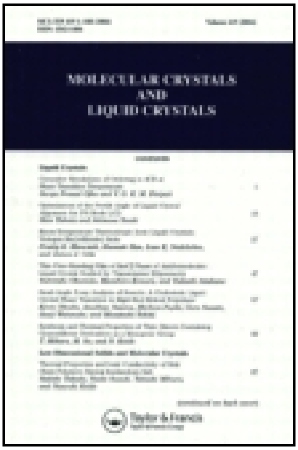

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Anomalous Behaviour of the Spontaneous Polarization of Ferroelectric, SmC* Liquid Crystals

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ANOMALOUS BEHAVIOUR OF THE SPONTANEOUS POLARIZATION OF FERROELECTRIC, SmC* LIQUID CRYSTALS

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A generalized, dimensionless Landau model of the ferroelectric, SmC* phase is presented. The equations governing the tilt, polarization and pitch of ferroelectric, SmC* liquid crystals are given. It is shown that the solutions of these equations agree with available experimental data. It is also shown that the introduction of a biquadratic coupling between tilt and polarization in the Landau expansion of the free-energy density, which is an essential part of the model, implies a cross-over behaviour of the polarization when plotted as function of temperature. This cross-over is essential when understanding the connection between the behaviour of the pitch, the ratio polarization/tilt and the polarization versus temperature.

I INTRODUCTION

The chiral smectic C* phase exhibits, in contrast to nonchiral smectics, ferroelectric behaviour[1], a fact which gives rise to interesting implications for the developing of electro-optical devices[2]. During the last years an increasing amount of experimental data concerning the thermodynamic properties of the SmC* phase has appeared in the literature[3], but only recently a coherent theoretical model which is in agreement with experiments has been presented[3,4]. In this paper we will give a brief summary of this model and show how it predicts the polarization to exhibit a cross-over behaviour, i.e. different square-root behaviour versus temperature close to and far from the SmA - SmC* phase transition temperature T_C. This behaviour has also been verified by several experimental observations[5-7]. We will also show how this cross-over regime is intimately associated with the maximum of the pitch which is usually observed[8,9] a few degrees below T_C.

II GENERALIZED, DIMENSIONLESS LANDAU MODEL OF THE FERROELECTRIC, SmC* PHASE

The theoretical model of the ferroelectric, SmC* phase which we will use in this work is based on the generalized Landau expansion of the free-energy density which has been introduced by us elsewhere[3,4]. 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[1,3] at right angle to $\vec{\xi}$. The coordinates we use are defined in Figure 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 $g_0(z)$ is now written as[3,4]

$$g_o(z) = \frac{1}{2} a (\xi_1^2 + \xi_2^2) + \frac{1}{4} b (\xi_1^2 + \xi_2^2)^2 + \frac{1}{6} c (\xi_1^2 + \xi_2^2)^3 - \Lambda (\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) +$$
$$+ \frac{1}{2} K_3 [(\frac{d\xi_1}{dz})^2 + (\frac{d\xi_2}{dz})^2] + \frac{1}{2\varepsilon} (P_x^2 + P_y^2) - \mu (P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz}) + C (P_x \xi_2 - P_y \xi_1) -$$
$$- \frac{1}{2} \Omega (P_x \xi_2 - P_y \xi_1)^2 + \frac{1}{4} \eta (P_x^2 + P_y^2)^2 - d (\xi_1^2 + \xi_2^2)(\xi_1 \frac{d\xi_2}{dz} - \xi_2 \frac{d\xi_1}{dz}) \qquad .....(1)$$

Only the term quadratic in tilt is assumed to be explicitely temperature dependent: $a = \alpha(T - T_0)$. The elastic modulus is denoted by K_3, the coefficient of the Lifshitz term responsible for the modulation is denoted by Λ while μ and C are the coefficients of the flexo- and piezo- electric bilinear coupling. The dielectric constant of the system in the high temperature limit of the SmA phase is denoted by ε, while Ω is the coefficient of the biquadratic coupling term inducing transverse quadrupolar ordering and the η-term has been added to stabilize the system. The d-term

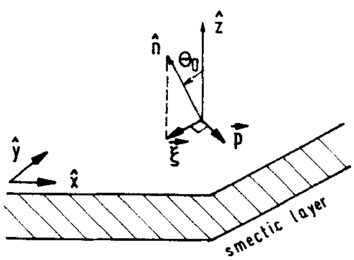

FIGURE 1 Definition of coordinates and the introduction of the order parameters $\vec{\xi}$ and $\vec{P}$.

is describing the monotonous increase of the pitch with temperature at low temperature. If the model shall be capable of describing the heat capacity of the system in a correct way, we also have to add[10] a sixth-order term in tilt to the free-energy density and for this purpose we introduce the constant c.

