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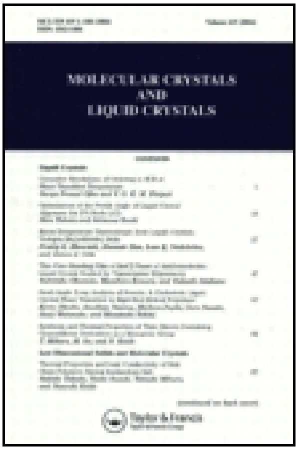

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# Quasi-Ferro- and Antiferroelectric Behaviour of Non-Chiral Smectics

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The pseudo-ferroelectric and pseudo-antiferroelectric states can exist in smectic phases possessing two-dimensional orientational order parameters and relatively strong flexoelectric effects. These states, in general, are the modulated structures with relatively large local polarization and chirality, but the smectic films with these modulations have no macroscopic, i.e., in average, spontaneous chirality and polarization because of the equivalence of both signs of wave number.

*Keywords:* non-chiral smectics; ferroelectrics; antiferroelectrics

## Introduction

The great interest to the non-chiral smectics consisting of banana-like molecules had arised recently[1,2] because of the observed unusual polarization properties which look like the ferro- and antiferroelectric ones. The problem of proper ferro- and antiferroelectricity is not solved yet, and,

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therefore, various approaches to the explanation of the observed phenomena are useful. For instance, it was shown[3] that sufficiently large flexoelectric coefficients in smectics provoke the appearance of the polarizarion modulations characterized by a spatial period critically depending on certain material parameters, the amplitude of modulations being dependent on the same coefficients as well as on the smectic order parameters. The present paper is devoted to the consideration of different situations in non-chiral smectics, which imitate some proper polarization properties.

**Spontaneous and induced modulations in non-chiral smectics C**

In vicinity of the smectic A - smectic C phase transition point $T_c$, the phenomenological expansion for the free energy density has the conventional form[4] taking into account the distributions of the director components $(n_x, n_y)$ and of the polarization components $(P_x, P_y)$ which are heterogeneous, for example, along the crystalline axis z:

$$f = tn_z^2\left(n_x^2 + n_y^2\right) + \frac{1}{2}Kn_z^2\left[\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right] + \frac{1}{\chi}\left(P_x^2 + P_y^2\right) + \frac{1}{2}g\left[\left(\frac{\partial P_x}{\partial z}\right)^2 + \left(\frac{\partial P_y}{\partial z}\right)^2\right] + \beta\left(n_z n_x \frac{\partial P_x}{\partial z} + n_z n_y \frac{\partial P_y}{\partial z}\right) \quad . (1)$$

Here, the coefficient $t = a'(T - T^*)$ is temperature-dependent, $T^*$ is close to the transition point, $a'$ is a constant; $K$ represents the average elastic constant, $\chi$ is the dielectric susceptibility and $\beta$ is the flexoelectric coefficient. The parameter $g$ characterizes the polarization inhomogeneities. The constants $K$, $g$ and $\chi$ are positive, the temperature dependent parameter $t$ is close to zero. The $z$-component of director turns out to be $n_z \cong 1$ in the approximation

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under consideration. If the modulation along the $z$-axis occurs, the in-plane director and polarization components are written as

$$n_x = \Theta\sin(qz),\ n_y = \Theta\cos(qz)\,;\ P_x = P\cos(qz),\ P_y = -P\sin(qz)\ . \quad (2)$$

By substituting Eqs.(2) into Eq.(1), the free energy $F$ over one period is

$$F = t\Theta^2 + \frac{1}{2}K\Theta^2q^2 + \frac{1}{\chi}P^2 + \frac{1}{2}gP^2q^2 - \beta\Theta Pq \quad . \qquad (3)$$

The minimization of the function (3) with respect to $P$ gives the relation

$$P = \frac{\chi\beta\Theta q}{2\left(1+\xi^2q^2\right)} \qquad (4)$$

where the parameter $\xi = \left(\chi g/2\right)^{1/2}$ plays the role of a correlation length.

By substituting (4) into (3), $F$ as a function of $q$ and $\Theta$ is obtained:

$$F = t\Theta^2 + \frac{1}{4}\Theta^2q^2\left(2K - \frac{\beta^2\chi}{1+\xi^2q^2}\right) \quad . \qquad (5)$$

The function (5) has a minimum at the effective value $q_{eff}$ given by

$$q_{eff} = \pm\frac{1}{\xi}\sqrt{\frac{\beta}{\beta_c}-1}\ ,\quad |\beta_c| = \left(2\frac{K}{\chi}\right)^{1/2} \quad . \qquad (6)$$

Thus, the finite wavenumber of this structure appears at sufficiently largevalues of the coefficient $|\beta| \geq |\beta_c|$, $\beta_c$ is the critical value[3].

Since both signs of wavenumber are equivalent, the set of short-pitch modulations have no, in average, chiral properties. This means that a possible domain area related to the defined chirality, i.e., to the defined sign of $q_{eff}$ , must be relatively small.. Though the local polarization value

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$$P_{eff} = \frac{\xi\beta_c\Theta}{g}\sqrt{\frac{\beta}{\beta_c}-1} \tag{7}$$

may be large, the macroscopic spontaneous polarization is absent. But the dielectric response of such a flexoelectric structure differs from the conventional one. For instance, the dielectric susceptibility has the correction $\Delta\chi$ of the order of

$$\Delta\chi \propto \frac{\chi^2\beta^2}{K} \tag{8}$$

for $\beta > \beta_c$ and $\Theta \sim 1$ [4]. This response describes, in fact, an unwinding of the modulations under the electric field action, the "critical" value $E_{unw}$ (the "unwinding" field value) being, for $\beta > \beta_c$ and $\Theta \sim 1$, of the order of

$$E_{unw} \sim \frac{Kq_e\Theta}{\chi\beta} \propto \frac{K^{3/4}}{\xi\chi^{3/4}\beta^{1/2}} \quad . \tag{9}$$

This magnitude may be small. Such a process of unwinding occurs if the threshold of the induced flexoelectric instability $E_{flexo}$ is larger than $E_{unw}$.

The estimate of magnitude $E_{flexo}$ is done by the consideration of the perturbations of tilt angle $\Theta'(z)$ induced by the external field $E_x$, which enter into the free energy density in the form of invariants

$$b\Theta^2\Theta'^2 \ , \ \frac{1}{2}\tilde{K}\left(\frac{\partial\Theta'}{\partial z}\right)^2 \quad . \tag{10}$$

In a weak electric field, small corrections $\Theta'(z)$ are found by the minimization of the free energy including terms (10) and term $-P_xE_x$:

$$\Theta'(z) \sim \frac{\chi\,\beta\Theta^2 qE_x}{2b\Theta^2 + \widetilde{K}q^2}\cos qz \ . \tag{11}$$

The corresponding macroscopic value of the induced polarization is of the order of magnitude

$$\overline{P}_x \propto \frac{\chi^2\beta^2\Theta^4 q^2}{2b\Theta^2 + \widetilde{K}q^2}E_x \ , \tag{12}$$

$$q^2 \propto \frac{\Theta^2}{\widetilde{K}}\left(\frac{\chi^2\beta^2 E_x^{\ 2}}{K} - 2b\right) , \qquad E_{flexo} \sim \frac{\sqrt{2bK}}{\chi\beta} \ , \tag{13}$$

if initially the modulations were unwound, i.e., if $E_x > E_{flexo} > E_{unw}$. These inequalities are filfulled at

$$b > \frac{\beta\sqrt{\chi K}}{\xi^2} \tag{14}$$

Condition (14) takes place at relatively large values of $b$ and at small values of $\beta$. This unwound structure is characterized by a relatively weak response at $E_x < E_{flexo}$, but above the threshold field value, for $b < \widetilde{K}q^2$, we obtain

$$\Delta\chi \propto \frac{\chi^2\beta^2}{\widetilde{K}} \ , \tag{15}$$

i.e., the dielectric response may increase. Such a behaviour simulates an "antiferroelectric" situation at which the increase in polarization occurs above a certain threshold field value.

