The phase emerging sequences that apparently change with decreasing the strength of antiferroelectricity as illustrated in Table 1 can naturally, though roughly, be explained by the phase diagrams illustrated in Figure 7 (b) and (c). Moreover, the figure reproduces the experimentally observed temperature variation of the SmC_α^* short-pitch, which characteristically depends on the phase emerging sequences summarized in Table 1. For example, the SmC_α^* short-pitch increases with temperature for sequence [i], whereas it decreases for sequences [v] and [vi] [22,34,35,45–48]. Although no detailed calculations have been made yet, the phase diagrams allow for the emergence of subphases other than Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$; see, in particular, the narrow temperature regions between Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$ and between Sm$C_A^*(1/2)$ and SmC^* in the $g - \widetilde{T}$ phase diagram given in Figure 6 [38,51].

Many remain unexplained, of course, as the intermolecular interactions are so complicated. For example, the first-order phase transition is observed between SmC_A^* and SmC_α^* and between SmC^* and SmC_α^* experimentally, but the above theoretical treatments always predict a continuous change but not the phase transition. We suspect that the elastic energy for the large twist in SmC_α^* critically depends on the director tilt angle and may cause the first-order transition observed experimentally [22]. Similarly, the boundary between the biaxial subphases and SmC_α^* is not easy to calculate accurately in the phase diagrams in Figure 7 (b) and (c). Furthermore, the most frequently observed subphase is Sm$C_A^*(1/3)$ empirically, but the most stable subphase that the above theoretical treatments predict is Sm$C_A^*(1/2)$. Things are much better than you think, though. We can improve the phase diagrams in various ways by taking account of various additional intermolecular interactions [51,52]. So far as we are aware of, four theoretical models for the LRILIs have been proposed, which can predict the emergence of subphases other than Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$ [38,53–55]. Among them, the Emelyanenko-Osipov model exactly grasps the essential points so that the emergence of Sm$C_A^*(0 < q_T < 1/3)$ and Sm$C_A^*(1/3 < q_T < 1/2)$ can be predicted appropriately. Note that their existence was insisted on by Isozaki *et al.* in the early stage of the subphase investigations [15,16,21].

4. Illuminating Remarks

Last year, Sandhya *et al.* further firmly established that there exist some additional intermediate subphases other than Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$. They measured the

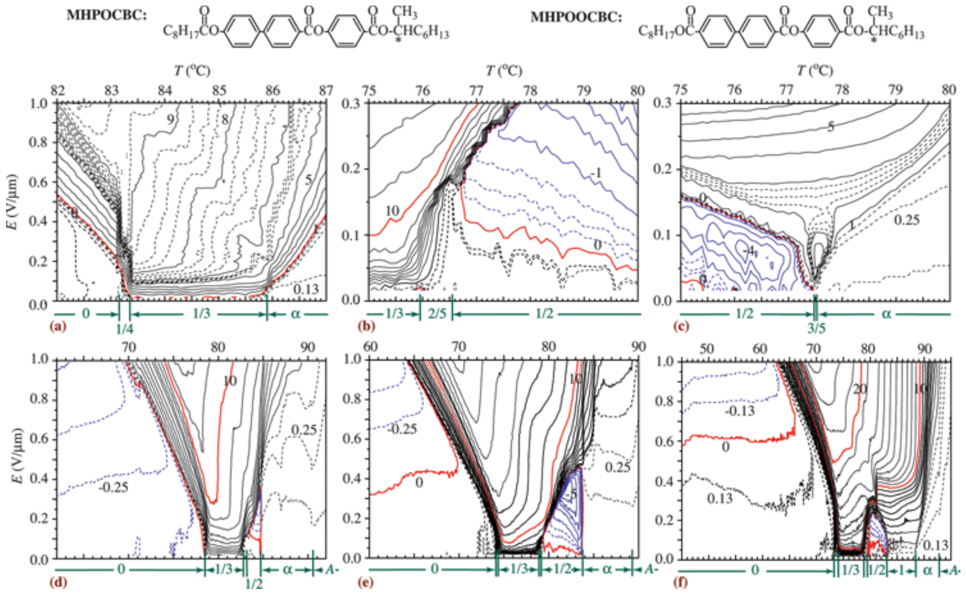

Figure 8. E–T phase diagrams with field-induced birefringence contours. We can see three additional subphases other than Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$ [(a), (b), and (c)], several field-induced stable states [(a), (d), (e), and (f)], and the staircase character of SmC_α^* [(d) and (e)]. MHPOOCBC concentrations are (a) 38, (b) 60, (c) 65, (d) 50, (e) 55, and (f) 70 wt.%. (Figure appears in color online.)

