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Elasticity and the electroclinic effect at the SmA–SmC phase transition

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The electroclinic effect has been investigated around the smectic A–smectic C phase transition in the materials SCE8 and SCE13. Attempts have been made to model this effect using the Landau–de Gennes mean field theory. Experiments carried out with low applied electric field at the transition show problems with this model, and we suggest the inclusion of elastic energy to describe the behaviour in this regime. The results indicate that the elastic term is important, and provides a fuller description of the electroclinic behaviour near the transition temperature.

1. Introduction

The electroclinic effect was first studied by Garoff and Meyer [1] in 1977. The effect occurs in a smectic A liquid crystal, at a temperature close to the smectic A to smectic C* phase transition, when an electric field is applied perpendicular to the molecular axis. Then the symmetry of the smectic A phase is broken and a tilt (perpendicular to the applied field) is induced in the molecular axis. Garoff and Meyer explained that the permanent dipole associated with each molecule aligns with the applied field, and that the tilt is coupled to this as in the smectic C* phase. They were therefore able to model the process using a Landau type expansion for the smectic A to smectic C* phase transition, together with additional terms for the interaction with the applied field.

Initially a linear relationship between the tilt angle and the field strength was observed, with the tilt angle rising rapidly near the phase transition [1]. However, as materials with higher electroclinic effect were manufactured, so a non-linear effect was observed at higher fields and at temperatures very close to the transition. This meant that the original Landau theory used by Garoff and Meyer had to be extended in order to allow for this effect [2]. Work has also been carried out to strengthen this model, with analysis of the dynamics of the molecular tilt [3–5] and temperature dependence of the Landau coefficients for chiral interactions [6]. Dynamic work carried out by Kimura *et al.* also includes surface interactions with the Landau theory [5].

Here we consider the Landau–de Gennes mean field theory (including terms up to the sixth order), at and around the smectic A–smectic C transition temperature for varying field strengths. We use the materials SCE8 and SCE13. Comparison between theory and experiment indicates that the basic mean field theory does not explain fully the behaviour of the liquid crystal close to the SmA–SmC phase transition. This is especially so at the transition temperature, where for small fields a cube root dependence in tilt with **E** is expected from the model, but not observed experimentally. We suggest that the theory requires the inclusion of elastic energy due to structure deformation.

2. Experimental

The test cells used here are 3 μm thick parallel aligned, rubbed, polyimide devices, filled with either the material SCE8 or SCE13. To measure the electroclinic response, we use the classical method of placing the cell between crossed polarizers, illuminating with a laser (here operating at 670 nm), and rotating the liquid crystal until the average molecular director (or optic axis) in the SmA phase (with zero field) is at 22.5 degrees to the polarizer axis, thereby maximizing the sensitivity of the transmission to changes in tilt angle. A square wave is applied to the liquid crystal device, the positive and negative polarity pulses inducing a tilt in the director in opposite directions. This leads to a change in the transmission corresponding to variation in the tilt angle and the optical anisotropy of the material. Often any changes in the optical anisotropy are ignored in this method. However it is quite easy to correct for any such changes which may take place by calculating the tilt angle from

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http://www.tandf.co.uk/JNLS/lct.htm
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the following equation:

$$\theta = \frac{1}{4}\sin^{-1}\left(\frac{T^{+} - T^{-}}{T_0 + \Delta T}\right) \tag{1}$$

where θ is the induced tilt angle, T^{+} and T^{-} are the transmissions with applied voltage pulses of positive and negative polarity, and T_0 is the transmission when no field is applied. ΔT is the change in maximum transmission due to any variation in optical anisotropy which may take place, and is given by the equation:

$$\Delta T = (T^{+} - T_0) + (T^{-} - T_0). \tag{2}$$

In principle this formulation allows changes in the optical anisotropy to be determined (as well as the induced tilt angle). For the materials studied here however, such effects appear to be minimal, although others have recently noted that large optical anisotropy changes can take place for the electroclinic effect in some materials [7].