We are looking for a helicoidal solution

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

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

which minimizes the free-energy of the system. Here $q = 2\pi/p$ is the wave vector of the helix. Substituting this ansatz into Eq.(1) we obtain an expression for the free-energy density, which, when minimized with respect to θ_0, P_0 and q, respectively, gives three equations determining the tilt, the polarization and the pitch, p, of the system as functions of temperature.

We have shown[3] that the equations governing the behaviour of the system which can be deduced from Eqs.(1)-(2) are most conveniently studied by rewriting them into dimensionless form. By doing so we reduce the eleven material parameters introduced in Eq.(1) to six independent dimensionless constants

$$\gamma = \frac{\tilde{b}\eta}{\Omega^2} \quad , \quad \beta = \frac{\eta^{1/2}\tilde{C}\tilde{\varepsilon}}{\Omega^{1/2}} \quad , \quad \rho = \frac{\tilde{c}\eta}{\tilde{\varepsilon}\Omega^3}$$

$$\lambda = \frac{\Lambda\eta^{1/2}\tilde{\varepsilon}^{1/2}}{K_3^{1/2}\Omega^{1/2}} \quad , \quad \nu = \frac{\mu\tilde{\varepsilon}^{1/2}}{K_3^{1/2}} \quad , \quad \delta = \frac{d\eta^{1/2}}{K_3^{1/2}\Omega^{3/2}\tilde{\varepsilon}^{1/2}} \qquad .....(3)$$

where $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, $\tilde{\varepsilon}$ and $\tilde{C}$ are renormalized constants given by

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

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

The physical quantities such as the polarization P_o, the tilt θ_o, the wave vector of the pitch q and the dielectric susceptibility χ will now be expressed in dimensionless form and will be denoted by a tilde above the corresponding symbol, while the characteristic units with which these are measured will be denoted by an asterisk (e.g. $\tilde{\theta}_o = \theta_o/\theta^*$). The reduced temperature however we denote by $\tau = (T_c - T)/T^*$. The characteristic units are chosen to be

$$\theta^* = \left(\frac{1}{\tilde{\varepsilon}\Omega}\right)^{1/2}, \quad P^* = \left(\frac{1}{\tilde{\varepsilon}\eta}\right)^{1/2}, \quad q^* = \frac{1}{z^*} = \left(\frac{\Omega}{\tilde{\varepsilon}\eta K_3}\right)^{1/2}, \quad \chi^* = \tilde{\varepsilon}, \quad T^* = \frac{\tilde{b}}{\tilde{\varepsilon}\alpha\Omega} \qquad \text{.....(5a)}$$

$$g^* = \frac{P^{*2}}{\chi^*}, \qquad C_p^* = \frac{P^{*2}}{\chi^* T^*}, \qquad E^* = \frac{P^*}{\chi^*} \qquad \text{.....(5b)}$$

The original eleven parameters (Eq.(1)) can thus be transformed into six dimensionless constants (Eqs.(3) and (4)), which determine the shape of the temperature dependence of the physical quantities, and into five characteristic units (Eq.(5a)). The characteristic units of the free-energy density, the heat capacity and the electric field are not independent and are given by Eq.(5b) for completeness.

