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# Effect of spontaneous polarization on smectic C*–smectic A* phase transition temperature and the thickness dependence of the spontaneous polarization of ferroelectric liquid crystal

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The influence of spontaneous polarization on the smectic C*–smectic A* phase transition was studied theoretically by means of Landau theory. It was observed from the theoretical calculations that the transition temperature from a non-chiral to chiral smectic C phase is shifted due to the effect of bilinear and biquadratic couplings. A qualitative relationship has also been derived between spontaneous polarization and cell thickness which supports the experimental observations of the increase of spontaneous polarization with the increase of cell thickness for surface-stabilized ferroelectric liquid crystals.

## 1. Introduction

During the last decade much progress has taken place in the field of ferroelectric liquid crystals (FLCs) from the view point of both fundamental and applied physical interest. The chiral smectic C* (SmC*) phase represents a spatially modulated structure [1]. The ferroelectric ordering in the SmC* phase is usually denoted by two order parameters [2]: one is the molecular tilt angle ($\theta$), the other is spontaneous polarization ($P$). The tilt angle of the long molecular axis with the smectic layer normal precesses from one smectic layer to the other, forming a helicoidal structure with helical axis coincident with the layer normal. Spontaneous polarization developed in the plane of smectic layers, perpendicular to the tilt plane, also precesses from layer to layer and forms a helix. Due to the existence of this helix, there is no net polarization on a macroscopic level. However the introduction of parallel bounding surfaces normal to the layers, which interact with the director as well as the spontaneous polarization, prevents the helix formation and leads to bookshelf or chevron geometry. This is the basis of the surface stabilized ferroelectric liquid crystal (SSFLC) [3]. For this reason it is important to study the physical properties of FLC molecules with varying cell thickness, i.e. distance between the bounding surfaces. Moreover the switching mechanism in electro-optical devices depends on cell thickness, surface condition, temperature and even on material parameters such as tilt angle and spontaneous polarization [4]. It is also observed from experimental data that the transition temperature [5, 6] and the magnitude of spontaneous polarization [7, 8] are also influenced by cell thickness.

In this paper we analyse theoretically the influence of spontaneous polarization on the SmC*–SmA* phase transition temperature using the generalized Landau model. We also discuss the cell thickness dependence of spontaneous polarization which has a definite practical significance.

## 2. Theory

In this section we present a calculation to show how the spontaneous polarization in the Landau free energy expression affects the transition temperature from non-chiral to chiral smectic phase. As a starting point we used the generalized Landau expansion of the free energy density of the system as discussed by several authors [9–11]. In the framework of phenomenological Landau theory, Gibbs free energy density $F$ of a non-chiral SmC phase at temperature $T$ is given by an even power series expansion of the tilt angle $\theta$, which is the primary order parameter of the SmC–SmA transition.

$$F = F_0 + \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 \qquad (1)$$

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where $a = \alpha(T - T_C)$, and $\alpha$, $b$, $c$ are positive constants. The values of these constants are very small near the transition temperature. $T_C$ is the SmC–SmA second order phase transition temperature, and $F_0$ is the singular part of $F$.

In the generalized Landau model, the expression for the Gibbs free energy density of an unwound system (for which the wave vector $q = 0$) for the SmC*–SmA* transition is given by [10]

$$F^*(\theta, P) = F_0 + \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 + \frac{1}{2\chi_0}P^2 - CP\theta - \frac{1}{2}\Omega P^2\theta^2 + \frac{1}{4}\eta P^4. \tag{2}$$

Chiral interactions are introduced in equation (2) by the term $P^2/2\chi_0$ ($\chi_0$ is the high frequency dielectric susceptibility), which is due to the effect of dipolar ordering. $C$ is the piezoelectric bilinear coupling term and $\Omega$ is the biquadratic coupling term, implying the competition between two ordering parameters $\theta$ and $P$. As proven by numerical calculations [12], the $\eta$ (a constant) term in equation (2), is not significant for a consistent description of the experimental data and is omitted in the calculation. The term ($\eta > 0$) has been added to stabilize the system. Recently Gouda *et al.* [13] also pointed out that the $\eta P^4$ term is related to the low temperature saturation of spontaneous polarization and is therefore irrelevant near the transition temperature.