However, for substances characterized by a small $b$ and by a large $\beta$,

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$b < \beta\sqrt{\chi K} / \xi^2$, we have the inequality $E_{unw} > E_{flexo}$, i.e., the modulations with $q = q_{eff}$ may occur and, correspondingly, we obtain

$$\overline{P}_x \propto \frac{\chi^2\beta^3}{b\beta_c\xi^2}E_x \quad , \quad \Delta\chi \propto \frac{\chi^2\beta^3}{b\beta_c\xi^2} \tag{16}$$

for $\beta > \beta_c$, $\Theta \sim 1$ and $b > \tilde{K}q_{eff}^{\ 2} \cong \left(\beta\tilde{K} / \beta_c\xi^2\right)$. Thus, the latter inequality may take place if the constant $K$ is larger than the constant $\tilde{K}$. This case reminds the "ferroelectric " situation at which the relatively large increase in polarization occurs in a weak field and, then, the high value of polarization is preserved though its increase becomes slower in strong fields.

## In-plane and other modulations in non-chiral smectics

The spontaneous in-plane modulations in non-chiral smectics C can betreated similarly[3] taking into account the invariants related to the orientational deformations $\left(\partial n_x / \partial x + \partial n_y / \partial y\right)$. If the homogeneous external field induces, due to the flexoelectric effect, a heterogeneous distribution of the ionic harge density $\rho$ then the additional terms in the free energy are of importance:

$$B\rho^2 + \frac{1}{2}G\,(\partial\rho/\partial r)^2 + \chi\tilde{\beta}E_z\rho n_z\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right) + \chi\tilde{\beta}E_x\rho n_z\left(\frac{\partial n_x}{\partial z}\right). \tag{17}$$

Now, the critical values $E_{unw}$ and $E_{flexo}$ are estimated as

$$E_{unw} \propto \frac{Kq_{eff}\,\Theta}{\chi\tilde{\beta}} \propto \frac{K^{3/4}\beta^{1/2}}{\xi\chi^{3/4}\tilde{\beta}} \quad , \; E_{flexo} \propto \frac{\sqrt{BK}}{\chi\tilde{\beta}} \tag{18}$$

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The condition $E_{unw} < E_{flexo}$ is filfulled at $B > \beta\sqrt{\chi K} / \xi^2$, which is similar to the case (14) (pseudo-antiferroelectric). In substances characterized by the inequality$B < \beta\sqrt{\chi K} / \xi^2$, the modulations with $q = q_{eff} \cong (\beta / \beta_c)^{1/2} \xi^{-1}$ may occur if, besides, $B > Gq_{eff}{}^2$, where $\beta_c$ is given by Eq.(6). In the latter case (pseudo-ferroelectric), the condition $\beta\sqrt{\chi K} / \xi^2 > B > Gq_{eff}{}^2$ means that the constant $K$ must be larger than the magnitude $\left(\beta / \widetilde{\beta}\right)^2 G$.

In general, the crystalline deformations $u_{zz}$ should be also considered similarly to magnitude $\rho$. The "elastic" constants of the type of $\widetilde{K}$ and $G$ are of importance for different competing threshold modulations. For instance, a relatively large stiffness of smectic planes may prevent the in-plane modulations.

Another remark should be done in connection with the forms of Eqs. (1) and (17) which contain the two-component orientational order parameter. For the biaxial A phase, where such an order parameter is composed from paired combinations of the director components describing the ordering of short molecular axes[4], the obtained results can be also applied and may explain the observed local chirality in such a phase[5].

As a secondary effect, in initially racemic mixture, the local separation of chiral components may occur due to the local twisting considered above. In such a case, the free energy expansion contains the terms similar to the ones in Eq.(19), where $\rho$ is the difference of concentrations, and, besides, the classical chiral term in the form $\rho\Theta P$ which vanishes at $\rho = 0$. As a result, the finite magnitude $\rho$ becomes directly proportional to the wave number $q$, $\rho \propto \left(\chi\beta\Theta^2 / B\right)q$, i.e., the type of chiral component which is in an excess directly depends on the sign of wave

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number in the proper area.

In conclusion, the pseudo-ferroelectric state shows an increase in polarization in weak electric fields, but the pseudo-antiferroelectric state possesses such a response when the field exceeds a certain threshold value. Since the flexoelectric modulated structures obviously have many structural defects[4], the mentioned responses must show a hysteresis behaviour.

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