Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article karabot, M. , Blinc, R. , Heppke, G. and Muevi, I.(2001) 'Electro-optic response of an antiferroelectric liquid crystal in submicron cells', Liquid Crystals, 28: 4, 607 — 613
To link to this Article: DOI: 10.1080/02678290010020166
URL: http://dx.doi.org/10.1080/02678290010020166

LIQUID CRYSTALS, 2001, VOL. 28, NO. 4, 607–613

Electro-optic response of an antiferroelectric liquid crystal in submicron cells

M. ŠKARABOT†, R. BLINC†‡, G. HEPPKE§ and I. MUŠEVIČ*†‡

†J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
‡Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, Ljubljana, Slovenia
§Iwan-N-Stranski-Institut, Technische Universität Berlin, Sekr. ER 11, Str. des 17 Juni 135, D-10623 Berlin, Germany

(*Received 4 September 2000; accepted 16 October 2000*)

The dynamics of chiral smectic phases of antiferroelectric liquid crystal MHPOBC in a confined geometry has been analysed. Using an electro-optic response technique, the temperature dependences of the relaxation rates and electro-optic strengths of the elementary excitations in thin, planar aligned, wedge-type cells of thickness from 0.3 to 4 μm have been measured and compared with those for a 50 μm hometropically aligned cell. The effects of the confined geometry are the following. (i) The smectic C^*_γ phase does not exist in planar aligned cells with thickness less than 4 μm. Instead of this phase, we have observed the coexistence of the ferroelectric smectic C* phase and the antiferroelectric smectic C^*_A phase over a very wide temperature range. (ii) The smectic C^*_α phase is stable at all measured thicknesses down to 0.3 μm. (iii) We have observed a decrease of the smectic A–smectic C^*_α phase transition temperature, proportional to the inverse of the cell thickness. (iv) Additional, thickness-independent phase modes have been observed above some critical value of the measuring electric field in all tilted phases.

1. Introduction

Much experimental and theoretical work has been performed over the last ten years on the characterization of tilted phases of antiferroelectric liquid crystalline materials. So far, several theoretical models have been proposed for the structure of intermediate smectic C^*_γ and smectic C^*_α phases, but none of them seems to be in perfect agreement with all experimental observations [1]. Moreover, there is a disagreement between the results from different experimental techniques obtained for ferrielectric phases, which remain poorly understood. For example, the resonant X-ray scattering experiment performed by Mach *et al.* [2] shows that the smectic C^*_α phase has a unit cell with length close to six smectic layers and this changes with temperature. On the other hand, the two ferrielectric smectic C^*_{FI1} (i.e. smectic C^*_γ) and smectic C^*_{FI2} phases have unit cells with three and four smectic layers, respectively. Whereas the structure of the smectic C^*_α phase is in agreement with optical measurements, the proposed three- and four-layer structures of the two ferrielectric phases are in clear disagreement with the high optical rotatory power exhibited by smectic C^*_{FI1} and smectic C^*_{FI2} phases [3].

*Author for correspondence; e-mail: igor.musevic@ijs.si

The behaviour of antiferroelectric liquid crystals in very thin planar cells has been almost exclusively reported in the context of their application in fast switching devices [4, 5]. It was observed, that below some critical thickness of a planar cell, the ferroelectric phase was nucleated within the antiferroelectric state. Ferroelectric regions, which are favoured by polar boundary conditions, were found in coexistence with the antiferroelectric state. In very thin cells, the antiferroelectric phase can be depressed for several tens of degrees [6] and the ferroelectric state is in general dominant. On the other hand, it has been observed that the ferrielectric phase is very unstable with respect to polar geometrical confinement [6, 7]. It usually disappears in pores or cells with a thickness smaller than a micron, but not many details are known.

The theoretical discrepancies and other open questions have motivated our studies of the behaviour of antiferroelectric materials in very thin planar cells, where the effects of geometrical confinement can reveal new properties of ferrielectric phases. In this paper we present detailed measurements of the electro-optic response of MHPOBC confined to wedge-type cells with variable thicknesses from 0.3 to 4 μm in the temperature range from the smectic A to the smectic C^*_A phase.

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010020166

2. Experimental

In the experiment we have measured the linear electro-optic response in the antiferroelectric liquid crystal *R*-MHPOBC, 4-(1-methylheptyloxycarbonyl)phenyl 4′-octylbiphenyl-4-carboxylate, as a function of temperature, thickness of liquid crystal and strength of the measuring electric field.

