Guided wave study of electroclinic effects in a homogeneously aligned smectic A liquid crystal

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Guided wave study of electroclinic effects in a homogeneously aligned smectic A liquid crystal

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Using the half leaky guided mode geometry, we have studied the electroclinic effect using a thin homogeneously aligned layer of C8, a material having a first order S_A to S_C^* transition in the bulk. Application of voltage in the S_A phase produces a small ($< 12°$), but easily measured director twist which is characterized over a range of temperatures in the S_A phase. Mean field theory is used to interpret the data recorded. At low applied fields ($\leqslant 6\,V\,\mu m^{-1}$), a linear voltage dependence of induced twist is found. For higher applied fields there is a non-linear dependence which is caused by an induced first order S_A to S_C^* transition at these fields. Fitting the voltage dependent induced twist yields the first three Landau coefficients for this transition. The voltage dependent results also provide a procedure for determining the S_A to S_C^* phase transition.

1. Introduction

The electroclinic effect in chiral smectic liquid crystals has recently received significant attention because of its potential for fast switching. Further, because there is a simple linear relationship between the applied field and the induced twist angle [1, 2] this phenomenon has analogue device potential. New materials designed to give stronger electroclinic effects have been synthesized allowing more detailed studies of non-linear effects particularly near the S_A–S_C^* phase transition in high fields [3–5]. Theories of the electroclinic effect predicting the dependence of the induced director twist angle on the applied field have been presented in several studies [1, 6–8]. It is found that the use of the Landau expansion of the free energy up to terms of order θ^4 quantitatively describes the non-linear behaviour of the twist angle, θ, observed at high fields near the phase transition temperature [1, 3–5].

Studies have been undertaken using thick cells ($> 6\,\mu m$) in order to examine the S_A–S_C^* phase transition under application of a field [9]. Bahr and Heppke [9, 10] have investigated the critical behaviour of the phase transition between the S_A and the S_C^* phases in a thick cell (about $100\,\mu m$) with a material having a first order S_A–S_C^* transition. They found that the simple Landau model, with a term including the linear coupling between the polarization and the induced angle, well describes their experimental results. The behaviour observed is

strikingly different to the normal second order S_A–S_C^* transition.

In this research, using the very sensitive half leaky guided wave technique [11], we study the electroclinic effect at the first order S_A–S_C^* transition of the material C8. The liquid crystal is aligned homogeneously in a thin cell ($> 2\,\mu m$) which causes severe boundary constraints upon the behaviour of the LC, limiting the electroclinic effect as well as changing the phase transition temperature which in this case is determined accurately from observations of the electroclinic effect. As far as we are aware, this is the first half leaky guided mode study of this behaviour at the first order S_A–S_C^* transition.

2. Experimental

In order to provide the required half leaky geometry, the cell is built of a high index glass plate ($n_1 = 1.733$ at 632·8 nm) and a low index glass substrate ($n_2 = 1.459$ at 632·8 nm). These two plates are each coated with a thin layer ($\sim 50\,nm$) of transparent conducting indium–tin oxide (ITO). On top of one of these electrodes is deposited a polyimide buffer layer and on both is deposited a thin rubbed nylon layer to provide low tilt homogeneous alignment. The two coated plates are placed together in a clean room with spacers of the order 1·5 μm and then filled with C8 in the isotropic phase. The cell is then cooled, and the high index plate placed into intimate optical contact with a high index prism using matching fluid. This complete sample assembly is shown in figure 1.
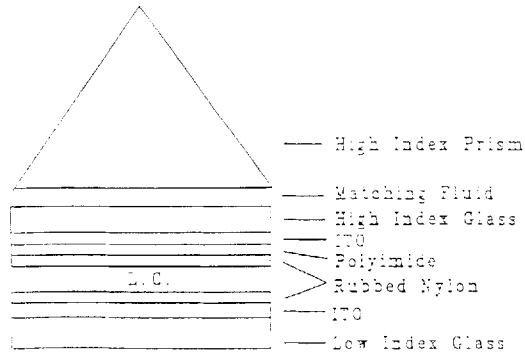
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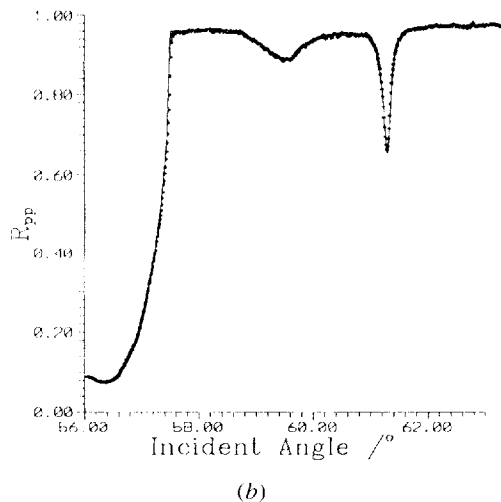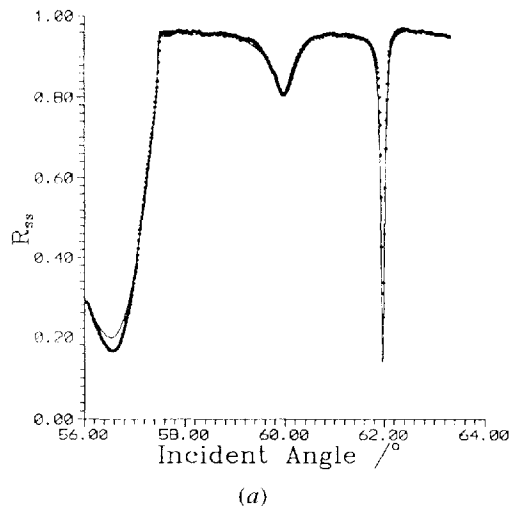Figure 1.   The sample geometry used in the experiments.

