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Direction of Flexoelectric Polarization in Smectic C_G^* Phases of Chiral Smectic Liquid Crystals

(Arah Pengutuban Fleksoelektrik dalam Fasa-fasa Smektik C_G^* bagi Hablur Cecair Khiral Smektik)

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ABSTRACT

Polarization in antiferroelectric liquid crystals has two origins: The piezoelectric polarization which is of chiral origin and the flexoelectric polarization which originates in different orientation of tilts in neighboring layers. The flexoelectric polarization is perpendicular to the tilt direction only if the structure is uniformly helicoidally modulated. In structures like SmC_{F11}^* *and* SmC_{F12}^* *the flexoelectric contribution might be significant and it can be non-parallel to the piezoelectric component. Hence it may deviates the direction of polarization from the perpendicular direction significantly. The angle formed by the polarization and the tilt is therefore general and as such the basic characteristic of the* SmC_G^* *phase can be recognized. It seems that this aspect was completely overlooked in the past. In this contribution we analyze the dependence of the polarization direction on the phase structures and on the values of piezoelectric and flexoelectric coefficients in the discrete phenomenological model.*

Keywords: Antiferroelectric liquid crystals; general tilt phase; multilayer structure

ABSTRAK

Pengkutuban di dalam hablur cecair antiferoelektrik berasal daripada dua sumber berikut: pengkutuban piezoelektrik yang berasal daripada sifat khiralnya dan pengkutuban fleksoelektrik yang berasal daripada 'tilt-tilt' di dalam lapisan terdekat yang berada dalam orientasi yang berbeza. Pengkutuban fleksoelektrik adalah berserenjang kepada arah 'tilt' sahaja jika struktur yang dikaji berbentuk 'kelopak bunga' yang seragam. Dalam struktur seperti SmC_{F11}^* *dan* SmC_{F12}^**,penyumbangan fleksoelektrik mungkin ketara dan ia adalah tidak selari kepada komponen piezoelektrik. Maka, ia mungkin menyimpangkan arah pengkutuban daripada arah berserenjang secara ketaranya. Sudut yang dibentuk daripada pengkutuban dan 'tilt' ini adalah dikatakan secara am dan ciri asal fasa* SmC_G^* *boleh dikenal pasti. Aspek ini tidak diambil kira sebelum ini. Dalam kertas ini, kami menganalisis arah pengkutuban dalam struktur tersebut berdasarkan pergantungan nilai parameter piezoelektrik dan fleksoelektrik dengan menggunakan model fenomenologi diskrit.*

Kata kunci: Fasa 'tilt' am; hablur cecair antiferoelektrik; struktur berbilang lapis

INTRODUCTION

Tilted smectic phases of antiferroelectric liquid crystals (Chandani et al. 1989) are already known for more than 20 years, and the newly discovered phenomena on the behaviours of these tilted smectic phases are still of great interest to many researchers (Fukuda et al. 1994; Takezoe et al. 2010). Smectic A (SmA) phase is the usual non-tilted smectic phase. Upon lowering the temperature, the chiral smectic liquid crystals may have phase variation according to the most general phase sequence such as: SmA $\rightarrow SmC_\alpha^* \rightarrow SmC^* \rightarrow SmC_{F12}^* \rightarrow SmC_{F11}^* \rightarrow SmC_A^*$ (Gorecka et al. 2002). The immediate phase, where the molecules within each layer tilt from the layer normal, after SmA is SmC_α^*. SmC_α^* phase is helically modulated with a pitch of only a few layers, where its behaviour depends strongly on the length of the helical modulation. The number of tilted smectic phases with distinguished polar properties is usually found within a narrow temperature region.

SmC^* and SmC_A^* phases are ferroelectric and antiferroelectric, respectively. In between these two phases, there might exist intermediate phases of SmC_{F12}^* and SmC_{F11}^* with primitive cells extending over 4 and 3 layers, respectively. These are the most complex structures in the phase sequence. It is well known now that all tilted phases have polar layers. Macroscopically, the SmC_A^* and the SmC_{F12}^* behave antiferroelectrically, while SmC_{F11}^* behaves ferrielectrically. Generally, the layer polarization is dependent on the tilt and its direction is 'expected' to be perpendicular to the tilt among these tilted smectic phases. Another smectic system of bent-core molecules can be polar even when the molecules are not tilted (Niori et al. 1996). In these materials the polar order within each layer does not depend on the tilt and layer polarization can take any general direction with respect to the direction of tilt. The smectic C phases with the general angle between the polarization and the tilt were named the SmC_G^* phase

(Bailey & Jákli 2007; Brand et al. 1998; Cladis et al. 1999; de Gennes 1993; Gorecka et al. 2008), where subscript G stands for 'general'.

