Field-Induced Superlattice Structures and Effective Long-Range Interlayer Interactions in Ferrielectric Liquid Crystals

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Microbeam resonant X-ray scattering experiments recently revealed field-induced superlattice structures that have unexpectedly large unit cells consisting of 12- and 15-layers [1]. We have tried to explain their emergence by the long-range interlayer interactions (LRILIs) based on the Emelyanenko-Osipov quasi-molecular model [2] together with our primitive way of understanding the frustration in clinicity [3].

Keywords: electric-field-induced subphases, RXRS, ferrielectric phases, E-T phase diagram, 12- and 15-layer unit cells

1. Formulation

To calculate the electric-field-induced superlattice structures, we used the dimensionless free energy given in Eq. (62) of Ref. [2] after adding an electric field effect,

\[ -\frac{\chi_{\beta}E}{\sin \theta \cos \theta B (1 + 2g)} \sum_{i=1}^{t} \cos \varphi_i. \]  

The only new parameter is the effective dimensionless electric field strength \( \tilde{E} \) and the remaining four are previously used [2]. By minimizing the dimensionless free energy thus formulated with respect to \( \varphi_i \), we obtain a set of \( t \) equations for \( \varphi_i \). Now the free energies of the field-induced superlattice structures with different-size unit cells as well as SmC* are compared with one another to select the field-induced subphase that has the global minimum free energy.

2. Numerical calculations

Figure 1 lists conceivable field-induced superlattice structures with simple \( q_E \)'s in the temperature region where the ferrielectric \( q_T=1/3 \) stably exists at zero filled. Iida et al. firmly established the field-induced subphase with \( q_E=2/3 \), the unit cell of which is unbelievably large and extending over 12 layers [1]. The 12-layer unit cell of the field-induced subphase with \( q_E=2/3 \) can be considered a much simpler array of the two ferrielectric and two ferroelectric building blocks. It is not pertinent to generalize the conclusion that any field-induced subphase in the \( q_T=1/3 \) temperature region consists of an orderly array of the ferrielectric and ferroelectric blocks, and the relative ratio of the ferroelectric block becomes larger with increasing applied field; the order must be produced by the interplay of

Figure 2: Six possible superlattice flat structures with \( q_E=1/3, 1/2, 3/5, \) and \( 2/3 \).

Figure 1: We considered possible unit cells consisting of up to 15 layers, for Iida et al. confirmed the existence of 15-layer periodicity pattern in RXRS [1].
the LRILIs and the applied field. Once we introduce this simplification, we only need to calculate the free energy for six possible superlattice structures with \( q_E = 1/3, 1/2, 3/5, \) and \( 2/3 \) shown in Fig. 2.

3. Calculated results

Actual calculations were performed for parameter values used in the classical paper [2], \( \chi c_p c_t/B = -0.12 \) and \( c_t/c_p = -1.0 \). Thus we reproduced their \( g-T \) phase diagram and chose 9 points for studying the electric field effect: For \( g = 0.1, \) \( T = -0.24, -0.21, \) and \( -0.18; \) for \( g = 0.2, \) \( T = -0.21, -0.16, \) and \( -0.09; \) and for \( g = 0.3, \) \( T = -0.09, -0.02, \) and \( 0.05. \) The \( q_{E=1} \) field-induced superlattice structure with the 3-layer unit cell is basically the temperature-induced \( q_T = 1/3 \) subphase and the stability range of \( q_{E=1} \) is pretty wide.

Among the five possible field-induced superlattice structures other than \( q_{E=1} \), the \( q_{E=5} \) superlattice structure with the 12-layer unit cell exists as the most stable field-induced subphase for all the \( g \) values and temperatures investigated. The second stable field-induced subphase is the \( q_{E=3} \) superlattice structure with the 15-layer unit cell and emerges in all temperatures investigated for \( g = 0.1 \) and \( 0.2. \) Its stability range of \( E \) is narrower in \( g = 0.2 \) than in \( 0.1; \) it is not stabilized at all for \( g = 0.3. \) The remaining \( q_{E=2}, 4, \) and \( 6 \) do not exist as the field-induced subphases.

Figure 3 shows the microscopic short-pitch helical structures of the \( q_{E=3} \) and \( q_{E=5} \) subphases with the 15-layer and 12-layer unit cells, respectively. The \( q_{E=3} \) helix makes three rotations in the 15-layer unit cell, whereas the \( q_{E=5} \) helix makes two rotations in the 12-layer unit cell. The director tilting directions of all smectic layers are arranged symmetrically with respect to the \( z-x \) plane. As we expected, the deviation from the flat structures is small in both subphases. At the same time, we notice that the deviation is slightly larger in the \( q_{E=3} \) helix than in the \( q_{E=5} \) helix, when we compare both helices carefully.

4. Discussions

The calculated results are consistent with the recent SOR microbeam RXRS data. In particular, the most stable calculated \( q_{E=5} \) with the 12-layer unit cell is the same as the one determined experimentally [1]. Regarding the 15-layer unit cell, the RXRS data given in Fig. 7 of Ref. [1] clearly indicates the emergence of a field-induced-subphase with a 15-layer unit cell but could not determine its planar structure because the signal intensity is weak. However, the RXRS data is consistent with the calculated result that an applied field may stabilize \( q_{E=3} \) but not \( q_{E=4}; \) the reflection intensities of 4/15 and 6/15 are about 1/4 of the intensity of 5/15 in \( q_{E=3}, \) whereas the intensities are about 1/24 in \( q_{E=4}. \)

Figure 3 indicates that EFIB in the \( q_{E=5} \) subphase is slightly smaller than that in the \( q_{E=3} \) subphase, and hence we can understand the sigmoid-shaped contours in the \( E-T \) phase diagram observed in other mixtures [3]. A weak point of this simplest way of treating the frustration lies in the fact that the free energy of actual SmC* is not treated appropriately. A more elaborate treatment should be made in the near future by taking into account the three-phase frustration among SmC* A, SmC*, and SmA.

References: