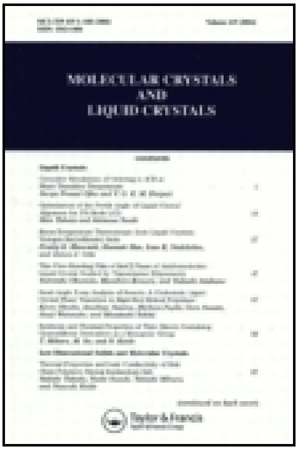

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Theoretical Prediction of Sign Reversal of the Spontaneous Polarization in the Ferroelectric, Chiral Smectic C* Phase

T. Carlsson [a] , B. Žekš [b c] , C. Filipič [c] & A. Levstik [c]
[a] Institute of Theoretical Physics, Chalmers University of Technology, S-41296, Göteborg, Sweden
[b] Institute of Biophysics, Medical Faculty, Lipičeva 2, YU-61105, Ljubljana, Yugoslavia
[c] J. Stefan Institute, Jamova 39, YU-61111, Ljubljana, Yugoslavia

To cite this article: T. Carlsson , B. Žekš , C. Filipič & A. Levstik (1987): Theoretical Prediction of Sign Reversal of the Spontaneous Polarization in the Ferroelectric, Chiral Smectic C* Phase, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 151:1, 155-163

To link to this article: http://dx.doi.org/10.1080/00268948708075327

Mol. Cryst. Liq. Cryst., 1987, Vol. 151, pp. 155-163
Photocopying permitted by license only

Printed in the United States of America

THEORETICAL PREDICTION OF SIGN REVERSAL OF THE SPONTANEOUS POLARIZATION IN THE FERROELECTRIC, CHIRAL SMECTIC C* PHASE

T. Carlsson[1], B. Žekš[2,3], C. Filipič[3] and A. Levstik[3]

[1]*Institute of Theoretical Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden*

[2]*Institute of Biophysics, Medical Faculty, Lipičeva 2, YU-61105 Ljubljana, Yugoslavia*

[3]*J. Stefan Institute, Jamova 39, YU-61111 Ljubljana, Yugoslavia*

With a generalized Landau expansion of the free-energy density as a basis, we have earlier presented a coherent model, with which we can calculate the temperature dependence of the tilt, polarization, pitch, dielectric susceptibility and heat capacity of the ferroelectric,SmC* phase in agreement with experiment (work submitted to Mol. Cryst. Liq. Cryst.). A brief review of this model is given and it is shown explicitely, that under certain circumstances the model predicts a sign reversal of the spontaneous polarization of the system. The nature of this transition is discussed and a simple expression of the tilt angle at the transition is derived.

I INTRODUCTION

Chiral SmC* liquid crystals exhibit ferroelectric behaviour[1] and have gained an increasing amount of interest during the last years. One reason for this is that the SmC* phase does not only lend itself to the study of many interesting physical phenomena, but also bears on the possibility of being used for developing electro-optical devices as was first pointed out by Clark and Lagerwall[2]. In this context the study of the spontaneous polarization of the system is of utmost importance. An increasing number of measurements of the temperature dependence of the polarization of the SmC* phase has recently been reported in the literature[3-10]. These measurements, which have been performed on several different compounds, all indicate a qualitatively similar temperature dependence of the polarization with one remarkable exeption. One compound studied by Goodby et al[10] showed a sign reversal of the polarization at a temperature which was roughly 25 K below the SmA - SmC* phase transition.

In order to describe the thermodynamical properties of the ferroelectric, SmC* phase, various theoretical models have been proposed in the literature[11-14]. These models are all based on Landau expressions of the free-energy density of the system. The early models[11,12] failed to describe the temperature dependence of the basic quantities of the system in a proper way. By proposing a more general form of the Landau expansion, Zeks[13] and Carlsson et al[14] however succeded to construct a thermodynamical model of the SmC* phase, which is capable of describing the full set of experimental data in at least a qualitatively correct way. It is the purpose of this paper to give a brief description of this model and to explicitely show that the sign reversal of the polarization, which was observed by Goodby et al[10], under certain circumstances comes out as a natural consequence of the model.