Substituting Eqs.(2) into Eq.(1) and eliminating q, we can derive the dimensionless form of the free-energy density by the use of Eqs.(3) - (5)

$$g_o = \frac{1}{2}(\beta^2 - \gamma\tau)\tilde{\theta}_o^2 + \frac{1}{4}\gamma\tilde{\theta}_o^4 + \frac{1}{6}\rho\,\tilde{\theta}_o^6 + \frac{1}{2}\tilde{P}_o^2 - \beta\tilde{P}_o\tilde{\theta}_o - \frac{1}{2}\tilde{P}_o^2\tilde{\theta}_o^2 + \frac{1}{4}\tilde{P}_o^4 - \nu\delta\tilde{\theta}_o^3\tilde{P}_o \qquad \text{.....(6)}$$

The equations for $\tilde{\theta}_o$ and $\tilde{P}_o$ are obtained by minimizing Eq.(6)

$$(\beta^2 - \gamma\tau)\,\tilde{\theta}_o + \gamma\tilde{\theta}_o^3 + \rho\tilde{\theta}_o^5 - \tilde{\theta}_o\tilde{P}_o^2 - (\beta + 3\nu\delta\tilde{\theta}_o^2)\,\tilde{P}_o = 0 \qquad \text{.....(7a)}$$

$$\tilde{P}_o^3 + (1 - \tilde{\theta}_o^2)\,\tilde{P}_o - (\beta + \nu\delta\tilde{\theta}_o^2)\,\tilde{\theta}_o = 0 \qquad \text{.....(7b)}$$

while $\tilde{q}$ is given by

$$\tilde{q} = \lambda + \nu\frac{\tilde{P}_o}{\tilde{\theta}_o} + \delta\tilde{\theta}_o^2 \qquad \text{.....(8)}$$

Eqs.(7) and (8) are the equations which govern the temperature dependence of the tilt, polarization and pitch. In Section III we will show how the cross-over behaviour of the polarization which was mentioned in the Introduction is a straightforward consequence of the polarization equation (7b).

III CROSS - OVER PROPERTIES OF THE POLARIZATION EQUATION

The polarization equation (7b) contains three of the constants defined by Eqs.(3) and (4). As the chirality of the system in question is of a weak character, one can generally expect[3] the magnitudes of the constants ν and δ to be considerably less than that of β. Furtheron, being interested of the behaviour of the polarization curve mainly close to the SmA - SmC* phase transition temperature T_C, i.e. where $\tilde{\theta}_o$ is small, we will assume that we can neglect the term $\nu\delta\tilde{\theta}_o^2$ in comparison with β. Doing this approximation and dividing Eq.(7b) by $\tilde{\theta}_o^3$ we get

$$\left(\frac{\tilde{P}_o}{\tilde{\theta}_o}\right)^3 + \left(\frac{1}{\tilde{\theta}_o^2} - 1\right)\frac{\tilde{P}_o}{\tilde{\theta}_o} - \frac{\beta}{\tilde{\theta}_o^2} = 0 \qquad .....(9)$$

This equation shows that the ratio $\tilde{P}_o/\tilde{\theta}_o$ as function of $\tilde{\theta}_o^2$ depends on one parameter only, namely β. From Eq.(9) we can furtheron deduce the limiting behaviour of $\tilde{P}_o/\tilde{\theta}_o$ close to and far away from T_C (τ being the reduced temperature)

$$\lim_{\tau\to 0}\frac{\tilde{P}_o}{\tilde{\theta}_o} = \beta \ , \qquad \lim_{\tau\to\infty}\frac{\tilde{P}_o}{\tilde{\theta}_o} = 1 \qquad .....(10)$$

We can assume without loss of generality that β is positive. This simply means[3] that we are dealing with a compound with a positive polarization (a (+) substance in the nomenclature of Clark and Lagerwall[11]).

In Figure 2 we have plotted $\tilde{P}_o/\tilde{\theta}_o$ and $\tilde{P}_o$ as functions of $\tilde{\theta}_o^2$ for three different values of β. The cross-over behaviour of the ratio $\tilde{P}_o/\tilde{\theta}_o$ versus $\tilde{\theta}_o^2$ is obvious from Eqs.(10) as soon as β is not equal to unity. More interesting are however the graphs of $\tilde{P}_o$ versus $\tilde{\theta}_o^2$. We notice that if β is small enough the polarization curve gets S-shaped, displaying different square-root behaviour close to and far from T_C. The limiting value of β for this behaviour to occur can be shown[3] to be around 0.5. We should also point out that, as $\tilde{\theta}_o$ is roughly proportional to $\sqrt{\tau}$ according to the model, the quantity $\tilde{\theta}_o^2$ can be considered as an approximate measure of the reduced temperature. The graphs $\tilde{P}_o(\tilde{\theta}_o^2)$ and $\tilde{P}_o(\tau)$ will consequently have the same qualitative apparence. We will see in the next

