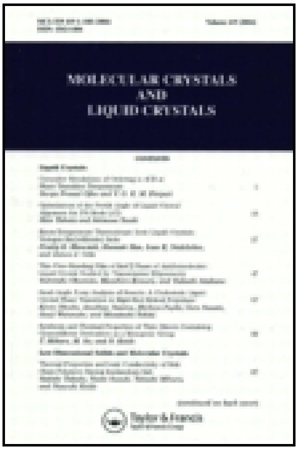

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Boštjan Žekš [a]
[a] Institute of Biophysics, Medical Faculty and J.Stefan Institute, Ljubljana, Yugoslavia
Version of record first published: 20 Apr 2011.

To cite this article: Boštjan Žekš (1984): Landau Free Energy Expansion for Chiral Ferroelectric Smectic Liquid Crystals, Molecular Crystals and Liquid Crystals, 114:1-3, 259-270

To link to this article: http://dx.doi.org/10.1080/00268948408071711

Mol. Cryst. Liq. Cryst., 1984, Vol. 114, pp. 259-270
0026-8941/84/1143-0259/$20.00/0

LANDAU FREE ENERGY EXPANSION FOR CHIRAL FERROELECTRIC SMECTIC LIQUID CRYSTALS

BOŠTJAN ŽEKŠ
Institute of Biophysics, Medical Faculty and J.Stefan Institute, Ljubljana, Yugoslavia

Abstract The biquadratic coupling between the tilt and polarization is added to the usual bilinear coupling in the Landau free energy density expansion describing the SmA - SmC* transition. The effect on the temperature dependence of the tilt, spontaneous polarization and the pitch of the helix is studied. The results agree qualitatively with measured data.

INTRODUCTION

The order parameter of the smectic A (SmA) to smectic C (SmC) transition is a two component tilt vector $\underline{\xi} = (\xi_1, \xi_2)$ describing the magnitude and the direction of the tilt of the long molecular axis from the normal to smectic layers. For chiral systems the tilt precesses around the normal to smectic layers as one goes from one layer to another resulting in a helicoidal smectic C* phase (SmC*). The tilt of a molecule breaks the axial symmetry around its long axis inducing an inplane polarization $\underline{P} = (P_x, P_y)$ perpendicular to the tilt[1]. Thermodynamic properties of the system are usually described by the phenomenological Landau type free energy Ansatz[2,3] including the bilinear coupling between the primary order parameter $\underline{\xi}$ and the secondary order parameter $\underline{P}$. This coupling is of a chiral character and does not exist in nonchiral systems where no ordering of molecules transverse to their long axes is induced by the tilt according to the model. The predictions of the model do not agree with experimental data[4] especially in a narrow temperature interval below the SmA - SmC* phase transition temperature T_c. The most evident discrepancy can be observed in the temperature dependence of the pitch of the helix (p) in the SmC* phase, which should be temperature independent according to the model. The measured pitch slowly increases with increasing temperature, reaches a maximum ~ 0.5 K below T_c and then sharply decreases with increasing temperature to a finite value at T_c[5,6].

There exist various modifications[7,8,9] of the model introduced to explain the anomalous temperature dependence of the pitch close to T_c. It has been proposed recently[9] that the non-chiral biquadratic coupling between the polarization and the tilt could explain the observed anomaly in p(T). In this paper we shall analyze the effect of biquadratic coupling terms on the temperature dependence of the pitch of the helix. Temperature dependence of the spontaneous polarization and of the tilt will be determined and some experiments will be proposed to test the model.

CLASSICAL LANDAU MODEL

The Landau free energy density describing the SmA - SmC* transition is usually expressed as[2,3]

$$g(z) = \frac{1}{2}a(\xi_1^2 + \xi_2^2) + \frac{1}{4}b(\xi_1^2 + \xi_2^2)^2 - \Lambda(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) +$$

$$+ \frac{1}{2}K_{33}\left[(\frac{d\xi_1}{dz})^2 + (\frac{d\xi_2}{dz})^2\right] + \frac{1}{2\varepsilon}(P_x^2 + P_y^2) -$$

$$- \mu(P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz}) + C(P_x\xi_2 - P_y\xi_1) \qquad (1)$$

where ξ_1 and ξ_2 describe the tilt of molecules from the normal (0, 0, 1) to smectic layers, P_x and P_y are the components of the in-plane polarization, $b > 0$, K_{33} is the elastic modulus, Λ the coefficient of the Lifshitz term responsible for the modulation and μ and C are the coefficients of the "flexo" - and "piezo" - electric coupling between the tilt and the polarization.