3. Results and discussion

The Gibbs free energy density (generalized Landau model [8]) of a chiral smectic material in the presence of an electric-field **E** can be written as [6]:

$$g = g_0 + \frac{a^*}{2}\theta^2 + \frac{b^*}{4}\theta^4 + \frac{c^*}{6}\theta^6 - \mathbf{PE} \tag{3}$$

where g_0 is the contribution to the free energy from the undisturbed smectic A liquid crystal, **P** is the total polarization, and a^*, b^*, and c^* are *chiral Landau coefficients* introduced by Giesselmann and Zugenmaier [6]. These coefficients are given by:

$$a^* = a - \frac{A_1^2}{\chi_0 T^2} = \alpha(T - T_{\mathrm{ac}}) - \frac{A_1^2}{\chi_0 T^2} \simeq \alpha(T - T^*_{\mathrm{ac}}) \tag{4}$$

$$b^* = b - \frac{2A_1^2 A_2}{\chi_0 T^3} \tag{5}$$

$$c^* = c - \frac{3A_1^2 A_2^2}{\chi_0 T^4}. \tag{6}$$

The coefficients a, b, and c are the standard mean field or Landau coefficients, while A_1 and A_2 are coupling constants related to dipolar and quadrupolar ordering, respectively. The constant A_2 vanishes when the polarisation $\mathbf{P} = \mathbf{P}_0\theta$ (i.e. **P** is linearly dependent on the induced tilt angle θ), which leads to $b^* = b$ and $c^* = c$. Giesselmann and Zugenmaier [6] showed that this was true for tilt angles up to around 0.24 radians or 14 degrees. Over a few Kelvin at absolute temperatures of several hundred K we would expect $A_1^2/\chi_0 T^2$ to be small and approximately constant; therefore it can be assumed that $a^* \simeq \alpha(T - T^*_{\mathrm{ac}})$, with an effective SmA–SmC* phase transition temperature, T^*_{ac} (where $T^*_{\mathrm{ac}} > T_{\mathrm{ac}}$).

Now if we assume the above approximations of polarization linearly dependent on θ and a small temperature range, then minimizing the Gibbs free energy with respect to θ, and reformulating the resulting equation, we obtain the following relationship between θ, $\Delta T = T - T^*_{\mathrm{ac}}$, and the voltage V applied to a liquid crystal cell of thickness d:

$$\Delta T\theta + B\theta^3 + C\theta^5 - qV = 0 \tag{7}$$

where

$$B = \frac{b^*}{\alpha}, \quad C = \frac{c^*}{\alpha}, \quad q = \frac{P_0}{\alpha d} \tag{8}$$

Solutions to equation (7) are shown in figure 1, using typical coefficients taken from the literature [9]. This shows clearly the change of the transition from discrete second order to continuous when a field is applied, and shows the commonly accepted electroclinic effect. Using equation (7) to model the electroclinic effect makes the assumption that θ is uniform over the thickness of the liquid crystal layer. This is equivalent to saying that either there is no surface anchoring present, or that θ is in a saturation regime with any variation taking place in thin boundary layers. We will discuss this issue later.

From equation (7) we can obtain approximations for temperature regimes well above, at the SmA–SmC transition, and also well below the transition.