This assembly is next placed into a temperature controlled environment on a computer controlled rotating table. It is then heated to convert the liquid crystal into the isotropic phase (about 65°C) and angular dependent half leaky guided wave data are recorded following the procedure described in detail elsewhere [11]. In the isotropic phase R_{ss} (s-polarized, transverse electric, input and output) and R_{pp} (p-polarized, transverse magnetic input and output) data are recorded. Fitting multilayer optics theory to these data gives the cell thickness, the isotropic LC index and approximate parameters for the ITO, polyimide and nylon layers. Fits for R_{ss} and R_{pp} are shown in figure 2.

The sample is now cooled slowly ($\sim$ 1·0°C per hour) into the S_A phase to give a well-aligned monodomain. Then with the cell configured so that the rubbing direction

Figure 2.   Reflectivity data (*a*) R_{ss}, (*b*) R_{pp} (crosses) for the isotropic phase and theoretically fitted results (solid line).
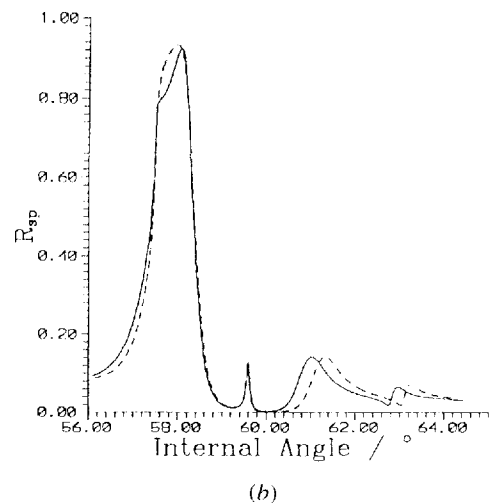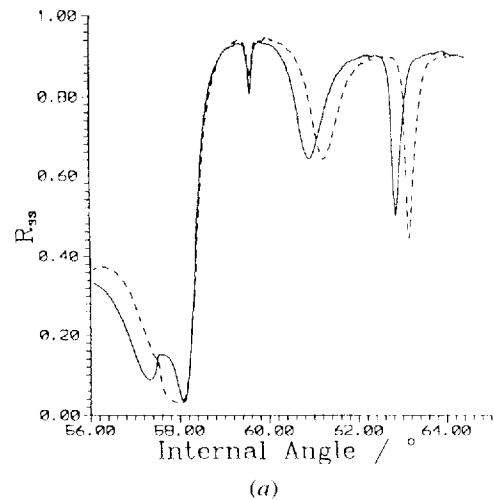

