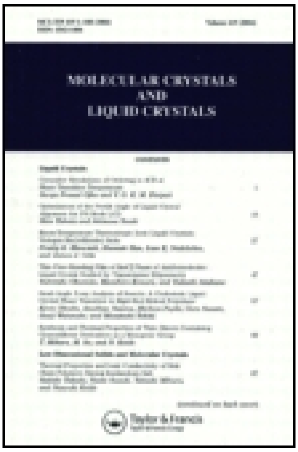

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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To cite this article: R. Blinc , I. Muševič & B. Žekš (1991): A Microscopic Explanation for the Anomalous Temperature Dependence of the Pitch in Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals, 202:1, 117-121

To link to this article: http://dx.doi.org/10.1080/00268949108035664

Mol. Cryst. Liq. Cryst., 1991, Vol. 202, pp. 117–121
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Printed in the United States of America

A Microscopic Explanation for the Anomalous Temperature Dependence of the Pitch in Ferroelectric Liquid Crystals

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(Received July 25, 1990)

A microscopic model of the ferroelectric smectic C* phase which takes into account both the small polar as well as the large quadrupolar ordering of the transverse molecular dipoles is shown to describe quantitatively the observed anomalous temperature dependence of the pitch of the smectic C* helix. The model is supported by the results of ^{14}N nuclear quadrupole as well as ^{13}C NMR studies.

Keywords: ferroelectric liquid crystals, pitch, dipolar order

I. INTRODUCTION

The anomalous temperature dependence of the pitch *p* of the smectic C* helix in ferroelectric liquid crystals seems to be one of the few unsolved problems in the physics of these systems. Whereas the classical Landau theory of ferroelectric liquid crystals[1,2] predicts that the pitch is temperature independent over the whole SmC* phase, a rather strong temperature dependence has been experimentally found close to T_c.[3–6] On approaching the SmC*-SmA transition temperature T_c from below, the pitch is at first constant, then increases with increasing temperature, reaches a maximum at T_c-T = 1–2 K and finally decreases to a finite value at T_c. Various different models[2,6,7] have been proposed but the real physical origin of the strong variation of the helical pitch close to T_c is still not clear.

Here we show that a microscopic model which takes into account both the small polar and the large quadrupolar ordering of the transverse molecular dipoles in the tilted SmC* phase is capable of describing quantitatively the observed temperature dependence of the pitch of the helix. The model is based on ^{14}N nuclear quadrupole and ^{13}C NMR studies[7] of the biasing of the rotation of the transverse molecular dipoles induced by the tilt of the long molecular axes on going from the smectic A into the ferroelectric smectic C* phase.

II. THE MICROSCOPIC MODEL

^{14}N nuclear quadrupole resonance (NQR) and ^{13}C NMR studies[7] showed that the biasing of the rotation of the molecules around their long axes consists of a relatively large quadrupolar part which is the same in the achiral Sm C and the chiral Sm C* phase and a small polar part which is specific for the Sm C* phase. Both of these contributions depend on the average molecular tilt θ and are thus absent in the Sm A phase, where the molecules are, on the average, oriented perpendicular to the layers. The single particle potential[8] for the rotation of a molecule around its long axis can be thus expressed as

$$V(\psi) = -a_1\theta \cos \psi - a_2\theta^2\cos(2\psi) \tag{1}$$

where ψ determines the orientation of the transverse molecular dipole. It is measured from the direction which is perpendicular to the tilt. The first term is linear in θ whereas the second term is quadratic in θ and is not of chiral character. The first term induces a polar—$\langle\cos \psi\rangle \neq 0$—and the second a quadrupolar—$\langle\cos 2\psi\rangle \neq 0$—ordering of the transverse molecular axes. ^{14}N NQR and ^{13}C NMR experiments have shown[7] that well below T_c $\langle\cos 2\psi\rangle \approx 10^{-1}$ whereas $\langle\cos \psi\rangle \approx 10^{-2} - 10^{-3}$.