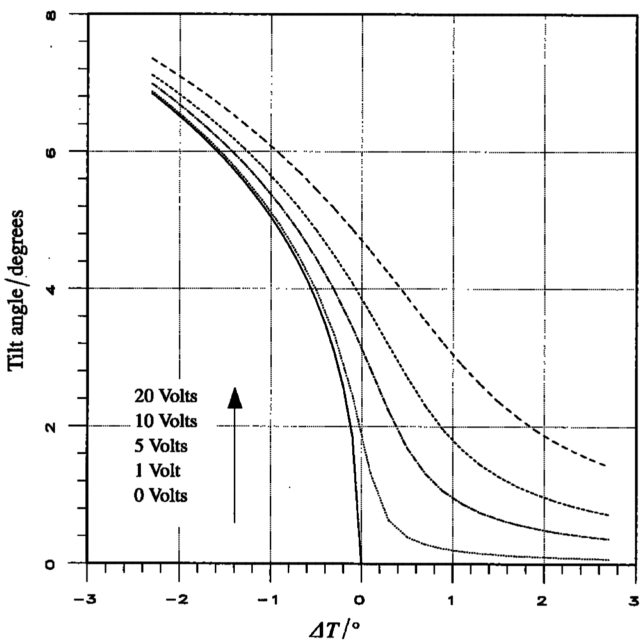

Figure 1. Typical electroclinic behaviour through the SmA–SmC transition, with various applied voltages: determined using equation (7) with typical values for the Landau coefficients B and C.

(i) At temperatures much greater than the transition temperature, the induced tilt angle is expected to be small; therefore the higher order terms in θ can be neglected, leading to:

$$\theta = \frac{qV}{\Delta T}. \tag{9}$$

This is the classical linear electroclinic effect as presented by Garoff and Meyer [1]. The assumption made in this approximation is that $\theta \ll (\Delta T / B)^{1/2}$.

(ii) At the transition $T = T^*_{ac}$ the first term in equation (7) disappears. The result then rearranges to give:

$$qV = \theta^3 (B + C\theta^2) \tag{10}$$

and for small θ, i.e. $\theta \ll (B/C)^{1/2}$:

$$\theta = \left(\frac{qV}{B}\right)^{1/3} \tag{11}$$

This equation clearly shows that at the transition, for low voltages, the Landau–de Gennes model leads to a cube root dependence between the tilt angle and the applied voltage.

(iii) Below the transition, we can substitute $\theta = \theta_e + \delta$ in equation (7), where θ_e is the tilt angle in the smectic C phase with no applied field, and δ is the change in θ due to the electroclinic effect when a field is applied. This leads to an expression for θ_e and an approximation for the electroclinic tilt angle δ. Assuming that δ is small ($\delta \ll \theta_e / 2$), and neglecting all higher order terms in δ we have:

$$\theta_e^2 = \frac{-B + (B^2 - 4\Delta T C)^{1/2}}{2C} \tag{12}$$

$$\delta = \frac{qV}{-4\Delta T - 2B\theta_e^2} \tag{13}$$

or

$$\delta = \frac{qV}{-2\Delta T + 2C\theta_e^4}. \tag{14}$$

Solutions to equations (9–14) are illustrated in figure 2, and are compared with numerical solutions for equation (7) (at $\Delta T \approx -2°$, $\Delta T = 0°$, and $\Delta T \approx 2°$). Again, all solutions use typical coefficients taken from