Figure 3.   (*a*) R_{ss} and (*b*) R_{sp} reflectivities at 51·2°C as a function of the incident angle with no voltage applied (solid line), and a d.c. applied voltage of 5·0 V (dashed line).
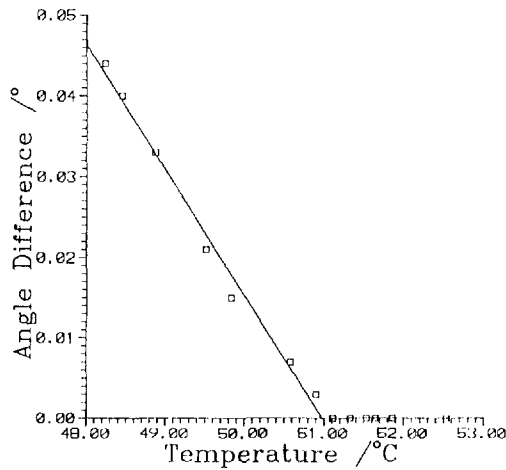
Figure 4. Difference in twist angle of the two relaxed states (zero volts), after application of + 5 or − 5 V pulses, as a function of temperature.

is at about 45° to the plane of incidence, both R_{ss} and the polarization conversion signal R_{sp} are recorded. The latter signal, which is very sensitive to director twist, is quite strong, peaking to about 80 per cent.

At different temperatures in the S_A phase, angle dependent reflectivity data were recorded for a range of applied d.c. fields. This strongly electroclinic material gives very significant changes in both the R_{ss} and R_{sp} data as shown in figure 3. Here the cell is at 51·2°C and data are presented for zero and 5 V. Full angle scan data sets of this nature were taken at seven different temperatures in the S_A phase for voltages up to 19 V.

Additionally, to determine the S_A to S_C^* transition temperature, we recorded accurately the dependence of the difference in angular position of the guided mode recorded at zero volts close to 63° after + 5 V and − 5 V, respectively had been applied to the cell. By plotting this small difference as a function of temperature, it is very simple to determine the phase transition, as shown in figure 4.

3. Results and discussion

Fitting the reflectivity data recorded for the isotropic phase to predictions from multilayer optics theory allows the determination of the boundary layer parameters. Such a fit is shown in figure 2. The ITO layers have a thickness of 49 nm and an optical permittivity of $\varepsilon = 3\cdot235 + i0\cdot018$. On the electrode on the high index plate there is a polyimide layer with a thickness of 20 nm and an $\varepsilon = 2\cdot528 + i0\cdot001$, while on top of this and the other ITO plate are thin, 26 nm, aligning nylon layers having $\varepsilon_{\parallel} = 2\cdot86 + i0\cdot001$ and $\varepsilon_{\perp} = 2\cdot30 + i0\cdot001$, with the uniaxial axis being the rubbing direction. All these parameters are approximate, being somewhat degenerate in choices of thickness and ε values. However, the exact values are not

as important as their optical equivalent thickness. The values found above are then used in all subsequent data fits.

From the rubbed nylon treatment, it is expected that the director of the S_A phase will be aligned homogeneously with the possibility of a small surface tilt. Fitting the data recorded at 52·3°C at zero applied field to a uniform slab model gives a uniform director tilt of 2·7°, with the director aligned along the rubbing direction. This fit (see figure 5) also gives a liquid crystal thickness of 1·4 μm and permittivities of $\varepsilon_{\parallel} = 2\cdot5580(\pm 0\cdot0002) + i0\cdot0004$ $(\pm 0\cdot0001)$ and $\varepsilon_{\perp} = 2\cdot2335(\pm 0\cdot0002) + i0\cdot00004$ $(\pm 0\cdot00001)$.

Application of a field now causes the director to twist out of the initial direction, and by fitting all the angle dependent reflectivities at different voltages, this induced twist is found. Figure 6 shows the voltage dependence of
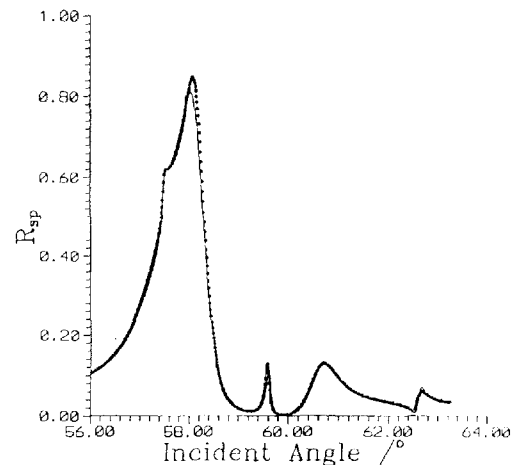