II GENERALIZED LANDAU MODEL OF THE FERROELECTRIC, SmC* PHASE

The Landau expansion of the free-energy density of the SmC* phase which we will use in this work has been introduced by us elsewhere[13,14]. The free-energy density of the system is expanded in two order parameters. These are the primary order parameter, the two component tilt vector $\vec{\xi}$, which is the projection of the director $\hat{n}$ into the smectic planes, and the two component in-plane polarization $\vec{P}$, which is always[1,14] at right angle to $\vec{\xi}$. The coordinates we use are defined in Fig. 1. The smectic planes are assumed to be parallel to the xy plane and the modulation of the system is along the z axis, while $\hat{n}$ and $\hat{z}$ are chosen with their signs in such a way that $\hat{n} \cdot \hat{z} > 0$. The free-energy density $g_o(z)$ is now written as[13,14]

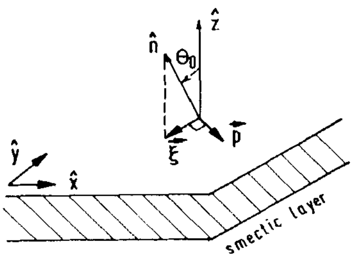

FIGURE 1 Definition of coordinates and the introduction of the order parameters $\vec{\xi}$ and $\vec{P}$.

$$g_o(z) = \frac{1}{2} a\,(\xi_1^2 + \xi_2^2) + \frac{1}{4} b\,(\xi_1^2 + \xi_2^2)^2 + \frac{1}{6} c\,(\xi_1^2 + \xi_2^2)^3 - \Lambda\,(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) +$$

$$+ \frac{1}{2} K_3 \,[(\frac{d\xi_1}{dz})^2 + (\frac{d\xi_2}{dz})^2] + \frac{1}{2\varepsilon}(P_x^2 + P_y^2) - \mu\,(P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz}) + C\,(P_x\xi_2 - P_y\xi_1) -$$

$$- \frac{1}{2}\Omega\,(P_x\xi_2 - P_y\xi_1)^2 + \frac{1}{4}\eta\,(P_x^2 + P_y^2)^2 - d\,(\xi_1^2 + \xi_2^2)(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) \qquad .....(1)$$

In Eq.(1) we have introduced $a = \alpha(T - T_o)$. The meaning of the eleven material parameters which are introduced in Eq.(1) is discussed by us elsewhere[14,15].

As the polarization vector $\vec{P}$ is mutually perpendicular to both $\vec{\xi}$ and $\hat{z}$, there are two possible directions of $\vec{P}$ for given $\vec{\xi}$ and $\hat{z}$. We will denote the polarization positive (a (+) substance) if $\vec{\xi}$, $\vec{P}$ and $\hat{z}$ form a right-handed coordinate system. If, on the other hand, $\vec{\xi}$, $\vec{P}$ and $\hat{z}$ form a left-handed coordinate system we will denote the polarization negative (a (-) substance). The notation of (+) and (-) substances was first introduced by Clark and Lagerwall[16]. Introducing the wave vector of the pitch $q = 2\pi/p$, p being the pitch, we thus can make the following ansatz of the order parameters:

$$\xi_1 = \theta_0 \cos qz \quad , \quad \xi_2 = \theta_0 \sin qz \qquad .....(2a)$$

$$P_x = - P_0 \sin qz \quad , \quad P_y = P_0 \cos qz \qquad .....(2b)$$

In Eq.(2) θ_o denotes the tilt angle while the magnitude of the spontaneous polarization is denoted by $|P_o|$.