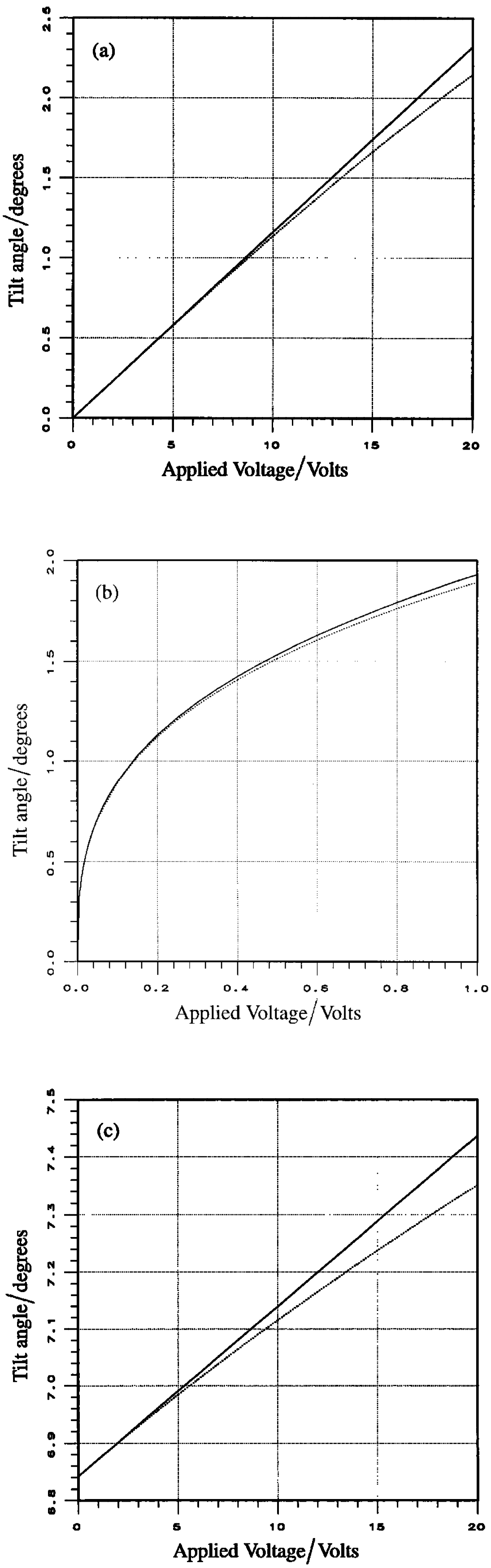

Figure 2. The director tilt angle as a function of applied voltage corresponding to the approximations (solid lines) given in equations (9–14) in the three regimes (*a*) $T \gg T^*_{ac}$, (*b*) $T = T^*_{ac}$, (*c*) $T \ll T^*_{ac}$; also a comparison with numerical solutions (dotted lines) using equation (7) ($B = 90$ K, $C = 5000$ K, $q = 0.0035$ K V^{-1}).

the literature. Figure 2 shows each relation within a regime of valid approximation, and the errors are seen to be reasonable.

We now compare the behaviour of the electroclinic effect predicted by the Landau model of equation (7) (and the approximations discussed above) with experimental data obtained for the liquid crystal SCE8. Data taken for an SCE8 filled cell are shown in figure 3 as the set of discrete points. These show how the tilt varies with temperature for a range of applied voltages. We would expect from the theory curves illustrated in figure 1 that at temperatures below $T = T^*_{\mathrm{ac}}$ the electroclinic effect should diminish and the data should converge on $\theta = \theta_{\mathrm{e}}(T)$; this can also be seen from equations (12–14). However the experimental data of figure 3 do not show this; the tilt angle below the transition at low voltages is significantly less than we might expect. If we look to the generalized Landau model of equation (3) we find it assumes a bookshelf type geometry, which is a reasonable assumption in the smectic A phase. However in the smectic C phase we would expect a chevron structure to form where the director is anchored at the surfaces of the cell and also at the centre of the cell. This chevron structure has been shown to form a permanent quasi-bookshelf structure when a high a.c. field is applied [10], but a permanent structure change is not observed here. It is more likely that a significant change in the smectic layer structure is not taking place and therefore the director configuration must take a form consistent with this [11], leading to a reduced average tilt for low voltages, saturating at higher fields. We can therefore suggest that once the director rotation around the cone saturates, the Landau theory will describe the average optic axial tilt angle approximately. The 'saturation voltage' required for this convergence would be expected to increase with decreasing temperature in the smectic C phase.

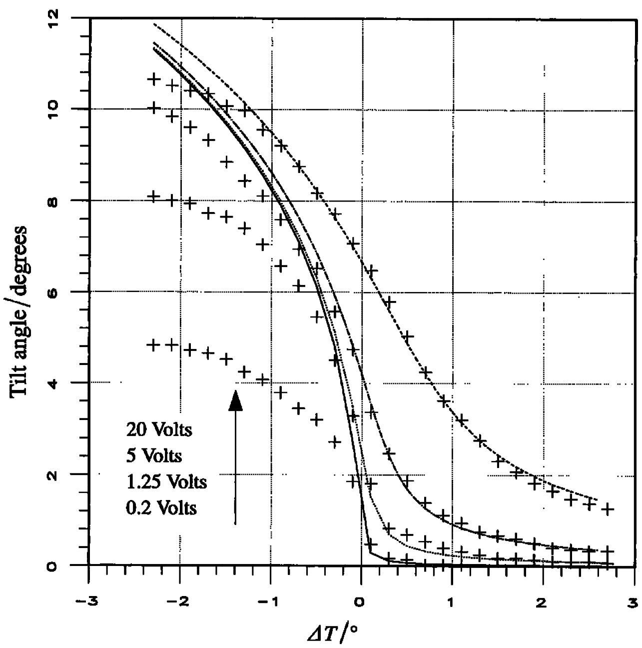

Figure 3. Plots of $\theta(T)$ through the SmA–SmC* transition for several applied voltages. Discrete points show experimental data from work carried out on SCE8. The lines show theoretical results using equation (17) with values for the coefficients as given in the table (SCE8 with K).

Experimental work carried out on SCE8 in the three regimes of the approximations, namely well above the transition, at the transition, and well below the transition reveal data as shown in figure 4. At a temperature around 2° above the transition ($\Delta T \approx 2°$), equation (9) implies that $\theta(V)$ should be linear over a large voltage range, which agrees well with the experimental data of figure 4 (a). The slope of the linear regime leads to a value for the parameter q of $q = 0.0035\ \mathrm{K\ V^{-1}}$.

At the transition, where a cube root dependence should exist at low voltages, the data show a dependence of tilt on voltage with much less curvature than we would expect, see figure 4 (b). This latter point is a strong indication that there are problems with the present Landau model very close to the SmA–SmC phase transition. Clearly the induced tilt rises much less quickly than the suggested cube root behaviour for low voltages. This indicates that the Landau model needs to be extended in a way which will limit the reorientation near to the phase transition temperature—this is discussed further below.

For $\Delta T \approx -2°$ the experimental data, shown in figure 4 (c), indicate that for $V \lesssim 5$ V the tilt angle change is significant—it can therefore be assumed that in this regime saturation of reorientation in the chevron structure has not been reached. Applying equations (12–14) to the experimental results for $V \gtrsim 5$ V, we find that $B \simeq 120$ K and $C \simeq -1400$ K. The negative value of C does not agree at all with values obtained in other work (see the table), and we therefore conclude that the model of equation (7) does not describe the behaviour below the smectic A–smectic C* phase transition. Again this may be because it ignores the presence of the chevron structure.

As noted above, we need to limit the reorientation near to $T = T^*_{\mathrm{ac}}$. We can achieve this by including a term associated with the elastic deformation which may accompany the electroclinic effect and therefore not make the assumption—implicit in equation (7)—that the reorientation is uniform over the thickness of the cell. Such a term has been considered before in describing the dynamics of the effect [4, 5], but the influence on the reorientation close to the phase transition was not considered.