Thickness dependence measurements were performed with ultra-thin wedge-type cells with homogenous orientation, which were made of commercial glass plates with ITO electrodes. No polymer coating was applied to the plates. The thickness of the cell was determined by the 4 μm glass spacers at one edge and a close contact at the other edge of the glass. The thinnest part of the cell was approximately 0.2 μm thick in order to avoid direct contact between the two ITO electrodes. The thickness of each individual cell as a function of position along the cell was determined by measuring the spectral transmission with an accuracy better than 0.05 μm. The cells were filled with the liquid crystal material in the isotropic phase and then slowly cooled in a strong magnetic field ($B = 6$ T) to the smectic A phase, where a good homogenous alignment was obtained. In addition, we have made measurements with homeotropically oriented cells with thickness 50 μm, which represent bulk material. These cells were made from glass plates treated with *N*,*N*-dimethyl-*N*-octadecyl-3-a minopropyltrimethoxysilyl chloride (DMOAP silane). One of the glass plates was covered with two ITO electrodes, separated by a 1 mm wide gap. Voltage applied across the ITO electrodes thus created a nearly homogenous electric field in the plane of the smectic layers at the measuring spot, located in the middle of the gap between the electrodes.

In the experiment, polarized He-Ne laser light was focused on the sample and the transmitted light was detected with a photodiode connected to a lock-in amplifier. The planar sample was put between crossed polarizers with the optical axis at 22.5° to the polarization of the incoming light. In the case of a homeotropically aligned sample, the angle between the light direction and the optical axis of the sample was set to give half the intensity of the transmitted light, thus yielding a maximum linear response from the sample. We have applied an oscillating measuring electric field in the plane of the smectic layers. In both cases, this field couples to the polar eigenmodes of the liquid crystal and the lock-in amplifier measures the real (in-phase) and imaginary (out-of-phase) parts of the linear electro-optic response. It has been shown that this method is an optical analogue to dielectric spectroscopy [8].

Typical frequency dependences of the linear electro-optic response are shown in figure 1 for different phases in a homeotropic sample and in the inset of figure 5 in

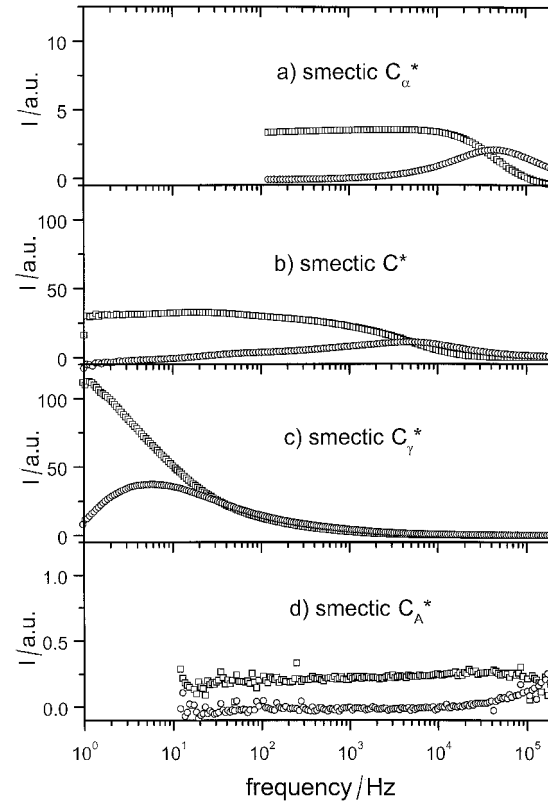

Figure 1. Real (i.e. in-phase, open squares) and imaginary (i.e. out-of-phase, open circles) parts of the linear electro-optic response in different phases of homeotropically aligned MHPOBC.

a homogenously aligned sample. We have determined the number of modes n and their relaxation rates (τ^{-1}) and strengths (ΔI) by fitting the measured spectra to the Cole–Cole equation

$$I = I_\infty + \sum_{i=1}^{n} \frac{\Delta I_i}{1 + \mathrm{i}\omega\tau_i^{1-\alpha_i}}.$$

Note that the electro-optic strength ΔI of a given mode is proportional to the dielectric strength $\Delta\varepsilon$, as described elsewhere [8].

3. Results and discussion

Figure 2(*a*). shows the temperature dependence of the relaxation rate τ^{-1} and the electro-optic strength ΔI in a very thick homeotropically oriented sample ($d = 50$ μm). We have observed a single mode relaxation in all phases, except in the smectic C* phase, where we have observed two modes, figure 1(*b*). In the smectic A phase, the relaxation rate of the soft mode decreases non-critically with decreasing temperature and the electro-optic strength of the soft mode increases. After the continuous transition to the smectic C_α^* phase, the decrease of τ^{-1} is much