In the polar smectic phases, the polarization occurs because of two reasons: Firstly, due to the hindered rotation because the molecules are tilted with respect to the layer normal – the piezoelectric effect – and secondly, because the structure is not homogeneous and the rotation is hindered due to the interactions with neighbouring layers as well – the flexoelectric effect. The induced flexoelectric polarization is rather small in the SmC* and the SmC$^*_A$ phases and it might be significant in the short pitch SmC$^*_\alpha$ phase. In these three phases the layer polarization direction is parallel to the piezoelectric polarization. In cases of SmC$^*_{F11}$ and SmC$^*_{F12}$, the flexoelectric component may not be parallel to the piezoelectric component and the resultant effect produces layer polarization which is not perpendicular to the tilt. Hence, in principle the layer polarization in these phases, which are denoted as the general SmC$^*_G$ structures, can have any directions with respect to the tilt. In reality, the tilted smectic phases with non-perpendicular layer polarization are extremely rare and are considered as a surprise.

In this article, we show that polar layers having the general SmC$^*_G$ structures exist in much simpler antiferroelectric liquid crystals formed of chiral elongated molecules. In these structures, the layer polarization deviates from the direction normal to the tilt with an angle, δ. In our calculations, we have shown the influence of flexoelectric coefficient μ and the structure of the smectic system on the deviation angle δ. In the next section, we reviewed the background of the theory on piezoelectric and flexoelectric components of polarization and the calculation leading to the layer polarization. Next, we give the calculations of δ and polarization which correspond to the structures of the smectic systems. The results and discussion on the influence of these polarization components for the structures of SmC$^*_\alpha$, SmC$^*_{F12}$ and SmC$^*_{F11}$ phases are shown in the following section. We conclude the study in the final section.

The Piezoelectric and The flexoelectric Components of Polarization

The piezoelectric polarization appears because the molecular rotation about the long axis is hindered (Čepič & Žekš 2001). If molecules are not perfectly symmetric, they tilt in order to reduce the voids between the molecules and when they are tilted all the orientations around the long molecular axis are not equivalent anymore if molecules are chiral. There exists one direction which is more favourable than the others and as a consequence the molecule spends on average more time oriented close to this direction. The result is that the ensemble average of molecular dipoles is not zero anymore and the polarization perpendicular to the tilt and the direction defined by the chirality of the molecules appears (Muševič et al. 2000). The phenomenon is called the piezoelectric effect because it appears when layers shrink due to the tilt although it is not the consequence of change in pressure (Lagerwall 1999). The contribution to the free energy is given by the phenomenological term $c_p\left(\vec{P}_j \times \vec{\xi}_j\right)_z$, where the c_p is the piezoelectric parameter which has opposite signs in enantiomers of the same material having the opposite handedness. The contribution to the free energy due to the flexoelectricity is $\frac{1}{2}\mu\vec{P}_j.\left(\vec{\xi}_{j+1} - \vec{\xi}_{j-1}\right)$, where the μ is the flexoelectric coefficient. This is the discrete form of the flexoelectric term in the continuous theoretical model for the ferroelectric liquid crystals by Pikin and Indebom (1978). The fact that different molecular orientations above and below the considered layer affect the molecular rotation along the long axis of the considered layer and as a consequence an additional polarization is induced. The free energy contribution due to the layer polarization is:

$$G_{P,j} = \frac{1}{2}b_0P_j^2 + \frac{1}{4}b_1\left(\vec{P}_j.\vec{P}_{j+1} + \vec{P}_j.\vec{P}_{j-1}\right) + c_p\left(\vec{P}_j \times \vec{\xi}_j\right)_z + \frac{1}{2}\mu\vec{P}_j.\left(\vec{\xi}_{j+1} - \vec{\xi}_{j-1}\right), \qquad (1)$$