With the helicoidal ansatz

$$\xi_1 = \theta \cos(qz) \quad , \quad \xi_2 = \theta \sin(qz) \qquad (2a)$$

$$P_x = - P \sin(qz) \quad , \quad P_y = P \sin(qz) \qquad (2b)$$

one obtains by minimizing the free energy (Eq. 1) with respect to the tilt θ, polarization P and the wave-vector of the helix q for $T < T_c$

$$p = \frac{2\pi}{q} = 2\pi \frac{K_{33} - \varepsilon\mu^2}{\Lambda + \varepsilon\mu C} \qquad (3a)$$

$$P = \varepsilon(C + \mu q)\theta \qquad (3b)$$

$$\theta = \sqrt{\frac{\alpha}{b}(T_c - T)} \qquad (3c)$$

where the transition temperature T_c is given by

$$T_c = T_o + \frac{1}{\alpha}[\varepsilon C^2 + (K_{33} - \varepsilon\mu^2)q^2] \qquad (4)$$

Within this model the pitch of the helix p does not depend on temperature in contrast to experiments. The spontaneous polarization is strictly proportional to the tilt and both show a classic square root temperature dependence.

BIQUADRATIC COUPLING BETWEEN THE POLARIZATION AND THE TILT

All chiral terms in Eq.(1) are expected to be small. This can be concluded from the large value of the pitch as compared to the molecular dimensions and from the extremely small difference in the transition temperatures $T_c - T_o$ between a chiral system and a corresponding racemic mixture. As the bilinear $\underline{P} - \underline{\xi}$ coupling terms are chiral and therefore small, the biquadratic coupling terms could become important in SmC* phase. On the other hand, NMR measurements show[10] no appreciable difference in the transverse ordering between chiral and non-chiral systems except perhaps very close to T_c. The observed quadrupolar ordering can be described by $P^2 \neq 0$ and is induced by the biquadratic $\underline{P} - \underline{\xi}$ coupling terms. We add therefore to the free energy expansion (1) the lowest nonchiral biquadratic coupling terms

$$g_a = - \frac{1}{2}\Omega(P_x\xi_2 - P_y\xi_1)^2 + \frac{1}{4}\eta(P_x^2 + P_y^2)^2 \tag{5}$$

The last term has been added to stabilize the system.

We shall as well include a higher order term

$$g_b = - d(\xi_1^2 + \xi_2^2)(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) \tag{6}$$

which is equivalent to replacing Λ by $\Lambda + d\theta^2$ and should describe the monotonous increase of the pitch with temperature at low temperatures.

The total free energy $g + g_a + g_b$ can be expressed with ansatz (2) as a function of θ, P and q as

$$g = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{2\varepsilon}P^2 - CP\theta - \frac{1}{2}\Omega P^2\theta^2 + \frac{1}{4}\eta P^4 +$$
$$+ \frac{1}{2}K_{33}q^2\theta^2 - \Lambda q\,\theta^2 - dq\theta^4 - \mu qP\theta \tag{7}$$

Minimization with respect to q gives for the wave vector of the helix

$$q = \frac{1}{K_{33}} (\Lambda + d\theta^2 + \mu\frac{P}{\theta}) \tag{8}$$

The temperature appears in q and therefore in the pitch $p = 2\pi/q$ in two ways: i) d-term gives a contribution at large θ(low T) and describes the low temperature increasing part of p(T) for $d > 0$, ii) the last term is proportional to the flexoelectric coupling coefficient μ and is temperature dependent only if P is not proportional to θ.