In order to derive the equations governing the tilt and the polarization of the system we now substitute the ansatz (2) into the free-energy density (1). After having eliminated the equilibrium value of q ($q_{eq} = \Lambda/K_3 + \mu P_o/K_3\theta_o + d\theta_o^2/K_3$) the free-energy density can be written[14]

$$g_o(z) = \frac{1}{2}\tilde{a}\,\theta_o^2 + \frac{1}{4}\tilde{b}\,\theta_o^4 + \frac{1}{6}\tilde{c}\,\theta_o^6 + \frac{1}{2\tilde{\varepsilon}} P_o^2 - \frac{1}{2}\Omega P_o^2\theta_o^2 + \frac{1}{4}\eta P_o^4 - (\tilde{C} + \frac{\mu d}{K_3}\theta_o^2)P_o\theta_o \qquad .....(3)$$

In Eq.(3) we have introduced the renormalized constants $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, $\tilde{\varepsilon}$ and $\tilde{C}$ according to

$$\tilde{a} = a - \frac{\Lambda^2}{K_3}\,, \qquad \tilde{b} = b - \frac{4\Lambda d}{K_3}\,, \qquad \tilde{c} = c - \frac{3d^2}{K_3}$$

$$\frac{1}{\tilde{\varepsilon}} = \frac{1}{\varepsilon} - \frac{\mu^2}{K_3}\,, \qquad \tilde{C} = C + \frac{\Lambda\mu}{K_3} \qquad .....(4)$$

By minimizing Eq.(3) with respect to θ_o and P_o we obtain the two coupled equations which determine the tilt and the polarization of the system.

$$\tilde{a}\,\theta_o + \tilde{b}\,\theta_o^3 + \tilde{c}\,\theta_o^5 - \Omega\,\theta_o P_o^2 - (\tilde{C} + \frac{3\mu d}{K_3}\theta_o^2)\,P_o = 0 \qquad .....(5)$$

$$\eta\,P_o^3 + (\frac{1}{\tilde{\varepsilon}} - \Omega\theta_o^2)\,P_o - (\tilde{C} + \frac{\mu d}{K_3}\theta_o^2)\,\theta_o = 0 \qquad .....(6)$$

We now introduce the designations tilt equation for Eq.(5) and polarization equation for Eq.(6).

III SOLUTION OF THE POLARIZATION EQUATION - THE POSSIBILITY OF SIGN REVERSAL OF THE POLARIZATION

Eq.(6) provides, for a given value of θ_o, a cubic equation in P_o. Dividing this equation by θ_o and taking the limit $\theta_o \to 0$, $P_o \to 0$ (i.e. $T \to T_C$) we get

$$\lim_{T\to T_C} \frac{P_o}{\theta_o} = \tilde{C}\,\tilde{\varepsilon} \qquad .....(7)$$

As the constant $\tilde{\varepsilon}$ must always be positive, and taking θ_o to be positive by definition, we notice that the sign of the polarization at T_C is determined by the sign of $\tilde{C}$. If the chirality of the system is weak, which seems to be the case for all presently known SmC* liquid crystals, the renormalization of the constant C, which is introduced by Eq.(4), is small and $\tilde{C}$ and C will have the same sign. Thus the sign of the constant C, which from Eq.(1) can be seen to be the coefficient of the piezoelectric bilinear coupling, determines whether a compound will appear as a (+) substance or as a (-) substance at T_C.

To write down the solution of the polarization equation (6) we first introduce the parameter x

$$x = \sqrt{\frac{27\eta}{2}}\ \frac{(\tilde{C} + \frac{\mu d}{K_3}\theta_o^2)\ \theta_o}{\left|\frac{1}{\tilde{\varepsilon}} - \Omega\theta_o^2\right|^{3/2}} \qquad .....(8)$$

The sign of x is determined by the factor $\tilde{C} + \mu d\theta_o^2/K_3$. It can be proven[14] that if the model shall exhibit a temperature dependence of the pitch in accordance with what is experimentally observed, *the signs of the constants $\tilde{C}$, d and μ must be chosen in such a way that (recalling that C and $\tilde{C}$ has* the same sign) the product $\tilde{C}d\mu$ is negative. Thus the two terms in the factor $\tilde{C} + \mu d\theta_o^2/K_3$ are always of opposite signs. Depending on the values of x and θ_o we have to chose the solution of the polarization equation to belong to one of the following three regimes[14]