The orientational free energy per molecule[8] is now obtained as $F_{\text{orient}} = \langle V\rangle + kT\,\langle\ln \rho\rangle$ where ρ is the density matrix. It can be expressed as an expansion in powers of the polar and quadrupolar order parameters $\langle\cos \psi\rangle$ and $\langle\cos 2\psi\rangle$:

$$F_{\text{orient}} = -a_1\theta\langle\cos \psi\rangle - a_2\theta^2\langle\cos 2\psi\rangle + kT\,\langle\cos \psi\rangle^2 - kT\,\langle\cos \psi\rangle\langle\cos 2\psi\rangle + \frac{1}{2}kT\,\langle\cos \psi\rangle^4 + kT\,\langle\cos 2\psi\rangle^2. \tag{2}$$

By minimizing F_{orient} with respect to the quadrupolar order parameter $\langle\cos 2\psi\rangle$ we find:

$$\langle\cos 2\psi\rangle = \frac{1}{2kT}\cdot a_2\theta^2 + \frac{1}{2}\langle\cos \psi\rangle^2. \tag{3}$$

By eliminating $\langle\cos 2\psi\rangle$ F_{orient} can be expressed as a function of the tilt and $\langle\cos \psi\rangle$:

$$F_{\text{orient}} = -\frac{1}{4}a_2^2\theta^4/kT - a_1\theta\langle\cos \psi\rangle - \frac{1}{2}a_2\theta^2\langle\cos \psi\rangle^2 + kT\,\langle\cos \psi\rangle^2 + \frac{1}{4}kT\,\langle\cos \psi\rangle^4. \tag{4}$$

The $\theta^2\langle\cos 2\psi\rangle$ term thus leads to an achiral biquadratic coupling term between the tilt and $\langle\cos\psi\rangle$, i.e., between the tilt and the polarization $P = n\mu_d\langle\cos\psi\rangle$. Here n is the number of molecules per unit volume and μ_d the molecular transverse dipole moment. Using the relation $g_{\text{orient}} = nF_{\text{orient}}$ and adding the inhomogeneous Lifshitz and elastic terms[1] as well as the diamagnetic anisotropy $-\chi_a$-coupling[1] g_H to the external magnetic field, we now find for the total free energy density

$$g(z) = g_{\text{orient}} + g_{\text{Lifshitz}} + g_H \tag{5a}$$

the expression:

$$g(z) = \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 - \Lambda\theta^2\phi' + \frac{1}{2}K_{33}(\theta'^2 + \theta^2\phi'^2) + \frac{1}{2\varepsilon}P^2 - \mu P\theta\phi'$$
$$- CP\theta - \frac{1}{2}\Omega P^2\theta^2 + \frac{1}{4}\eta P^4 - d\theta^4\phi' - \frac{1}{2}\chi_a H^2\theta^2\cos^2\phi. \tag{5b}$$

where polar coordinates were used $P_x = -P\sin\phi(z)$, $P_y = P\cos\phi(z)$, $n_x n_z = \theta\cos\phi(z)$, $n_y n_z = \theta\sin\phi(z)$, and $a = \alpha\,(\mathrm{T} - \mathrm{T_c})$.

The above free energy density has the same form as the extended Landau model proposed by Žekš[9] and Dumrongrattana and Huang[10] where however the origin of the anomalously large biquadratic coupling term Ω between the polarization and the tilt was not clear. The coefficients of the Landau expansion can be here related to the parameters of the microscopic model and one finds:

$$\Omega = a_2/(n\mu_d^2), \qquad C = a_1/\mu_d, \qquad \varepsilon = n\mu_d^2/(2\mathrm{kT}), \qquad \eta = \mathrm{kT}/n^3\mu_d^4). \tag{6}$$

It is thus the achiral quadrupolar ordering which is responsible for the large value of the Ω-term.