From the condition

$$\frac{\partial F^*}{\partial P} = \left(\frac{1}{\chi_0} - \Omega\theta^2\right)P - C\theta = E \tag{3}$$

we define $E$, the quantity thermodynamically conjugate to the polarization $P$. Hence,

$$\frac{\partial E}{\partial P} = \left(\frac{1}{\chi_0} - \Omega\theta^2\right). \tag{4}$$

From equation (3) we have

$$P = \frac{(E + C\theta)}{\left(\dfrac{1}{\chi_0} - \Omega\theta^2\right)} = \frac{\chi_0(E + C\theta)}{(1 - \chi_0\Omega\theta^2)} \tag{5}$$

also, from equation (5), we have

$$P = (E + C\theta)\left(\frac{\partial P}{\partial E}\right) = P_{\mathrm{A*C*}} + \delta P \tag{6}$$

where

$$\delta P = C\theta\frac{\partial P}{\partial E}. \tag{7}$$

At the second-order transition $\theta = 0$, and we have from equations (4) and (6),

$$P = P_{\mathrm{A*C*}} = E\left(\frac{\partial P}{\partial E}\right) = E\chi_0. \tag{8}$$

The additional term $\delta P = C\theta(\partial P/\partial E)$ in the polarization is related to the tilt angle. In the case of a continuous transition $\theta \to 0$ and $\delta P \to 0$, and in the case of a first-order transition the increment $\delta P$ is proportional to that of $\theta$. On transforming $F^*(\theta, P)$ into a potential depending on the field variable $E$

$$\begin{aligned} F(\theta, E) &= F^*(\theta, P) - EP \\ &= \frac{1}{2}(a - C^2\chi_0 - E^2\Omega\chi_0^2)\theta^2 \\ &\quad + \frac{1}{4}(b - 2\Omega C^2\chi_0^2 - 4\chi_0^3\Omega^2E^2)\theta^4 \\ &\quad + \frac{1}{6}(c - 6\Omega^2C^2\chi_0^3)\theta^6 \end{aligned} \tag{9}$$

we obtain a remarkable analogy to the Landau expression, equation (1), for the non-chiral SmC phase, if chiral coefficients $a^*$, $b^*$, $c^*$ are introduced

$$F(\theta, E) = \frac{1}{2}a^*\theta^2 + \frac{1}{4}b^*\theta^4 + \frac{1}{6}c^*\theta^6. \tag{10}$$

The renormalized coefficients are obtained as follows from equation (10)

$$a^* = \alpha'(T - T_C^*) = (a - C^2\chi_0 - E^2\Omega\chi_0^2) \tag{11}$$

$$b^* = (b - 2\Omega C^2\chi_0^2 - 4\chi_0^3\Omega^2E^2) \tag{12}$$

$$c^* = (c - 6\Omega^2C^2\chi_0^3). \tag{13}$$

Now when a second order transition (SmC–SmA) occurs, $a = 0$. Thus from equation (11) at $T = T_C$ we have

$$T_C^* = T_C + \frac{C^2\chi_0}{\alpha'} + \frac{P^2\Omega}{\alpha'} \tag{14}$$

where $T_C^*$ is the SmC*–SmA* phase transition temperature. Mean-field coefficients $C$, $\Omega$, $\alpha'$, $\chi_0$ have been calculated by Gießelmann and Zugenmaier [12] and are found to be positive. The temperature $T_C^*$ calculated from equation (14) always increases since the last two terms are always positive. Hence from (14) we note that the transition temperature is displaced in a chiral compound compared with its non-chiral analogue, due to the effect of both bilinear and biquadratic coupling, and we always have $T_C^* > T_C$. The transition temperature $T_C^*$, as shown in equation (14), is similar to that obtained by Padmni *et al.* [14]; an additional term ($P^2\Omega/\alpha'$) appears in equation (14) due to biquadratic coupling.

We see that all the terms except polarization in the R.H.S. of equation (14) are nearly constant for a particular FLC compound, thus it is clear that the transition temperature increases with the increase of the polarization $P$ for a FLC compound. Naturally transition temperature ($T^*_C$) reaches maximum value $T^*_{C\max}$ when $P$ becomes $P_{\max}$. Hence, equation (14) can be written

$$T^*_{C\max} = T_C + \frac{C^2\chi_0}{\alpha'} + \frac{(P_{\max})^2\Omega}{\alpha'} \tag{15}$$

where $P_{\max}$ and $T^*_{C\max}$ are the maximum values of polarization and transition temperature respectively. Again from equation (14) it can be shown that any shift of SmC*–SmA* phase transition temperature $T^*_C$ of a FLC compound is mainly due to the polarization-dependent term and we have

$$\Omega = \frac{\alpha'}{2P}\frac{\mathrm{d}T^*_C}{\mathrm{d}P} > 0 \tag{16}$$

i.e. the biquadratic coupling term $\Omega$ is always greater than zero and determines the shift of transition temperature.