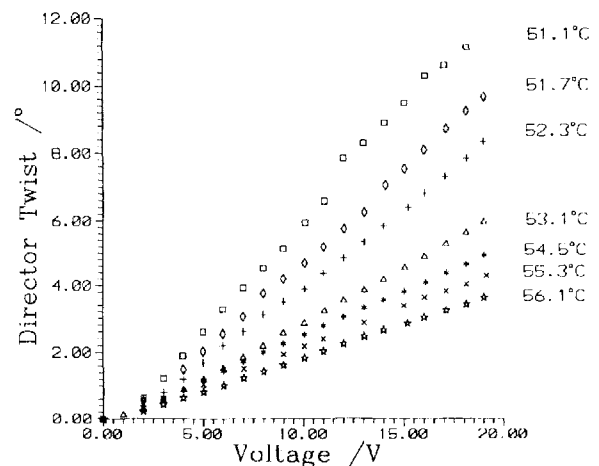Figure 5. R_{sp} reflectivity data (crosses) and the theoretical fit (solid line) at 52·3°C.

Figure 6. The voltage dependence of the induced twist for different temperatures in the S_A phase.

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the induced twist for seven temperatures in the S_A phase. The error on the measurement of twist is less than $0.1°$.

In this thin cell, the phase transition temperature is rather different from that in the bulk [12], and it is necessary to establish this temperature if we wish to fit the electroclinic effect data to theory. As indicated above, using the half leaky guided mode measurements together with the electroclinic effect, it is a simple matter to determine this phase transition temperature in the cell. In the S_A phase, after application of either a positive or negative field, the deformed director will return, at zero volts, to its original undeformed state, which is the same regardless of the voltage direction. However as soon as the liquid crystal enters the S_C^* phase, this is no longer true. The two zero volt relaxed states after the application of a positive or negative voltage pulse will be slightly different, one being associated with the dipole pointing 'up', the other with the dipoles pointing 'down'. By monitoring accurately the position (at $\sim 63°$) of the first order guided mode in the R_{ss} data (the mode which is most sensitive to director twist) and plotting the difference in its position after positive and negative voltage application to the cell, we may monitor accurately the phase transition. This difference is shown as a function of temperature in figure 4. It is clear from these data that the transition temperature, T_C, for this cell is $51.00 \pm 0.05°C$. This is significantly lower than the bulk transition temperature of $53.8°C$ for this material.

Of course we have to exclude the possibility that the temperature T_C we have measured as the S_A–S_C^* transition is not the true transition temperature, but a monostable–bistable transition in the S_C^* phase. If this were true, the S_A–S_C^* transition is at a higher temperature than T_C. This is readily shown not to be the case, since in the S_C^* phase the director twists out of the rubbing direction. As the temperature rises through T_C, if the material is still in the S_C^* phase, but monostable due to the asymmetry of the cell, then the director twist would be still measurable and would slowly change with temperature. Our reflectivity data show clearly that there is no director twist above T_C. Alternatively, if the monostable state were arranged with the director staying at the top of the cone in the S_C^* phase, then the director tilt would change with temperature as the cone angle is reduced. Again this does not appear in our data. Therefore it is clear that we have determined the S_A–S_C^* transition T_C, and not some temperature below this corresponding to a monostable to bistable transition.

Now, having established T_C, we return to fitting the electroclinic data for the S_A phase. Examination of figure 6 reveals an apparent threshold voltage of the order 1 V, followed by a linear dependence of the induced twist at low voltages. However, near the phase transition and at higher voltages this linearity is obviously lost. Ignoring for

the time being the threshold field, this behaviour may be explained using the Landau theory.

If we consider a first order transition, with linear coupling between the polarization and the tilt angle, the Landau free energy expression for the ferroelectric liquid crystal takes the form [9]

$$F = F_0 + \frac{1}{2}a(T - T_0)\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}d\theta^6$$

$$+ \frac{1}{2\chi_0\varepsilon_0}P^2 - cP\theta - EP. \qquad (1)$$

Here T_0 is the racemic mixture transition temperature, θ is the director twist (cone angle), P is the polarization, χ_0 is the susceptibility at fixed tilt angle, E is the applied electric field, and c is the director twist-polarization coupling constant. Further the constants a, b and d are such that a, $d > 0$ and $b < 0$. Minimizing (1) with respect to both θ and P leads to

$$E = \frac{1}{c\chi_0\varepsilon_0}[(a(T - T_0) - c^2\chi_0\varepsilon_0)\theta + b\theta^3 + d\theta^5], \qquad (2)$$

which may be more conveniently written as

$$E = \alpha(T - T_C')\theta + b'\theta^3 + d'\theta^5 \qquad (3)$$

where $\alpha = a/(c\chi_0\varepsilon_0)$, $b' = b/(c\chi_0\varepsilon_0)$, $d' = d/(c\chi_0\varepsilon_0)$ and $T_C' = T_0 + [(c^2\chi_0\varepsilon_0)/a]$.