Eliminating q from Eq. (7) one obtains the free energy as a function of θ and P

$$g = g(\theta) + g(P,\theta) \tag{9}$$

where

$$g(\theta) = \frac{1}{2}(a - \frac{\Lambda^2}{K_{33}})\theta^2 + \frac{1}{4}(b - \frac{4\Lambda d}{K_{33}})\theta^4 - \frac{d^2}{2K_{33}}\theta^6 \tag{10}$$

and

$$g(P,\theta) = \frac{1}{2}\left[(\frac{1}{\varepsilon} - \frac{\mu^2}{K_{33}}) - \Omega\theta^2\right]P^2 + \frac{1}{4}\eta P^4 - \left[(C + \frac{\Lambda\mu}{K_{33}})\theta + \frac{\mu d}{K_{33}}\theta^3\right]P \tag{11}$$

In the "potential" for P (Eq. 11) we expect the last term to be small because of its chiral character. The potential is therefore of a single-minimum type for $\theta^2 < \theta_o^2$, where

$$\theta_o^2 = \frac{1}{\Omega}(\frac{1}{\varepsilon} - \frac{\mu^2}{K_{33}}) \tag{12}$$

The polarization in this regime is proportional to θ but small because it is induced only by a small chiral term linear in P. For $\theta^2 > \theta_o^2$ we get a double-minimum potential for P and the chiral term only chooses between the two minima. For $\theta^2 \gg \theta_o^2$ P is again proportional to θ but the ratio $P/\theta = (\Omega/\eta)^{1/2}$ is larger than in the small θ regime. The flexoelectric contribution to the wave vector of the helix, i.e. the last term in Eq. (8) is large for $\theta^2 \gg \theta_o^2$ and small for $\theta^2 \ll \theta_o^2$ and the flexoelectric coefficient μ has to be negative to give the measured temperature dependence of the pitch.

The minimization of $g(P, \theta)$ (Eq. 11) with respect to P leads to a cubic equation for P

$$\eta P^3 + \left(\frac{1}{\varepsilon} - \frac{\mu^2}{K_{33}} - \Omega\theta^2\right)P - \left(C + \frac{\Lambda\mu}{K_{33}} + \frac{\mu d}{K_{33}}\,\theta^2\right)\theta = 0 \quad (13)$$

Its minimal free energy solution is given by

$$P(\theta) = \frac{C + \Lambda\mu/K_{33} + \mu d\theta^2/K_{33}}{|C + \Lambda\mu/K_{33} + \mu d\theta^2/K_{33}|}\,\frac{2}{\sqrt{3\eta}} \times$$

$$\times \sqrt{\left|\frac{1}{\varepsilon} - \frac{\mu^2}{K_{33}} - \Omega\theta^2\right|}\; Y(X) \quad (14)$$

where

$$X = \frac{3^{3/2}\eta^{1/2}\theta\,|C + \Lambda\mu/K_{33} + \mu d\theta^2/K_{33}|}{2\,|1/\varepsilon - \mu^2/K_{33} - \Omega\theta^2|^{\,3/2}} \quad (15)$$

and

$$Y(X) = \begin{cases} \mathrm{sh}\left(\frac{1}{3}\mathrm{sh}^{-1}X\right) & \text{for } \theta^2 < \theta_o^2 \\ \mathrm{ch}\left(\frac{1}{3}\mathrm{ch}^{-1}X\right) & \text{for } \theta^2 > \theta_o^2 \text{ and } X > 1 \\ \cos\left(\frac{1}{3}\cos^{-1}X\right) & \text{for } \theta^2 > \theta_o^2 \text{ and } X < 1 \end{cases} \quad (16)$$

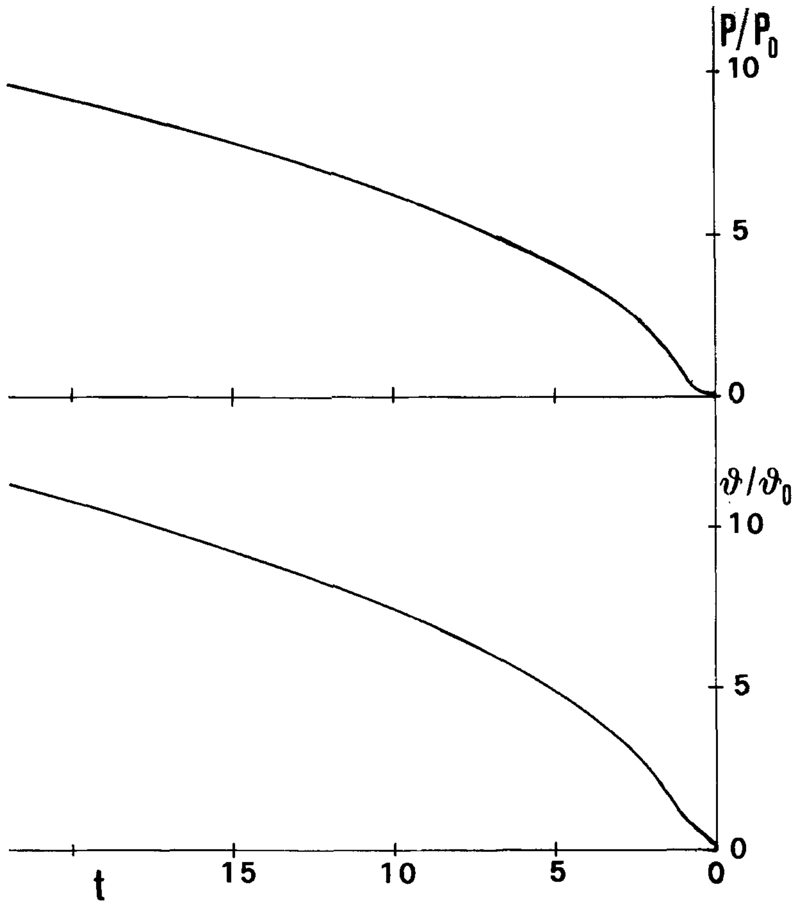

FIGURE 1. Temperature dependence of the spontaneous polarization P and of the tilt θ in SmC* phase.

The equation for θ can be obtained by minimizing the free energy g(Eq. 9) with respect to θ

$$(a-\frac{\Lambda^2}{K_{33}})\theta+(b-\frac{4\Lambda d}{K_{33}})\theta^3-\frac{3d^2}{K_{33}}\theta^5-(C+\frac{\Lambda\mu}{K_{33}}+\frac{3\mu d}{K_{33}}\theta^2)P(\theta)-$$

$$-\Omega\theta P^2(\theta)=0 \tag{17}$$

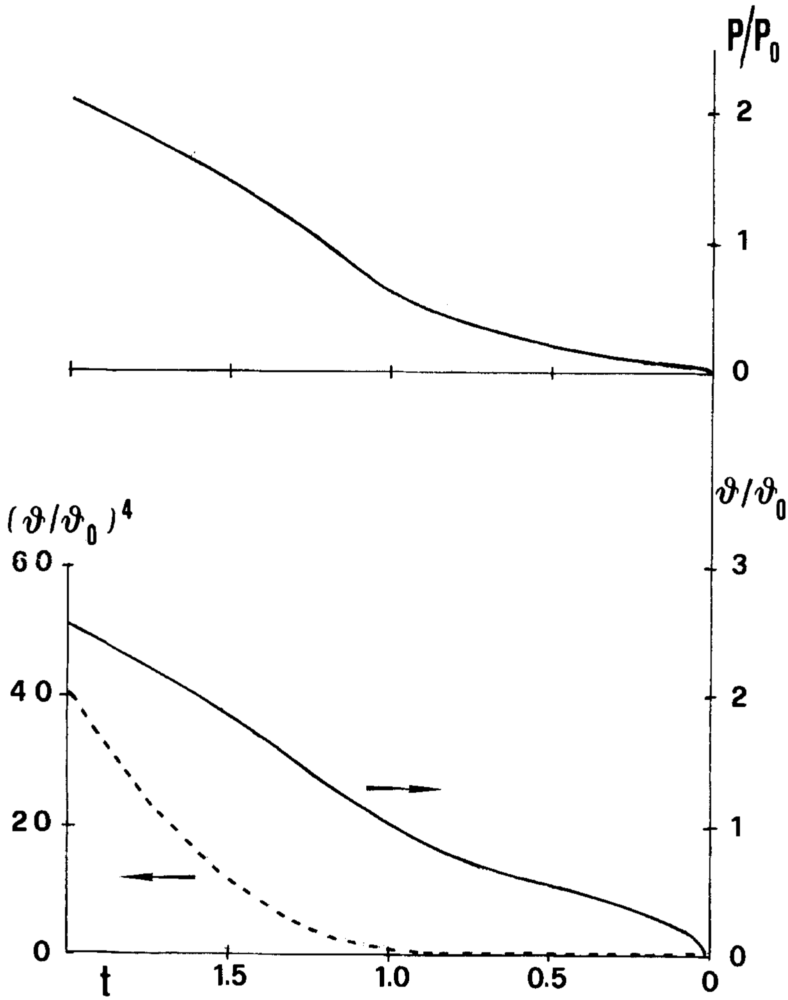

FIGURE 2. Temperature dependence of P and θ close to T_c in SmC* phase. The broken line represents $(\theta/\theta_0)^4$.