where the first two terms express the electrostatic energy due to the induced polarization (b_0) and the electrostatic interactions of dipoles in neighbouring layers (b_1). For a general system having different tilts and different polarization within layers, the polarization can be obtained by the minimization of the polar part of the free energy (1) which could be given in the matrix form as (Čepič & Žekš 2001):

$$G_P = \frac{1}{2}\,\mathbf{P{\cdot}B{\cdot}P} + \mathbf{P{\cdot}C{\cdot}\xi}, \qquad (2)$$

where $\mathbf{P}$ and ξ are $2N$ dimensional vectors which give the structures for the whole system of N layers and are defined as:

$$\mathbf{P} = \{P_{1x}, P_{2x}, \ldots, P_{jx}, \ldots, P_{Nx}, P_{1y}, \ldots, P_{Ny}\}$$
$$\boldsymbol{\xi} = \{\xi_{1x}, \xi_{2x}, \ldots, \xi_{jx}, \ldots, \xi_{Nx}, \xi_{1y}, \ldots, \xi_{Ny}\}. \qquad (3)$$

The matrix $\mathbf{B}$ is the block matrices formed of the equal $N \times N$ tridiagonal symmetric matrices $\tilde{\mathbf{B}}$ that give the couplings between polar interactions within the layer and between the neighbouring layers expressed phenomenologically.

$$\mathbf{B} = \begin{bmatrix} \tilde{\mathbf{B}} & 0 \\ 0 & \tilde{\mathbf{B}} \end{bmatrix}. \qquad (4)$$

The elements of the tridiagonal symmetric matrix are $\tilde{B}_{j,j} = b_0$ and $\tilde{B}_{j,j+1} = \tilde{B}_{j,j-1} = \frac{1}{2}b_1$. The matrix $\mathbf{C}$ is composed from four matrices forming the off diagonal anti-symmetric matrix as:

$$\mathbf{C} = \begin{bmatrix} \tilde{\mathbf{M}} & \tilde{\mathbf{C}} \\ -\tilde{\mathbf{C}} & \tilde{\mathbf{M}} \end{bmatrix}. \qquad (5)$$

The nonzero elements of the matrices are $\tilde{C}_{j,j} = c_p$ and $\tilde{M}_{j,j+1} = \tilde{M}_{j,j-1} = \frac{1}{2}\mu$. If the structure of the phase is known, one can calculate the layer polarization from the minimized equations as shown:

$$\mathbf{P} = -\mathbf{B}^{-1}\cdot\mathbf{C}\cdot\xi. \tag{6}$$

Assuming that the interlayer electrostatic polar interactions b_1 are much weaker than the polar interactions within the layer b_0, the polarization in the j-th layer can be written as:

$$\vec{P}_j = \frac{c_p}{b_0}\left(\vec{n}\times\vec{\xi}_j\right) + \frac{1}{2}\frac{\mu}{b_0}\left(\vec{\xi}_{j+1} - \vec{\xi}_{j-1}\right), \tag{7}$$

where $\vec{n}$ is the layer normal. From (7), it is clearly seen that the polarization has two contributions – the piezoelectric (c_p) and the flexoelectric (μ). In the ferroelectric SmC* phase and in the antiferroelectric SmC_A^* phase the helical modulations are long and the changes of tilt directions within the layer above and layer below which contribute to the flexoelectric polarization within the layers is very small. Therefore, even for systems where the flexoelectric coefficient μ is comparable to the piezoelectric c_p, the flexoelectric contribution is negligible.

THE INDUCED POLARIZATIONS IN SmC_α^*, SmC_{F12}^* AND SmC_{F11}^* PHASES

Within the phase sequence of antiferroelectric liquid crystals, the phase differences, i.e. the angle formed by tilts in neighbouring layers, for SmC_α^*, SmC_{F12}^* and SmC_{F11}^* can be large. Hence the component of polarization induced from flexoelectric effect cannot be neglected. The schematic structures for these three phases are given in Figure 1.

In the SmC_α^* phase, the tilts are helically modulated but the magnitude is constant in each layer. The period of this helical modulation usually extends over a few tens of layers or several layers only, which means that the phase difference between tilts in neighbouring layers can be larger than a few tenths of degrees. In this SmC_α^* phase, polarizations induced from flexoelectric and piezoelectric effects are perpendicular to the tilt (Figure 2) and the magnitude of these two components can be comparable. The magnitude of the polarization is equal in all layers and it is given by $P = (c_p + \mu)\theta$.

The SmC_{F12}^* phase has a four-layer structure with two different phase differences which sum-up to approximately π radian (Figure 3(a)). The orientations of tilts in the nearest neighboring layers above and below a reference layer are different. The flexoelectric induced polarization, represented by the difference of the tilt order parameters in subsequent layers (7), is not perpendicular to the tilt as it is illustrated in Figure 3(a). The polarization deviates from its usual perpendicular direction to the tilt with an angle δ, where δ is given by:

$$\tan\delta = \frac{\mu\cos(\alpha)}{c_p + \mu\sin(\alpha)} = \frac{(\mu/c_p)\cos(\alpha)}{1+(\mu/c_p)\sin(\alpha)}. \tag{8}$$

The sign of δ alternates from layer to layer and the direction of polarization in the odd layers forms an angle $\frac{\pi}{2}+\delta$ with the tilt. While in the even layers this angle between the tilt and the polarization is $\frac{\pi}{2}-\delta$, as shown in Figure 3(a). The deviation angle δ is the largest for

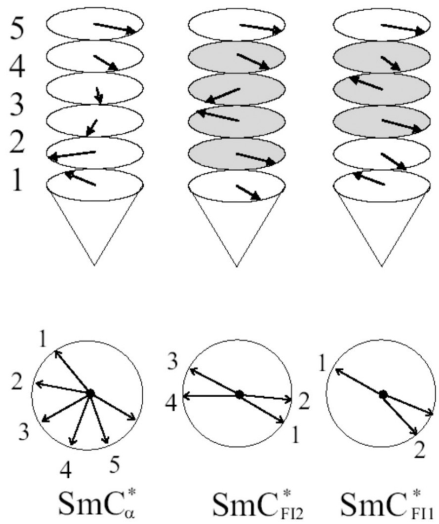

FIGURE 1. The schematic structures of the three phases (a) the SmC_α^* phase, (b) the four-layer SmC_{F12}^* phase and (c) the three-layer SmC_{F11}^* phase. Arrows denote the order parameter in the layer. The structures are presented in a 'quazi' 3D view (above) and as a projection onto the lowest layer in the structure (below)

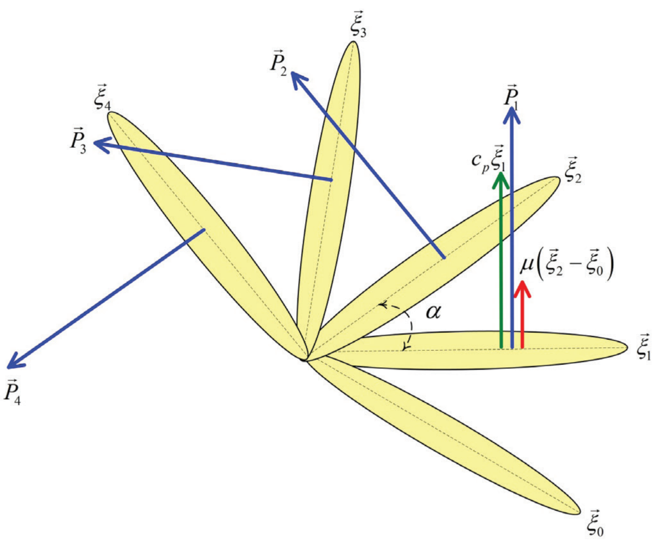

FIGURE 2. The layer polarization in the SmC_{α}^{*} phase. The polarization consists of two parts which both are perpendicular to the tilt

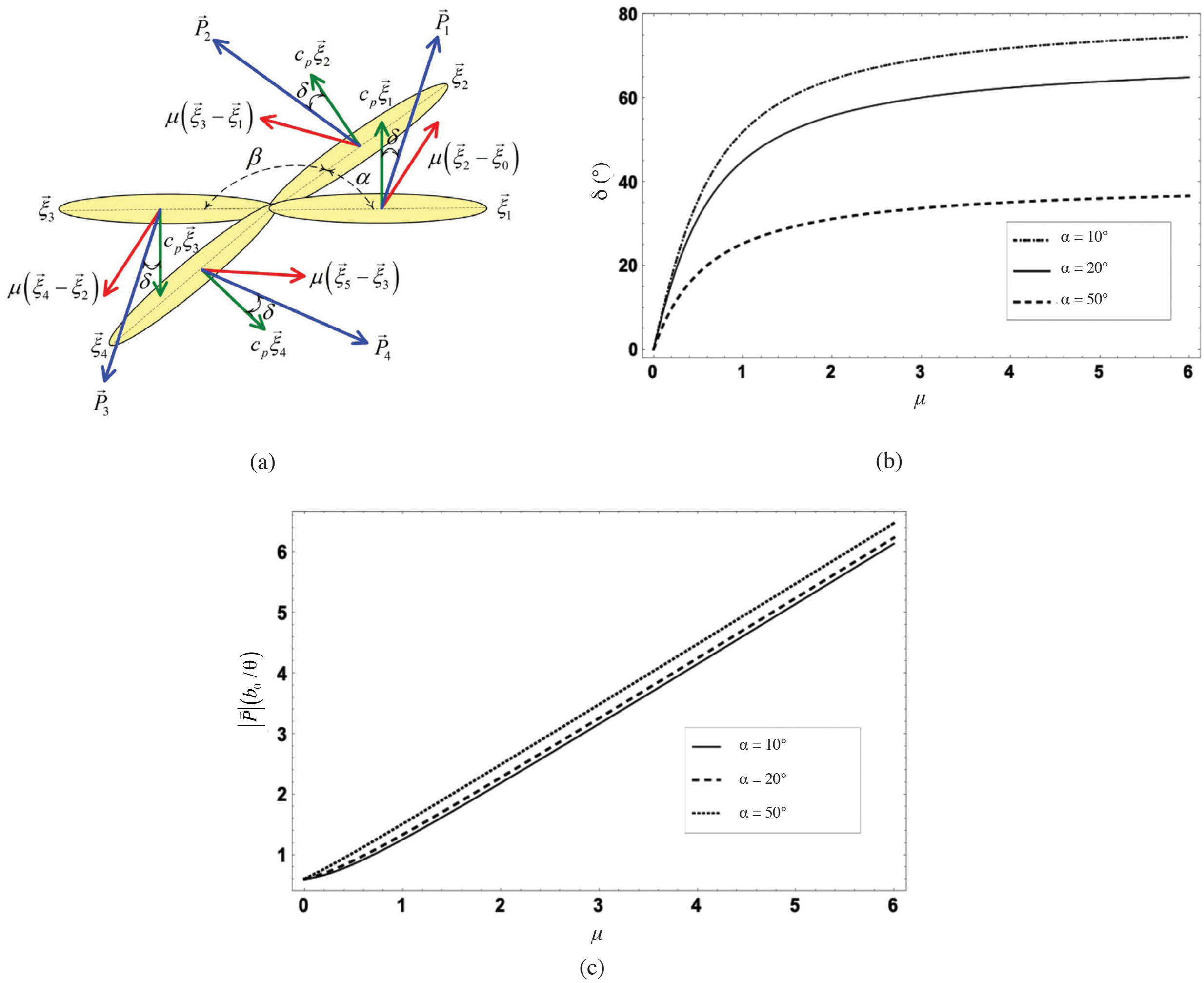

FIGURE 3. (a) The layer polarization in the four-layer SmC_{F12}^{*} phase. The polarization consists of two parts, the piezoelectric contribution is perpendicular to the tilt (green arrow) and the flexoelectric contribution (red arrow) is in the direction of the tilt difference in layers above and below. The μ dependence for three various phase difference between the neighboring layers α of (b) the deviation angle δ and (c) magnitude of polarization for the four-layer SmC_{F12}^{*} phase

the Ising-like structure of the SmC^{*}_{F12}, where the phase differences alternate between 0 and π radian. However, δ becomes 0 for the non-distorted structure where the polarization is perpendicular to the tilt and the structure is actually the structure of the SmC^{*}_{α} phase with the four-layer pitch. Figure 3(b) shows the flexoelectric μ dependence for three various phase difference between the neighboring layers α of deviation angle δ for the four-layer structure. The magnitude of the polarization (9) can be significantly different from the piezoelectric component of the polarization if the μ is significant, as shown in Figure 3(c).

$$\left|\vec{P}\right| = \left(\frac{c_p\theta}{b_0}\right)\sqrt{\left\{\left[\left(\frac{\mu}{c_p}\right)\cos(\alpha)\right]^2 + \left[1+\left(\frac{\mu}{c_p}\right)\sin(\alpha)\right]^2\right\}}. \tag{9}$$