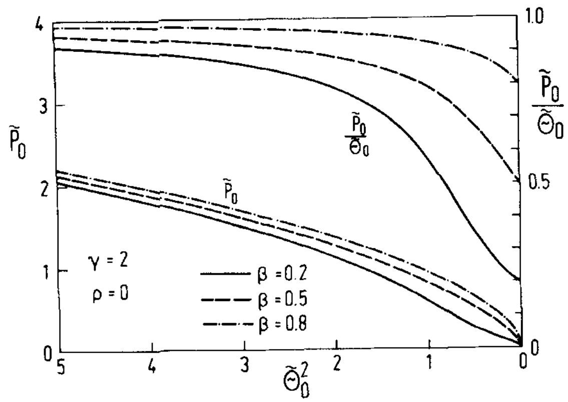

FIGURE 2 Calculated $\bar{P}_o/\bar{\theta}_o$ and $\bar{P}_o$ versus $\bar{\theta}_o^2$. We notice how the tendency of S-shape of the polarization curve is connected to the dip of $\bar{P}_o/\bar{\theta}_o$ close to T_C, i.e. to a small value of β.

section that, in order for the model to describe the experimentally observed behaviour[8,9] of the pitch correctly, we must choose a value of the parameter β which is considerably smaller than unity. This choice of β, which is directly connected to the dip of $\bar{P}_o/\bar{\theta}_o$ close to T_C, has also been verified by direct measurements by Parmar et al[7]. Thus the tendency of the polarization curve to exhibit the S-shaped behaviour, which is intimately connected to the smallness of β, is indirectly supported by both measurements of the pitch and of the ratio polarization/tilt.

IV THE CONNECTION BETWEEN THE POLARIZATION AND THE PITCH TEMPERATURE DEPENDENCE

The wave vector of the pitch can be calculated by Eq.(8). If we restrict the discussion to the case of a (+) substance with a right-handed helix the quantities entering this equation have the following signs[3]: $\lambda > 0$, $\nu < 0$, $\bar{P}_o/\bar{\theta}_o > 0$ and $\delta > 0$. More conveniently we now write the expression of $\bar{q}$ as

$$\bar{q} = \lambda - |\nu| \frac{\bar{P}_o}{\bar{\theta}_o} + \delta \bar{\theta}_o^2 \qquad .....(11)$$

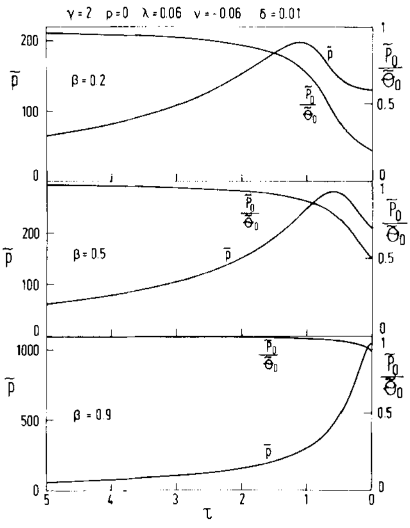

FIGURE 3 Demonstration of the connection between the maximum of the pitch and the "knee" in the Polarization/tilt curve.

and consequently all quantities entering Eq.(11) are positive. The general experimental behaviour[8,9] of $\tilde{q}$ as function of $\tilde{\theta}_o$ is such that it starts from a finite value at T_C, decreases towards a minimum approximately 1 K below T_C and then slowly increases with increasing value of $\tilde{\theta}_o$ (decreasing absolute temperature). This behaviour is obtained from Eq.(11) if the ratio $\tilde{P}_o/\tilde{\theta}_o$ (Fig.2) exhibits a strong enough dip at T_C. This dip will, as is seen from the equation, decrease $\tilde{q}$ if the temperature is decreased starting at T_C. Decreasing the temperature further, $\tilde{P}_o/\tilde{\theta}_o$ will saturate and $\tilde{q}$ will increase due to the $\delta\tilde{\theta}_o^2$ term. Thus $\tilde{q}$ will have a minimum (maximum of the pitch) somewhere in the region of the "knee" of the $\tilde{P}_o/\tilde{\theta}_o$ curve. In this way it is clear how the cross-over behaviour of the polarization curve is connected to the presence of the maximum of the pitch just below T_C. In Figure 3 we show the outcome of a calculation of the pitch (solid line) and the ratio polarization/tilt (dashed line) for a given set of the parameters γ, ρ, λ, δ and ν while β is varied. The figure clearly demonstrates how the maximum of the pitch is related to the form of the $\tilde{P}_o/\tilde{\theta}_o$ curve, i.e. to the value of the parameter β.