The polarization is here not simply proportional to the tilt as in the classical model but is for the homogeneous case given by a solution of the equation

$$\left(\frac{1}{\varepsilon} - \Omega\theta^2\right)P + \eta P^3 - C\theta = 0. \tag{7}$$

The ratio P/θ has one value—$P/\theta = \varepsilon/C$—close to $\mathrm{T_c}$, where θ and P are small, and another value—$P/\theta = (\Omega/\eta)^{1/2}$ far below $\mathrm{T_c}$ where θ is large.

For helicoidal systems the pitch of the helix $p = 2\pi/q$ is obtained as:

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

and is—in contrast to the classical case[1]—temperature dependent.

III. RESULTS AND DISCUSSION

The temperature variation of the helical pitch of chiral *p*-decyloxybenzilidene-*p'*-amino-2-methylbutyl cinnamate (DOBAMBC) below the SmA-SmC* transition is shown in Figure 1. The monodomain sample was prepared by slowly cooling (1°C/h) the system through the isotropic-smectic A transition in a magnetic field of 6 T which was parallel to the sample walls. The mono-domain sample acted as a one-dimensional diffraction grating. It was 240 μm thick to avoid surface effects. The determination of the temperature dependence of the pitch was performed by measuring the diffraction maxima of the scattered He–Ne laser light on a screen behind the sample with a Si phototransistor.

The form of the temperature dependence is similar to the one found by Ostrovsky *et al.*,[3] Martinot-Lagarde *et al.*,[4] and Takezoe.[5] The data can be fitted by expression[8] with the experimentally observed P/θ and θ values.[10]

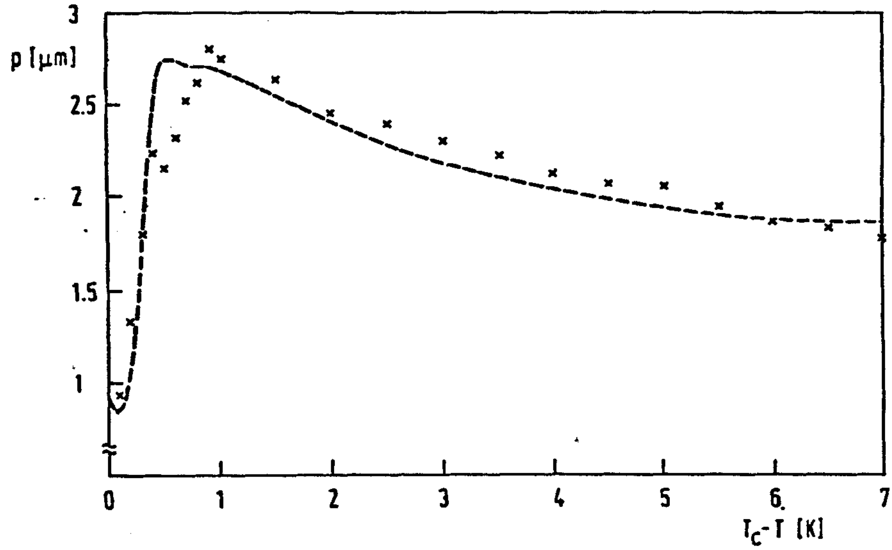

FIGURE 1 Comparison between the experimental (---) and theoretical (xxx) temperature dependences of the helical pitch of chiral DOBAMBC below the SmA-SmC* transition. The fit is based on Equation (8) with the experimental 0 and P/O data.[10]

The fit is nearly perfect and supports the microscopic model where the quadrupolar as well as the dipolar order of the transverse molecular dipoles is taken into account. It should be stressed that the values of the model parameters which describe the experimental data are in agreement with the ^{14}N NQR and ^{13}C NMR measurements such that the polar ordering is much smaller than the quadrupolar ordering everywhere except close to T_c at very small tilt angles θ. This explains the anomalous form of the Landau expansion used by Žekš[9] to describe dielectric and thermodynamic properties of ferroelectric liquid crystals.

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