From equation (3), we can see that when the induced director twist, θ, is small ($< 5°$), the θ^3 and θ^5 terms may be neglected, leading to a simple linear dependence of θ on E:

$$\theta = \frac{1}{\alpha(T - T_C')}E, \qquad (4)$$

or $\theta = C_E E$, where C_E is the electroclinic coefficient. Fitting the slope of the low field data of figure 6 gives, for C8, a C_E which varies from $(1.44 \pm 0.04) \times 10^{-8} \text{mV}^{-1}$ at $51.1°C$ to $(0.45 \pm 0.01) \times 10^{-8} \text{mV}^{-1}$ at $56.1°C$. A graph of C_E^{-1} against temperature produces a straight line, whose intercept is T_C' and with a slope α. Such a graph, shown in figure 7, very neatly confirms the straight line behaviour, giving T_C' as $(48.80 \pm 0.05)°C$ with $\alpha = (2.98 \pm 0.02) \times 10^7 \text{V(m°C)}^{-1}$. Note T_C' is removed from T_0 by the factor $(c^2\chi_0\varepsilon_0)/a$, which is positive; thus T_0 (the racemic transition temperature) is significantly lower than T_C, the phase transition temperature for the S_C^* phase in this thin cell.

Further examination of the data at higher voltages and closer to T_C' shows clear deviation from linear dependence of θ on E arising from higher order terms in equation (3). For director twists less than $6°$ we neglect the θ^5 term and equation (3) become
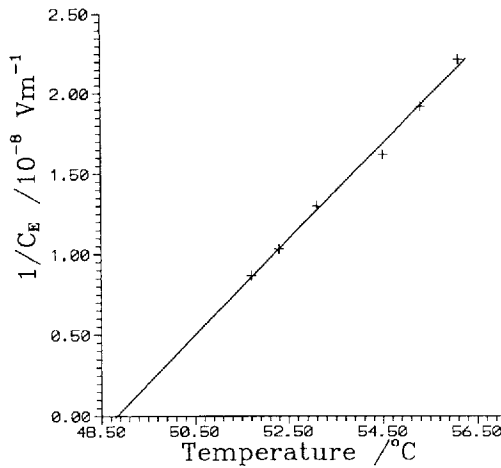
$$E = \alpha(T - T_C')\theta + b'\theta^3. \qquad (5)$$

Figure 7. The temperature dependence of the inverse of C_E in the S_A phase.

Figure 8. The theoretical fit of equation (3) (solid line) to the data taken at temperatures closer of T_C.

Since $b' < 0$, the induced director twists will be larger than for the simple linear dependence. This is obviously true for data at 53·1°C and for lower temperatures. Fitting the data at 53·1°C to equation (5) with $\alpha = 2·98 \times 10^7 \, V(m°C)^{-1}$ gives the constant b' as $(-5·0 \pm 0·2) \times 10^8 \, V m^{-1}$. For data taken at temperatures even closer to T_C and for higher voltages, we finally need to include the θ^5 term. Data at 52·3°C, 51·7°C and 51·1°C were all fitted to equation (3), with α and b' as already obtained. Such fits are shown in figure 8 and give d' as $(8·5 \pm 0·2) \times 10^9 \, V m^{-1}$. A further test of the Landau–de Gennes formulation (equation 3) is provided by plotting $[(E/\theta) - \alpha(T - T'_C)]\theta^{-2}$ against θ^2 for these higher twists and lower temperature data. Such a plot, shown in figure 9, gives an intercept of $b' = (-5·3 \pm 0·2) \times 10^8 \, V m^{-1}$ and a slope of $d' = (9·6 \pm 0·2) \times 10^9 \, V m^{-1}$. In so far as this is fully self consistent, these are the chosen b' and d' values for further analysis.

It must be emphasized that in this very thin cell the surface constraints, which suppress the phase transition, also inhibit the first order phase transition behaviour, making it very weak. The anticipated sharp jump in director twist at some voltage, typical of a first order transition, is strongly suppressed. Thus it must be stressed that although the Landau–de Gennes expression in θ fits the data, the parameters obtained are specifically for a thin, surface constrained, cell.