In the case of the SmC^{*}_{F11} phase, it has a three-layer structure where the phase differences between the neighboring layers are in the sequence of α, β, β. The sum of these phase angles are approximately 2π radian ($\alpha + 2\beta \approx 2\pi$) and the smaller of the angles α is less than $2\pi/3$, as shown in Figure 4(a). The asymmetric primitive cell has a few consequences: The tilts in neighboring layers are not equal (Dolganov et al. 2002; Fernandes et al. 2006); hence, the flexoelectric induced polarization should be different in different layers. However, one would assume that the tilts are almost equal as the x-ray measurements have shown only extremely weak signal at the three-layer periodicity. On the other hand, as the smaller of the angles α can be very different for different materials, the magnitudes of the polarizations in layers $(3j+1)$, $(3j+2)$ and $(3j)$ can be very different in direction and in magnitude. As the

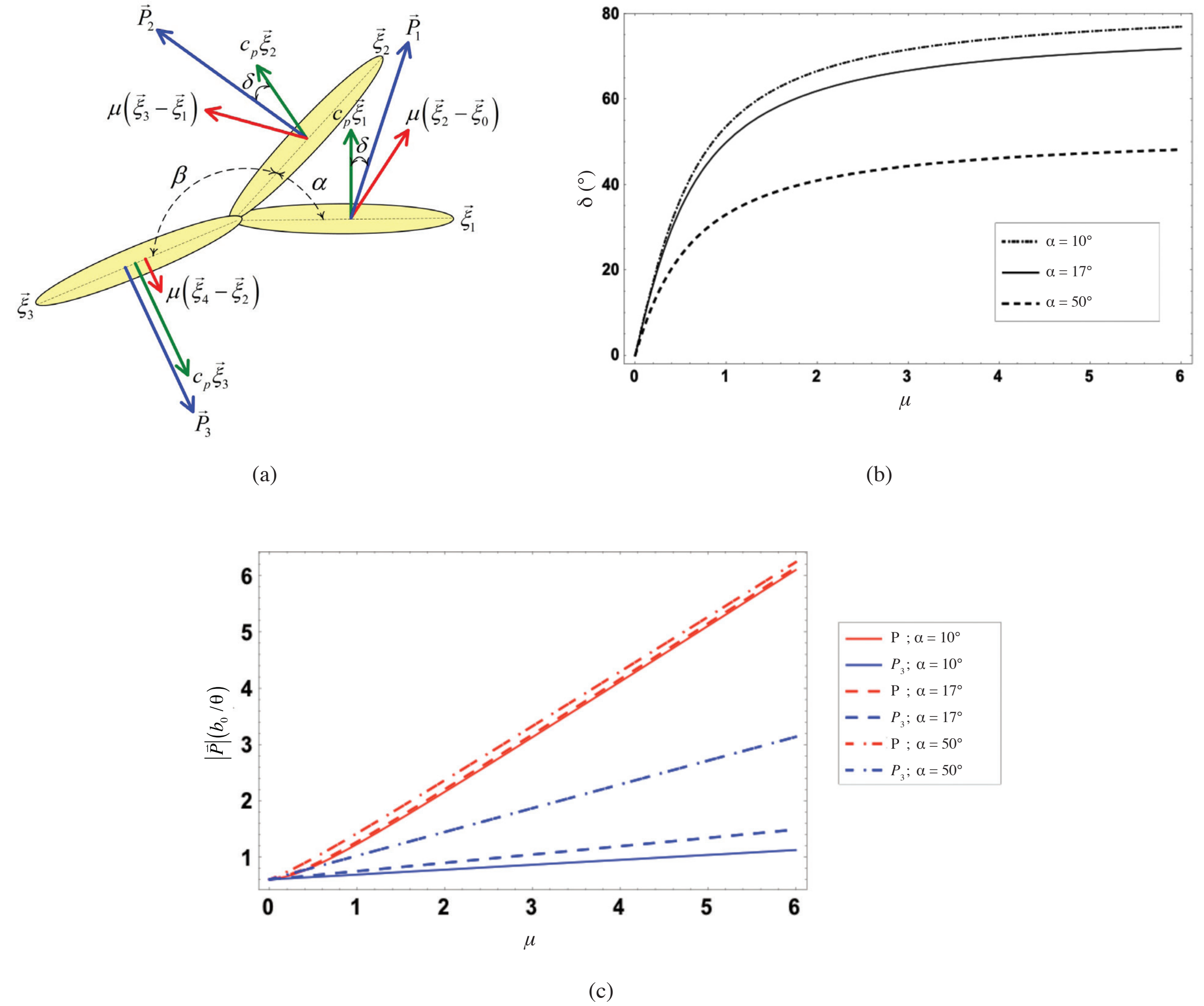

FIGURE 4. (a) The layer polarization in the three-layer SmC^{*}_{F11} phase. In the layers where the neighbouring polarization forms the smaller of the two angles, the polarization consists of two parts, where the piezoelectric contribution is perpendicular to the tilt (green arrow) and the flexoelectric contribution (red arrow) has a general direction with respect to the direction of the tilt difference in layers above and below. The flexoelectric component in the third layer is perpendicular to the tilt in this layer. The μ dependence for three various phase difference between the neighboring layers α of (b) the deviation angle δ and (c) magnitude of the polarizations P, P_3 for the three-layer structure of the SmC^{*}_{F11} phase

structure has a period of three layers, let us introduce a simpler notation such as $\vec{P}_{3j+1} = \vec{P}_1, \vec{P}_{3j+2} = \vec{P}_2$ and $\vec{P}_{3j} = \vec{P}_3$.

The symmetry analysis shows that the general polarization direction with respect to the tilt is found only in the two of the three layers in the primitive cell i.e. for the $\vec{P}_1$ and $\vec{P}_2$, as shown in Figure 4(a).