REGIME 1 : $\theta_o^2 < 1/\tilde{\varepsilon}\Omega$

$$P_o = \frac{2}{\sqrt{3\eta}}\left(\frac{1}{\tilde{\varepsilon}} - \Omega\theta_o^2\right)^{1/2} \sinh\left(\frac{1}{3}\sinh^{-1}x\right) \qquad .....(9)$$

REGIME 2 : $\theta_o^2 > 1/\tilde{\varepsilon}\Omega$; $|x| > 1$

$$P_o = \frac{x}{|x|}\ \frac{2}{\sqrt{3\eta}}\left(\Omega\theta_o^2 - \frac{1}{\tilde{\varepsilon}}\right)^{1/2} \cosh\left(\frac{1}{3}\cosh^{-1}|x|\right) \qquad .....(10)$$

REGIME 3 : $\theta_o^2 > 1/\tilde{\varepsilon}\Omega$; $|x| < 1$

$$P_o^+ = \frac{2}{\sqrt{3\eta}}\left(\Omega\theta_o^2 - \frac{1}{\tilde{\varepsilon}}\right)^{1/2} \cos\left(\frac{1}{3}\cos^{-1}x\right) \qquad ....(11a)$$

$$P_o^- = -\frac{2}{\sqrt{3\eta}}\left(\Omega\theta_o^2 - \frac{1}{\tilde{\varepsilon}}\right)^{1/2} \cos\left(\frac{1}{3}\cos^{-1}(-x)\right) \qquad ....(11b)$$

It is easy to see from Eqs.(9) - (11) that there are two ways in which the solution for P_0 can change sign as the temperature of the system is lowered, starting at T_C(i.e. as θ_0 is increased, starting from the value $\theta_0 = 0$). The solution of regime 1 is an odd function of x, the sign of which is determined by the factor $\tilde{C} + \mu d\theta_0^2/K_3$. As was mentioned before, $\tilde{C}$ and μd should be expected to be of different signs implying that the factor will always change sign for large enough θ_0. However, the solution of Regime 1 is only valid for small θ_0 ($\theta_0^2 < 1/\tilde{\varepsilon}\Omega$). This fact makes it improbable that the solution of Regime 1 will change sign before θ_0 has increased so much that Regime 2 has been entered.

The solution of Regime 2 will of course never change sign because in this regime $|x| > 1$, implying that here x can never go through zero.

Concerning the solution of Regime 3, which is valid for large enough tilts ($\theta_0^2 > 1/\tilde{\varepsilon}\Omega$), the situation is somewhat different. In this regime Eq.(6) has three real solutions, two of which correspond to local minima of the free-energy density (3). These are the two solutions given by Eqs.(11a) and (11b). From these two,we now have to chose the one for which the free-energy density is the least. Before doing so we must however realize a small complication of the problem. At a given temperature, i.e. for a given value of a, we have to solve Eqs.(5) and (6) simultaneously. We then end up with two solutions, (T, θ_0^+, P_0^+) and (T, θ_0^-, P_0^-), corresponding to local minima of the free-energy density. Due to the nature of the equations, the tilt is slightly shifted between these two solutions, i.e. $\theta_0^+ \neq \theta_0^-$. This forces us to solve the problem numerically in order

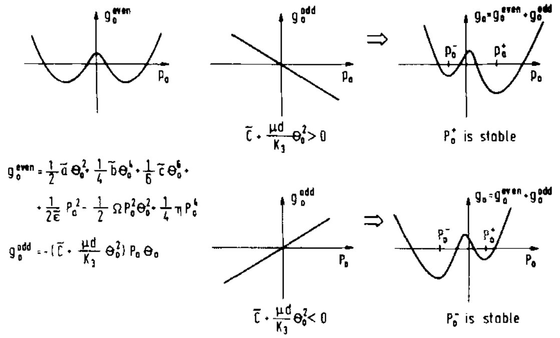

FIGURE 2 The free-energy density is composed of two parts of which one is even and one is odd in P_0. In the figure is demonstrated how the sign of the factor multiplying the $P_0\theta_0$ term determines for which of the solutions P_0^+ and P_0^- the free-energy density will adopt its minimum.