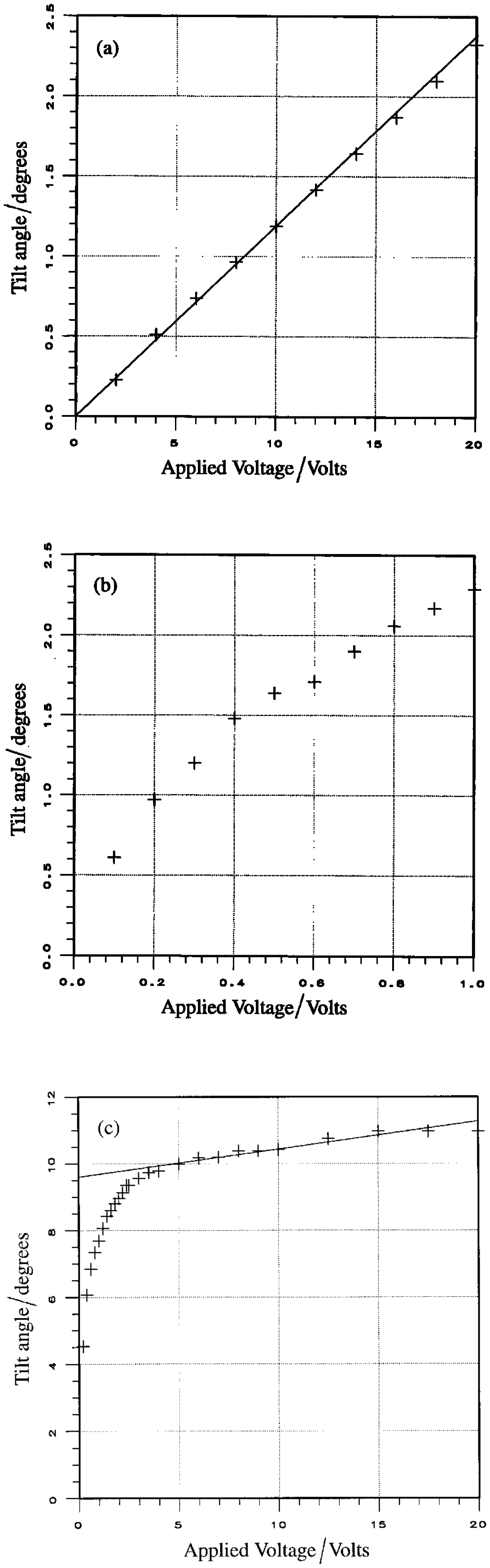

Figure 4. Demonstration of the analytical approximations applied to the corresponding experimental data for (*a*) $\Delta T \approx 2$ K ($0 \rightarrow 20$ V, $0° \rightarrow 2.5°$), (*b*) $\Delta T = 0$ K ($0 \rightarrow 1$ V, $0° \rightarrow 2.5°$), and (*c*) $\Delta T \approx -2$ K ($0 \rightarrow 20$ V, $0° \rightarrow 12°$).

The elastic free energy term which is required is given by

$$g_{\text{elas}} = \frac{K}{2}\left(\frac{\partial \theta}{\partial z}\right)^2. \tag{15}$$

Therefore the Landau free energy after the inclusion of the elastic free energy term is:

$$g = g_0 + \frac{a^*}{2}\theta^2 + \frac{b^*}{4}\theta^4 + \frac{c^*}{5}\theta^6 + \frac{K}{2}\left(\frac{\partial \theta}{\partial z}\right)^2 - \mathbf{PE} \tag{16}$$

where z is the direction perpendicular to the surface of the cell (and is chosen to be zero at the centre of the liquid crystal layer). Making the same approximations and substitutions made in deriving equation (7) and minimizing the free energy with respect to θ gives:

$$\Delta T\theta + B\theta^3 + C\theta^5 - \frac{K}{\alpha}\left(\frac{\partial^2 \theta}{\partial z^2}\right) - qV = 0. \tag{17}$$

The approximation for well above the phase transition is now dependent upon z, with $\theta(z)$ given by:

$$\theta(z) = \frac{qV}{\Delta T}\left\{1 - \frac{\cosh\left[\left(\frac{\Delta T}{K/\alpha}\right)^{1/2} z\right]}{\cosh\left[\left(\frac{\Delta T}{K/\alpha}\right)^{1/2} \frac{d}{2}\right]}\right\} \tag{18}$$

where d is the thickness of the liquid crystal cell. The boundary conditions applied assume infinite surface anchoring, and therefore $\theta = 0°$ at the surfaces of the cell where $z = -d/2$ and $z = d/2$. Integrating equation (18) leads to a modified equation for $\theta_{\text{av}}(V)$ given by:

$$\theta_{\text{av}} = \frac{qV}{\Delta T}\left\{1 - \frac{2}{d}\left(\frac{K/\alpha}{\Delta T}\right)^{1/2} \tanh\left[\left(\frac{\Delta T}{K/\alpha}\right)^{1/2} d\right]\right\}. \tag{19}$$

Therefore we can see that although the addition of the elastic term leads to a cosh-like solution for $\theta(z)$, the average tilt angle which would be observed is still linearly dependent on V, with only a small temperature dependent term reducing the gradient of the linear dependence. In order to illustrate this graphically, we use a relaxation solution to solve equation (17) (and estimated parameters) and obtain director profiles as shown in figure 5. The dashed lines show solutions for

Table. Parameters determined here (bold type) listed together with those obtained by others.