The influence of cell thickness on the spontaneous polarization of a FLC molecule can be derived with the help of equation (15). According to Pikin and Yoshino [6] the critical temperature $T^*_C$ for a SSFLC can be written as follows

$$T^*_C = T^*_{C\max} - \left(\frac{\pi^2 g}{2\alpha'}\right)\frac{1}{\left(d + \frac{2g}{|W|}\right)^2} \tag{17}$$

where $T^*_{C\max}$ is the maximum critical temperature when $d$ (cell thickness)→ ∝, $g$ is the elastic modulus and $W$ is the effective anchoring energy. From equations (14) and (15), we have

$$T^*_C = T^*_{C\max} + \frac{\Omega}{\alpha'}(P^2 - P^2_{\max}). \tag{18}$$

Comparing equations (17) and (18), we get

$$P^2 = P^2_{\max} - \left(\frac{\pi^2 g}{2\Omega}\right)\frac{1}{\left(d + \frac{2g}{|W|}\right)^2}$$

i.e.

$$P = \left[P^2_{\max} - \left(\frac{\pi^2 g}{2\Omega}\right)\frac{1}{\left(d + \frac{2g}{|W|}\right)^2}\right]^{1/2}. \tag{19}$$

Hence, from equation (19) it is clear that as $d \to \propto$, $P \to P_{\max}$, i.e. spontaneous polarization increases with the increase of cell thickness. Also from (19) we see that when $|W|d \gg g$, one has

$$P = \left[P^2_{\max} - \left(\frac{\pi^2 g}{2\Omega}\right)\frac{1}{(d)^2}\right]^{1/2}. \tag{20}$$

At $|W|d \ll g$ the dependence of $P(d)$ on cell thickness is very small.

## 3. Possible application of the theory

The temperature dependence of spontaneous polarization has been investigated experimentally by several authors [7, 8] as a function of cell thickness. The above equation (19) describes the experimental results [7, 8] of the thickness dependence of spontaneous polarization quite nicely. It has also been experimentally observed [5, 6] that the transition temperature $T^*_C$ increases remarkably with the increase of cell thickness, particularly for SSFLCs. The shift of the transition temperature $T^*_C$ vs the thickness of the measuring cell can be explained by considering equations (14) and (19), which state that an increase of cell thickness increases the spontaneous polarization, and that in turn increases $T^*_C$ in a thicker cell. By knowing the value of $P_{\max}$, $g$, and the quadrupole coupling coefficient $\Omega$, we can easily compute from equation (20) the trends of decrease of $P$ with decrease of cell thickness. The figure shows the theoretical curve of the thickness dependence of spontaneous polarization. Here $P_{\max}$ has been taken as $2\,\mathrm{nC\,cm^{-2}}$ from the literature value [7]. It was experimentally observed that $g$ is of the order of $10^{-5}$ dyn s and $\Omega$ of the order of $10^3\,\mathrm{V\,cm\,nC^{-1}}$ for materials of low spontaneous polarization; in computing the theoretical curve these $g$ and $\Omega$ values have been taken into consideration. It is also possible to determine the value of $g/\Omega$ from the experimental value of spontaneous polarization at different cell thickness from equation (20); if $g/\Omega$ is very small then polarization is almost independent of cell thickness.

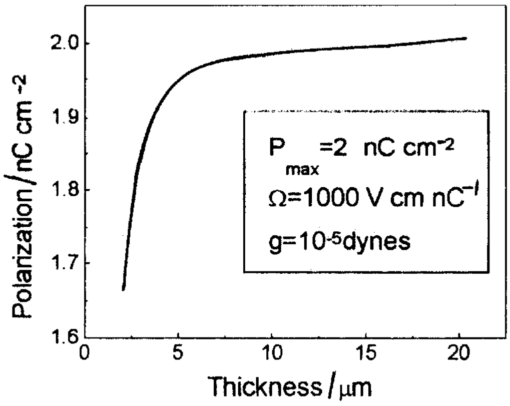

Figure. Variation of spontaneous polarization with cell thickness.

## 4. Conclusions

A theoretical relationship has been developed from the Landau free energy expansion between the SmC*–SmA* phase transition temperature of a chiral smectic compound and that of its non-chiral analogue. It has been shown that the bilinear and the biquadratic couplings between tilt and polarization are responsible for the increase of the $T_C$ of a chiral compound in comparison with that of its non-chiral analogue. It has also been shown that spontaneous polarization increases with the increase of cell thickness in SSFLCs, but is independent of cell thickness where the product of anchoring energy and cell thickness is much less than the elastic modulus of the system.

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