where $P(\theta)$ is given by Eq.(14). Temperature dependence of θ can be obtained numerically from Eq. (17) because $a = \alpha(T - T_o)$ and then $P(T)$ and $q(T)$ or $p(T)$ can be

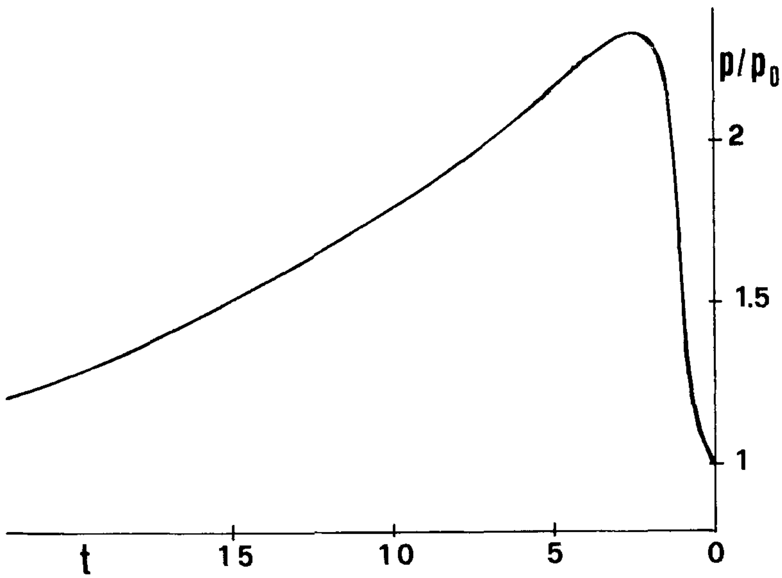

FIGURE 3. Temperature dependence of the helical pitch p in SmC* phase.

calculated from Eq. (14) and Eq. (8).

Figures 1.-4. show the obtained temperature dependences for one set of the parameters

$3^{3/2}\eta^{1/2}(C + \Lambda\mu/K_{33})/2\Omega^{3/2}\theta_o^2 = 1$

$3^{3/2}\eta^{1/2}\mu d/2K_{33}\Omega^{3/2} = - 0.001$

$9\eta d^2\theta_o^2/4\Omega^2 K_{33} = 3 \times 10^{-6}$

$3\eta(b - 4\Lambda d/K_{33})/4\Omega^2 = 0.8$

$3^{3/2}\eta^{1/2}\Lambda/2\Omega^{1/2}\mu = - 3.5$

The normalized temperature $t = (T_c - T)/(T_c - T_1)$ is defined so that $t = 1$ at $T = T_1$ where $\theta = \theta_o$. In Figures 1.-4. the spontaneous polarization is given in units of $P_o = 2\Omega^{1/2}\theta_o/3^{1/2}\eta^{1/2}$ and the pitch in units of its value