Material	q/K V^{-1} × 10^{-3}	B/K	C/K	K/α/m^2 K × 10^{-15}
SCE8[a]	3.5	120	– 1400	—
SCE8 (no K)	3.08	15.5	1393.3	—
SCE8 (with K)	3.51	26.0	702.9	17.9
SCE8 thick[b]	—	96	6000	2.9
SCE8 thin[b]	—	87	3625	2.6
SCE13 (no K)	9.39	71.1	498.3	—
SCE13 (with K)	10.7	56.6	502.2	61.2
SCE13 (A)[b]	—	59	240	0.28
SCE13 (B)[b]	—	27	133	0.85
SCE13[c]	—	95	500	—

[a] Parameters determined using equations (9), (13), and (14).
[b] From [9], using free-standing films technique.
[c] From [12], using the Half Leaky Guided Mode (HLGM) technique.

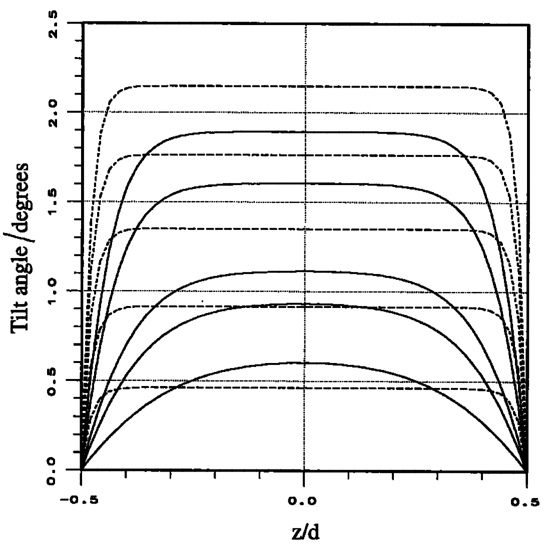

Figure 5. Theoretical director profile through the cell after introduction of the elastic term ($K/\alpha = 2.7$) with increasing voltage at $T = T^*_{ac}$ and $\Delta T \approx 2°$. The applied voltages for $T = T^*_{ac}$ (solid lines) are 0.04, 0.12, 0.2, 0.6, and 1.0 V, and for $\Delta T \approx 2°$ (dashed lines) are 4, 8, 12, 16, and 20 V.

$\theta(z)$ at $\Delta T \approx 2$ K showing a relatively unchanged director profile through the cell as voltage increases.

The regime of greatest interest is at the phase transition where the use of equation (11) has dictated a cube root dependence between tilt and applied field at low voltages. The solid lines in figure 5 are profiles for $\theta(z)$ at $T = T^*_{ac}$. This shows how the introduction of the elastic constant leads to a voltage dependent profile for $\theta(z)$, which at low voltages is broadly curved across the cell, thereby reducing the average director tilt angle, $\theta_{av}(V)$, which is what we require in order to explain the experimental results at the transition.