to be able to compare the free-energy density of the two solutions. By doing so one realizes[14] that the shift in tilt is so small that the approximation $\theta_0^+ = \theta_0^-$ will introduce a relative error in the results by a factor 10^{-3}. We thus introduce the approximation $\theta_0^+ = \theta_0^- = \theta_0$. As all the terms in the free-energy density of Eq.(3) are even in P_0 except the term $-(\tilde{C} + \mu d\theta_0^2/K_3)P_0\theta_0$, the sign of the coefficient of this last term will determine which of the two solutions P_0^+ and P_0^- will be stable. This reasoning is sketched in Fig.2 and from the definition of x (Eq.(8)) it is clear, that the free-energy density of the system will be minimized by the solution P_0^+ if $x > 0$ and by P_0^- if $x < 0$. This means that at one critical angle, θ_C, the sign of the polarization will change and the system will undergo a discontinuous transition from a (+) to a (-) substance or vice versa depending on the sign of $\tilde{C}$. This transition should of course be smeared out due to the presence of thermal fluctuations. The expression of the critical tilt angle which is determined by the condition $x = 0$ is the same as the one of the (less probable) transition within Regime 1 and is given by

$$\theta_C^2 = \left| \frac{\tilde{C}K_3}{\mu d} \right| \qquad .....(12)$$

While the change of sign of polarization within Regime 1 would be continuous it is discontinuous within Regime 3 and the value of the polarization at the transition is given by

$$P_C = \frac{1}{\sqrt{\eta}} \left(\left| \frac{\Omega\tilde{C}K_3}{\mu d} \right| - \frac{1}{\varepsilon} \right)^{1/2} \qquad .....(13)$$

For this transition to occur we still must demand that the values of the ingoing parameters of Eq.(12) are such that θ_C is within the feasible experimental range. This does not seem to be the case for most compounds, but recently Goodby et al have reported[10] the observation of change of sign of polarization in one case. We thus conclude that in such a case our model is able to describe this transition in a simple way if one just choses a suitable set of material parameters.

IV DISCUSSION

The earliest Landau models which were introduced[11,12] in order to describe the ferroelectric SmC* phase were evidently too simple. These models predicted for instance both the pitch and the ratio polarization/tilt to be temperature independent, predictions which are contradicted by experiments[6,7,9]. Also the dielectric susceptibility which can be calculated by these models is not in accordance with experiments[15]. Motivated by this we have introduced[13-15] the generalized Landau expansion of Eq.(1) in which the terms proportional to c, Ω, η and d represent the generalization. By the use of this expansion we have been able to construct a coherent model with which we can calculate[14] the temperature dependence of the tilt, polarization, pitch, dielectric susceptibility and heat capacity of the ferroelectric, SmC* phase in agreement with experiment.

It is the purpose of this paper to show that our generalized Landau model in addition to the features mentioned above also predicts that under some circumstances the polarization will change sign at a certain temperature. As was discussed in Section III this transition can be of two types. In both cases the transition occurs when the tilt is so large that the quantity $\tilde{C} + \mu d\theta_0^2/K_3$ changes sign (we recall the previous statement that the two terms entering this quantity can be expected to always be of opposite signs). If this transition takes place at a comparatively small tilt angle ($\theta_C^2 < 1/\tilde{\varepsilon}\Omega$) the transition takes place within Regime 1 of the solution of the polarization equation (c.f. Eq.9) and would be continuous. If on the other hand the condition $\theta_C^2 > 1/\tilde{\varepsilon}\Omega$ is fulfilled, the transition takes place within Regime 3 (c.f. Eqs.(11)) and is discontinuous, possibly smeared out by thermal fluctuations. In both cases the critical tilt angle at which the transition takes place is given by Eq.(12). The two types of transitions are schematically illustrated in Fig.3.