V DISCUSSION

From Figures 2 and 3 is clearly demonstrated the connection between the dip in the $\bar{P}_0/\bar{\theta}_0$ curve close to T_C, the tendency of the polarization curve to exhibit S-shaped behaviour and the presence of the maximum of the pitch just below T_C. It is also clear from the figure that the cross-over behaviour is more pronounced, the smaller is the magnitude of β. This in turn means that the cross-over behaviour gets the more important, the larger the biquadratic coupling (the Ω-term) between tilt and polarization in the free-energy density is compared to the bilinear coupling (the $\bar{C}$-term) as $\beta \propto \bar{C}/\Omega^{1/2}$. The presence of the biquadratic coupling is thus an essential ingredience of the generalized Landau model which is used in this paper. This is also emphasized by the fact that the early models of the SmC* phase , in which the biquadratic coupling is missing predict[12] a temperature independent $\bar{q}$, a temperature independent $\bar{P}_0/\bar{\theta}_0$ and a pure square-root behaviour of as well tilt as polarization versus temperature. This model is thus totally incapable of describing the experimental data of the SmC* phase in a correct way.

Finally we conclude in pointing out that while some authors[5-7] confirm the S-shaped behaviour of the polarization curve, others[13,14] argue strongly against it. Dumrongrattana and Huang[13] in a recent paper claim that if one choose the parameters of the model in such a way that the three first terms in the Landau expansion of Eq.(1) is about 1000 times larger than the other terms, the possibility of producing S-shaped polarization curves by the model is eliminated. This division of the terms into groups containing terms of different orders of magnitude seems to be a sound approach, as it is well known that as well the chirality as the polarization can be regarded as "small disturbances" to the system. That the statement by Dumrongrattana and Huang, concerning the possibility of producing S-shaped polarization curves with this division, is misleading is however easily shown by Figure 4. The solid line is the calculated polarization using the parameter values of DOBAMBC chosen by Dumrongrattana and Huang[14]. The dashed line is the polarization curve obtained by making the following changes in these parameter values: $b \to b/2$, $c \to c/2$, $\eta \to \eta/3$, $\Omega \to \Omega\sqrt{2}$, all other parameters being unchanged. It is quite clear that the relative magnitudes of the terms in the free-energy density are unaltered by this transformation. Still, however, we notice a pronounced S-shaped kink in the last case. We thus conclude that as well S-shaped as non S-shaped polarization curves are well contained within the realistic sets of material parameters. It is also obvious that the solutions of Eqs.(7) exhibit an in-built cross-over behaviour, the magnitude of which is determined by the parameter β. This behaviour is introduced into the model due to the presence of the biquadratic coupling between tilt and polarization.

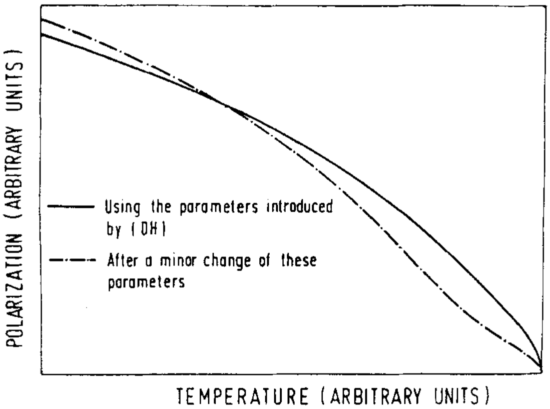

FIGURE 4 Calculated polarization as function of reduced temperature. The solid line is calculated by the use of the material parameters of DOBAMBC given by reference 14. For the calculation of the dashed line a minor change of these parameters has been made: $b \rightarrow b/2$, $c \rightarrow c/2$, $\eta \rightarrow \eta/3$ and $\Omega \rightarrow \Omega\sqrt{2}$. This shows that as well S-shaped as non S-shaped polarization curves are well contained within the realistic sets of parameters.

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