Using the model of equation (17), it is difficult to develop analytical approximations at $T = T^*_{ac}$ and for $T \ll T^*_{ac}$, therefore in order to test this approach we perform a least squares fit on the data taken for the SCE8 cell with B, C, q, and also K (the elastic constant we have now introduced) as the free parameters. We simultaneously fit three sets of data: data taken at 20 V over a 4° temperature range around the SmA–SmC* transition; data at $T = T^*_{ac}$ for voltages up to 1 V; and data at $\Delta T \approx 2°$. The solid lines in figure 3 show the results of this procedure, where we have assumed that the experimentally determined tilt angle is θ_{av}. For comparison we also fit the data using the model of equation (7) with B, C, and q as the free parameters. For this second fit, we ignore data for low V near the transition, because this regime is most influenced by K—and therefore does not compare well with the model of equation (7). The resulting parameters from both fits are given in the table, and both sets give good agreement with the experimental data at high V, which we would expect, as in this regime elasticity is less important. We also compare directly the results from both least squares fits and the experimental data, in the regime of low V at $T = T^*_{ac}$. This comparison is illustrated in figure 6, where we have again assumed that the experimentally determined tilt angle is θ_{av}. As can be seen, the Landau model with the addition of the elasticity provides excellent agreement between theory and experiment, limiting the reorientation at the transition in a similar way to that seen in the data presented here. Similar analysis was undertaken for the material SCE13, with the theory again requiring elasticity in order to limit the reorientation at the transition and be in agreement with experiment. These results are also given in the table for both the basic Landau model and the model with the inclusion of the elasticity. Additionally comparison is made with results on SCE8 and SCE13 from other work [9, 12].

The results in the table show clearly that the influence of the elasticity is large when considering the electroclinic effect at the smectic A–smectic C transition. Comparing

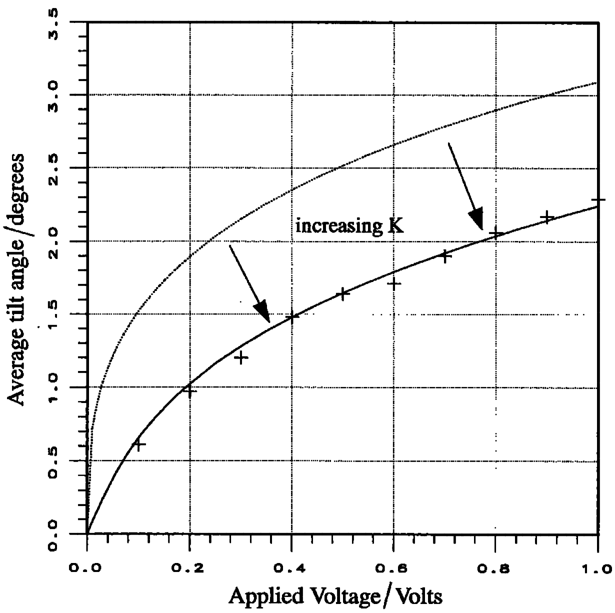

Figure 6. Experimental data for SCE8 (shown as discrete points) with low applied voltages at $T = T^*_{ac}$ and equivalent theoretical plots showing the effect of the introduction of the elastic term (dotted line—no K; solid line—with K).

the values for K obtained here with those obtained by others [9], the elastic constants determined for SCE8 and SCE13 are significantly larger, the SCE13 results differing by two orders of magnitude. However the values determined for B and C (SCE8 and SCE13) compare well with those from previous work [9, 12]. The wide difference between the values of K obtained here and those obtained by studying free-standing films [9] is most likely to be because of the nature of the distortions involved. In the free-film work, only director distortions are present, the smectic layers being free to take up their equilibrium configuration. Here however there may be layer stresses present in the electroclinic effect due to the tendency of smectic layers to tilt when director tilt takes place. As we have made no attempt to include such a process explicitly in the modelling, such stress (which will limit the reorientation taking place) will tend to increase the effective elasticity, resulting in a larger value for K.

4. Conclusions

It is seen that the basic Landau model cannot explain the electroclinic behaviour of a liquid crystal cell close to the smectic A to smectic C* phase transition for applied voltages of $\lesssim 1$ V. We have shown that the elastic deformation energy is a necessary addition to the model, with the contribution in this regime shown to be large. The Landau model with the addition of the elastic deformation energy presented here therefore provides a fuller description of the electroclinic behaviour near the transition.

Despite the success of including the deformation energy as an extension to the Landau model, it does not provide a description of the formation of the chevron structure through the phase transition, and thus cannot explain effects for $T < T^*_{ac}$. We have also noted that the layer stresses resulting from the electroclinic effect appear to lead to a large effective elastic constant. In future work we intend to address these issues.

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