As was discussed earlier, the sign of the bilinear, piezoelectric coupling constant C determines the sign of the polarization close to T_C. The "driving force" of the sign reversal of the polarization is then connected to the $\mu-$ and d-terms. The μ-term is proportional to the flexoelectric bilinear

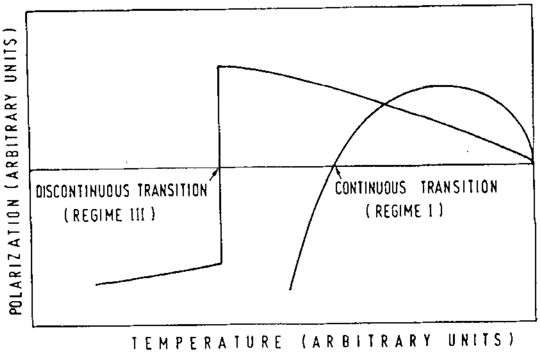

FIGURE 3 Continuous and discontinuous sign reversal of the spontaneous polarization. The nature of the transition will depend on in which regime of the solution of the polarization equation the transition takes place.

coupling and the d-term was introduced into the model in order to describe the temperature dependence of the pitch far from T_C correctly[14]. If the transition shall take place within the experimentally feasible range these two couplings must be large. A small value of the elastic constant K_3 would of course also favour the transition. It should also be pointed out that within the simpler Landau models[11,12], where the d-term is missing, the critical angle of the transition goes to infinity. This makes the transition to a new feature, predicted by our generalized model only, and to one possible way of explaining the experimentally observed sign reversal of the polarization which was recently observed by Goodby et al[10].

Another possible way of explaining the observed polarization sign reversal is to include into the free-energy density the term

$$g_o' = C'(\xi_1^2 + \xi_2^2)(P_x\xi_2 - P_y\xi_1) \qquad .....(14)$$

which leads to an effective tilt dependent piezoelectric coefficient $C + C'\theta_o^2$ giving the polarization sign reversal at $\theta_C^2 = - C/C'$ for $C/C' < 0$. The structure of such a renormalization of the piezoelectric coefficient is the same as the one in Eq.(3). The C'-term (Eq.(14)) therefore in general leads to the same two possible types of the sign reversal as the ones shown in Fig.3.

REFERENCES

1. R. B. Meyer, L. Liebert, L. Strzelecki and P. J. Keller, *J. Physique Lett.* 36, L69 (1975)
2. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* 36, 899 (1980)
3. B.I. Ostrovski, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov and S. A. Taraskin, *Ferroelectrics*, 20, 189 (1978)
4. J. Hoffman, W. Kuczynski and J. Malecki, *Mol. Cryst. Liq. Cryst.* 44, 287 (1978)
5. K. Skarp, I. Dahl, S. T. Lagerwall and B. Stebler, *Mol. Cryst. Liq. Cryst.* 114, 283 (1984)
6. C. Filipič, A. Levstik, I. Levstik, R. Blinc, B. Žekš, M. Glogarova and T. Carlsson, *Ferroelectrics* (in press)
7. S. Dumrongrattana and C. C. Huang, *Phys. Rev. Lett.* 56, 464 (1986)
8. K. Skarp and G. Andersson, *Ferroelectrics Lett.* 6, 67 (1986)
9. D. Parmar, M. A. Handschy and N. A. Clark, *Poster presented at the 11th International Liquid Crystal Conference*, Berkeley 1986
10. J. W. Goodby, E. Chin, J. M. Geary and J. S. Patel, *Poster presented at the 11th International Liquid Crystal Conference*, Berkeley 1986
11. S. A. Pikin and V. L. Indenbom, *Uspheki Fiz. Nauk.* 125, 251 (1978)
12. R. Blinc and B. Žekš, *Phys. Rev.* A 18, 740 (1978)
13. B. Žekš, *Mol. Cryst. Liq. Cryst.* 114, 259 (1984)
14. T. Carlsson, B. Žekš, C. Filipič, A. Levstik and R. Blinc, *Mol. Cryst. Liq. Cryst.* (submitted)
15. A. Levstik, T. Carlsson, C. Filipič, I. Levstik and B. Žekš, *Phys. Rev.* A 35 (in press)
16. N. A. Clark and S. T. Lagerwall, *Ferroelectrics*, 59, 25 (1984)