Additionally, as indicated earlier, the data of figure 6 point to a threshold voltage of the order 1 V before any induced twist is created at any temperature. This also suggests a strong interplay between surface anchoring and bulk forces in this cell. This we tentatively correlate with the 2·7° layer tilt. Further work concerning this threshold voltage is needed to reveal its exact cause.
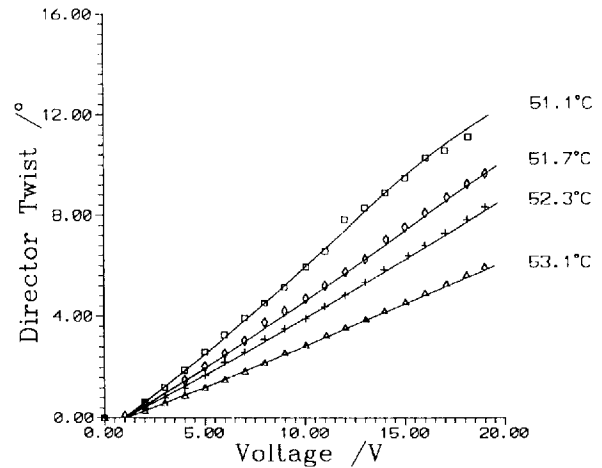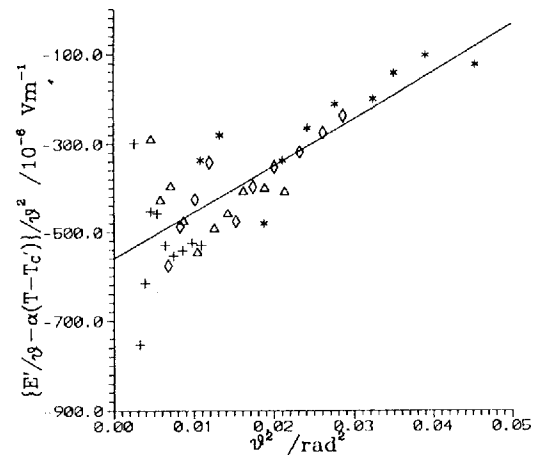

Figure 9. $[(E/\theta) - \alpha)(T - T'_C)]\theta^{-2}$ against θ^2 for different temperatures and different voltages (* relates to data at 51·5°C, ◇ at 51·7°C, △ at 52·3°C and + at 53·1°C). The line is the best (unweighted) straight line fit to the data.

4. Conclusions

Using the half leaky guided mode geometry, we have explored the electroclinic effect in the vicinity of a first order S_A to S_C^* phase transition in the material C8. The results are well explained by the Landau–de Gennes mean field theory. Fitting data to this theory gives an α coefficient (defined as in equation (3)) of $(2·98 \pm 0·02) \times 10^7 \, V(m°C)^{-1}$, which is 20 times that for C7 [13], while b' and d' are $(-5·3 \pm 0·2) \times 10^8 \, V m^{-1}$ and $(9·6 \pm 0·2) \times 10^9 \, V m^{-1}$, respectively. This gives finally the ratio $b/a = (-17·8 \pm 0·8)°C$ and $d/a = (3·22 \pm 0·08) \times 10^2 °C$ for the Landau coefficients for this material in this constrained geometry. The implication from these ratios is that only for θ less than 10^{-1} ($\sim 6°$) may the θ^5 term be ignored (≤ 3 per cent correction),

while the θ^3 term may only be ignored for θ less that ~ 0.05 ($\sim 3°$). Of course, for higher temperatures the $\alpha(T - T'_C)$ term will progressively dominate. It is therefore important in fitting theory in this manner that T'_C is well established. This is here done by plotting the inverse electroclinic coefficient against temperature (see figure 7), the intercept giving T'_C as $(48.80 \pm 0.05)°C$.

The S_A to S^*_C phase transition temperature is also independently determined by examining the relaxed (zero volt) state of the cell after application of both positive and negative voltage pulses. In the S^*_C phases, the resulting states are different, as is easily distinguished by observation of the s to p reflectivity conversion signal. This allows the phase transition temperature to be established; in this case it is $51.00 \pm 0.05°C$.

All of the phase information is altered by the boundary walls of the cell. It is clear that the constraints imposed by the wall are very severe, depressing the phase transition temperature and almost eliminating the sudden increase in twist expected of a first order phase transition at some applied field.

Further work needs to be undertaken with different anchoring strength surfaces to allow a fuller study of the electroclinic effect in this strongly electroclinic material, and to explore the unexplained and hitherto unreported threshold field.

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