$$\tan\delta = \frac{\left(\frac{\mu}{c_p}\right)\cos\left(\frac{3\alpha}{4}\right)\cos\left(\frac{\alpha}{4}\right)}{1+\left(\frac{\mu}{c_p}\right)\sin\left(\frac{3\alpha}{4}\right)\cos\left(\frac{\alpha}{4}\right)}. \qquad (10)$$

Figure 4(b) shows the deviation angle δ for polarization $\vec{P}_1$ versus μ for different values of α. δ is smaller for smaller value of μ and it decreases with increasing α. The polarization $\vec{P}_3$ is always perpendicular to the tilt in the layer. The magnitudes of polarization in layer 3_{j+1} and layer 3_{j+2} are equal, $P_1 = P_2 = P$ and the magnitudes of $\vec{P}_1$ and $\vec{P}_2$ are larger than that of $\vec{P}_3$, the difference diminishes as α increase as shown in Figure 4(c).

$$\left|\vec{P}\right| = \left(\frac{c_p\theta}{b_0}\right)\sqrt{\left\{\left[\left(\frac{\mu}{c_p}\right)\cos\left(\frac{3\alpha}{4}\right)\cos\left(\frac{\alpha}{4}\right)\right]^2 + \left[1+\left(\frac{\mu}{c_p}\right)\sin\left(\frac{3\alpha}{4}\right)\cos\left(\frac{\alpha}{4}\right)\right]^2\right\}}$$

$$\left|\vec{P}_3\right| = \left(\frac{c_p\theta}{b_0}\right)\sqrt{\left\{\left[\sin\left(\frac{\alpha}{2}\right)+\frac{1}{2}\left(\frac{\mu}{c_p}\right)-\frac{1}{2}\left(\frac{\mu}{c_p}\right)\cos(\alpha)\right]^2 + \left[-\cos\left(\frac{\alpha}{2}\right)-\frac{1}{2}\left(\frac{\mu}{c_p}\right)\sin(\alpha)\right]^2\right\}}. \qquad (11)$$

CONCLUSION

For a long time, the polarization component is believed to be perpendicular to the tilt in the structures formed by chiral rod-like molecules. In this calculation, we analyzed the contribution of piezoelectric and flexoelectric effects on polarization for three-layer SmC^*_{F11} and four-layer SmC^*_{F12} phases within the framework of discrete phenomenological model. We have shown that the effects of piezoelectric and flexoelectric on polarization contribute to the total polarization of the system and these effects influence the angle δ, the deviation of layer polarization from the direction normal to the tilt. We found that for the structures of three-layer SmC^*_{F11} and four-layer SmC^*_{F12} phases, the polarization is not perpendicular to the tilt but forms a general angle with respect to the tilt.

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