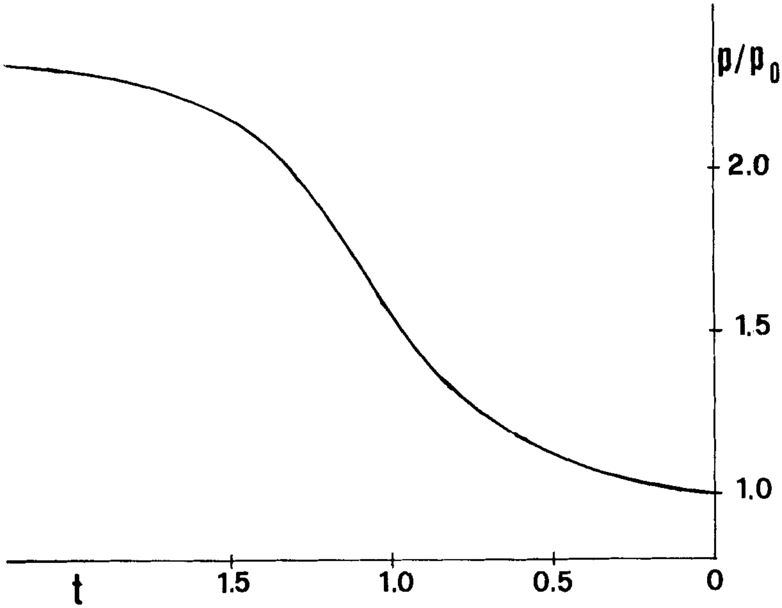

FIGURE 4. Temperature dependence of the pitch close to T_c in SmC* phase.

at T_c, i.e. p_o.

Figure 1. shows the temperature dependences of the spontaneous polarization and of the tilt in a broad temperature interval below T_c in the SmC* phase while in Figure 2. a narrower temperature interval at T_c is shown. Both $P(T)$ and $\theta(T)$ show classical behaviour very close to T_c and far below T_c with a cross-over regime with positive second derivatives around $t = 1$. Preliminary measurements of $P(T)$ in DOBAMBC show close to T_c an anomaly of the type shown in Figure 2. and more careful measurements are in progress. The expected anomaly in $\theta(T)$ is less pronounced and can be seen more clearly if one plots the fourth power of θ/θ_o which is shown as a broken line in Figure 2. Its value is

very small close to T_c and starts to increase rapidly at $t \sim 1$. Similar behaviour has been observed[4] in the temperature dependence of the intensity of the first diffraction sattelite which is expected to be proportional to θ^4.

The temperature dependence of the helical pitch is shown in Figures 2. and 3. The pitch increases with temperature at low temperatures, reaches a maximum at $t \sim 2.5$ and drops then to its finite value at T_c. The results agree qualitatively with measured data[4].

CONCLUSIONS

It has been shown that the anomalous temperature dependence of the helical pitch close to the SmA - SmC* transition can be explained by introducing the biquadratic coupling between the tilt of the molecules and the spontaneous polarization. The measured p(T) dependence can be obtained if

i) the non-chiral biquadratic coupling terms are large compared to the chiral bilinear terms and become relevant already very close to T_c in the SmC* phase, and

ii) the flexoelectric coefficient μ is negative.

The condition i) represents a reasonable assumption justified with the fact that chirality is in general a small perturbation in these systems. On the other hand it is not clear at present how the sign of μ is related to the anisotropy of a molecule and of the intermolecular interactions.

The consequence of biquadratic coupling terms is also an anomalous $P(T)$ and $\theta(T)$ dependence in the temperature interval where the pitch is strongly temperature dependent. Some preliminary results[4,11] show such anomalies but better measurements of the spontaneous polarization, the tilt and the pitch in a narrow temperature interval below T_c are needed.

REFERENCES

1. R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, J. Phys. (Paris) Lett., 30, L69 (1975).
2. S. A. Pikin and V. L. Indenbom, Uspekhi Fiz. Nauk, 125, 251 (1978).
3. R. Blinc and B. Žekš, Phys. Rev. A, 18, 740 (1978).
4. R. Blinc, B. Žekš, I. Muševič and A. Levstik, Proceedings of the 4th European Winter Conference on Liquid Crystals of Low-Dimensional Order and Their Applications, Bovec, March 26-30, 1984.
5. B. I. Ostrovski, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov and S. A. Taraskin, Ferroelectrics, 20, 189 (1978).
6. Ph. Martinot-Lagarde, R. Duke and G. Durand, Mol. Cryst. Liq. Cryst., 75, 249 (1981).
7. M. A. Osipov and S. A. Pikin, Sov. Phys. JETP, 55, 458 (1982).
8. M. Yamashita and H. Kimura, J. Phys. Soc. Jpn., 51, 2419 (1982); 52, 333 (1983).
9. B. Žekš, Proceedings of the 5th European Meeting on Ferroelectricity, to be published in Ferroelectrics.
10. R. Blinc, M. Vilfan, and J. Seliger, Bulletin of Magnetic Resonance, 5, 51 (1983).
11. A. Levstik, private communication.