electric-field-induced birefringence by using a photoelastic modulator, and drew its contour lines in the Electric-field–Temperature (E–T) phase diagrams, some typical of which are shown in Figure 8 [22]. We can identify several phases at zero field as indicated at the bottom of each diagram by the q_T numbers: 0 means the SmC_A^* main phase, 1/3 and 1/2 are the well-known biaxial Sm$C_A^*(1/3)$ and Sm$C_A^*(1/2)$ subphases, and α is the uniaxial SmC_α^* subphase. In addition, we can see three additional biaxial subphases, Sm$C_A^*(0 < q_T < 1/3)$, Sm$C_A^*(1/3 < q_T < 1/2)$, and Sm$C_A^*(1/2 < q_T < 1)$. Their existence is much clearer in the expanded figures. Following the Emelyanenko-Osipov model as well as the characteristic patterns of the contour lines in Figure 8, their simplest possible assignments are Sm$C_A^*(1/4)$, Sm$C_A^*(2/5)$, and Sm$C_A^*(3/5)$. The subphase Sm$C_A^*(1/4)$ is antiferroelectric and has a unit cell consisting of 8 smectic layers, the detailed structure of which has been calculated by Emelyanenko and Osipov [38]. In the temperature region of $0 < q_T < 1/3$, it is trivial that there exist no subphase with a unit cell consisting of 6 smectic layers; the unit cell of Sm$C_A^*(1/6)$ contains 12 smectic layers and Sm$C_A^*(2/3)$ that has 6-layer periodicity does not belong to this region. The subphase Sm$C_A^*(2/5)$ is also antiferroelectric and has a 10-layer unit cell. Since Emelyanenko and Osipov performed numerical calculations by considering subphase superstructures with unit cells consisting of up to 9 smectic layers, no detailed superstructure has been obtained for Sm$C_A^*(2/5)$. Although much simpler Sm$C_A^*(3/7)$ belongs to the region of $1/3 < q_T < 1/2$, this is ferrielectric but not antiferroelectric. The subphase Sm$C_A^*(3/5)$ is ferrielectric and has a 5-layer unit cell, the detailed superstructure of which has been obtained by Osipov and Gorkunov [56]. The emergence of antiferroelectric SmC_A^*(2/3) has been predicted by Matsumoto *et al.*, Hamaneh and Taylor, and Dolganov *et al.* [53–55]. I really wish to check the assignments by resonant X-ray scattering. Then we can prove the appropriateness of the Emelyanenko-Osipov model.

Most recently, Wang *et al.* observed the superstructure with 6-layer unit cell by resonant X-ray scattering [57]. I am deeply impressed by this observation, as I have kept insisting on the emergence of subphases with unit cells larger than 4 smectic layers. But the mixtures they studied exhibit the unusual phase sequence, where the 4- and 6-layer phases emerge at higher temperatures than SmC^* [58–60]. Consequently, we need to reconsider the fundamental premise that SmC_A^* is the low-temperature main phase of SmC^*. The extraordinary variety of intermolecular interactions sometimes makes it possible to stabilize SmC^* absolutely at lower temperatures instead of SmC_A^*. Such a situation is typically seen in the binary mixture phase diagram of MC881 and MC452 studied by Song *et al.* [61]. The border line between SmC_A^* and SmC^* runs almost parallel to the ordinate temperature axis, so we can define the critical concentration, r_c. The antiferroelectric main phase, SmC_A^*, does not seem to be stabilized even at the absolute zero temperature in the concentration range above r_c. So, modifying the SRILIs appropriately, the same effective LRILIs resulting from Eq. (6) must reproduce the observed unusual phase sequence. Such calculations have not yet been performed.

This mixture system gave us another very interesting phenomenon, the continuous change from SmC_A^* to SmC^*, as reported by Ken Ishikawa on Monday (I5) and by Jagdish Vij on Thursday (O87) in this Conference. Here I just would like to refer to the importance of the degeneracy lifting due to the thermal linkage of the two minima in Eq. (3). Usually, we resort to the absolute zero temperature approximation and do not consider any thermal linkage between the two minima, but near the critical concentration, the free energy difference between the minima must be extremely small in a very wide temperature range. Consequently, solitary wave movements may link these two minima thermally [32,61]. If the thermal excitation is described by the Boltzmann-type distribution, the q_T number changes continuously from 0 to 1 with increasing temperature [62].

Escaping from the absolute zero temperature approximation, we will be excited and hot in LC research !!! Let's roll up our sleeves and get ready to work with SOR, I mean, Synchrotron Orbit Radiation. Three steps must be important:

1. Draw such *E–T* phase diagrams as illustrated in Figure 8 for samples containing S, Se, or Br.
2. Look for staircases and find out stable states other than ordinary SmC_A^*(1/3) and SmC_A^*(1/2), not only in the subphases at zero field, but also in field-induced stable states of biaxial subphases and of uniaxial SmC_α^*.
3. Clarify the detailed structures of these pinpointed stable states by resonant X-ray scattering experiments.

I would like to keep a healthy respect for the complexity of liquid crystals, along with my insatiable curiosity.

In the course of my 45-year research and educational activities I have been indebted to a very large number of people and organizations; specifically I have met many attractive scientists through attending ILCCs and other related conferences and meetings from whom I have gained a great deal of enlightenment and help. I am deeply grateful to all of them for what they have done for me. Last but not least

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