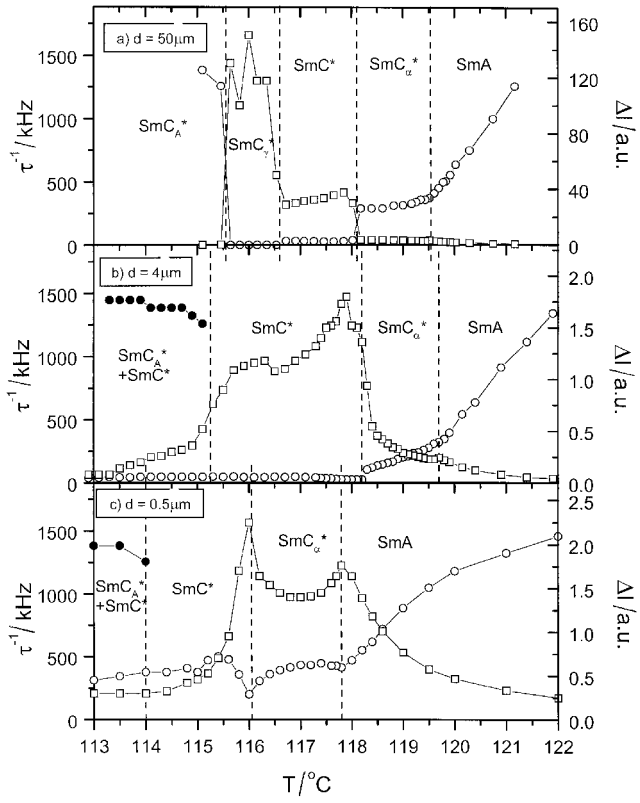

Figure 2. Temperature dependence of the relaxation rate τ^{-1} (open and closed circles) and the electro-optic strength ΔI (open squares) for three different thicknesses of planar aligned MHPOBC. The ferroelectric phason mode in the antiferroelectric phase is denoted by filled circles.

slower and both τ^{-1} and ΔI have almost constant values in this phase. At the first order phase transition into the ferroelectric smectic C* phase, we observed a discontinuous drop of τ^{-1} and a corresponding increase of ΔI of nearly ten times. In the ferroelectric smectic C* phase, τ^{-1} has an almost constant value, increasing only slightly with decreasing temperature. At the phase transition into the smectic C^*_γ phase, a strong and fast ferroelectric response is replaced by a strong, but very slow mode with a relaxation rate of $\tau^{-1} \approx 5$ Hz. Finally, in the antiferroelectric smectic C^*_A phase, the linear response becomes very small and fast. This mode represents phase excitations of the ferroelectric order parameter which have a very small amplitude in the antiferroelectric phase [8]. Here, we should stress that it is nearly impossible to achieve reasonably good alignment of the ferrielectric phase, and the results (i.e. absolute value of the response) in this phase should be considered with caution.

The dynamics in thin wedge-type homogenous cells have been measured as a function of temperature for a large number of different cell thicknesses from 0.3 to 4 μm. Figures 2 (*b*) and 2 (*c*) show two typical temperature dependences of the relaxation rates τ^{-1} and the electro-optic strengths ΔI for thicknesses of 4 and 0.5 μm, respectively. For a 4 μm cell, one can see that the ferrielectric phase has completely disappeared and has been replaced by a ferroelectric state. This state persists also for several degrees into the antiferroelectric phase and we have a coexistence of ferro- and antiferro-electric ordering. For a 0.5 μm thickness, figure 2 (*c*), the general picture is the same as for the 4 μm thickness, but the temperature range of coexistence of ferro- and antiferro-electric order further increases. We also observe a significant downwards shift in all phase transition temperature and a significant singularity at the phase transition between the smectic C^*_α and smectic C* phase.

A detailed analysis of the temperature dependences of the relaxation rates at different thicknesses has led to the following conclusions.

The confined geometry of the smectic A has almost no influence on its dynamical properties. We observed only a slight increase of the soft mode relaxation rate τ^{-1} at the transition to the smectic C^*_α phase. However, we have observed a strong decrease in the smectic A–smectic C^*_α phase transition temperature with decreasing thickness, a decrease which is proportional to the inverse of the cell thickness, as shown in figure 3.

The smectic C^*_α phase is stable at all measured thicknesses down to 0.3 μm and the confinement does not seem to have any significant influence on the dynamics and stability of this phase. We have observed that the relaxation rate τ^{-1} (i.e. the phase mode) in this phase decreases faster with temperature in the homogenous cell with thickness 4 μm than in the homeotropic cell with thickness 50 μm. This is an indication that the short-period helix of this phase is influenced to a smaller extent by polar surface coupling that tends to 'unwind' the helix. The helical arrangement of the smectic C^*_α phase is therefore more easily perturbed (i.e. unwound) in the vicinity of the phase transition into the ferroelectric phase. Furthermore, the relaxation rate of the phase mode τ^{-1} increases significantly with decreasing cell thickness. This is a general phenomenon, which can also be observed in the ferroelectric smectic C* phase and is related to the lateral geometrical confinement, which gives rise to the $1/d^2$ increase in the phason relaxation rates (i.e. the so-called thickness mode) [8, 9].

In the smectic C^*_α–smectic C* phase transition, for large thicknesses the phason relaxation rate exhibits a discontinuous jump, which is an indication of a first order character of the transition, reflected in an abrupt change of the helical period. This discontinuity in the dynamics is accompanied by a discontinuity in the temperature dependence of the tilt angle [10]. However, at thicknesses lower than 1 μm, the discontinuity is replaced by a very strong, nearly divergent behaviour of

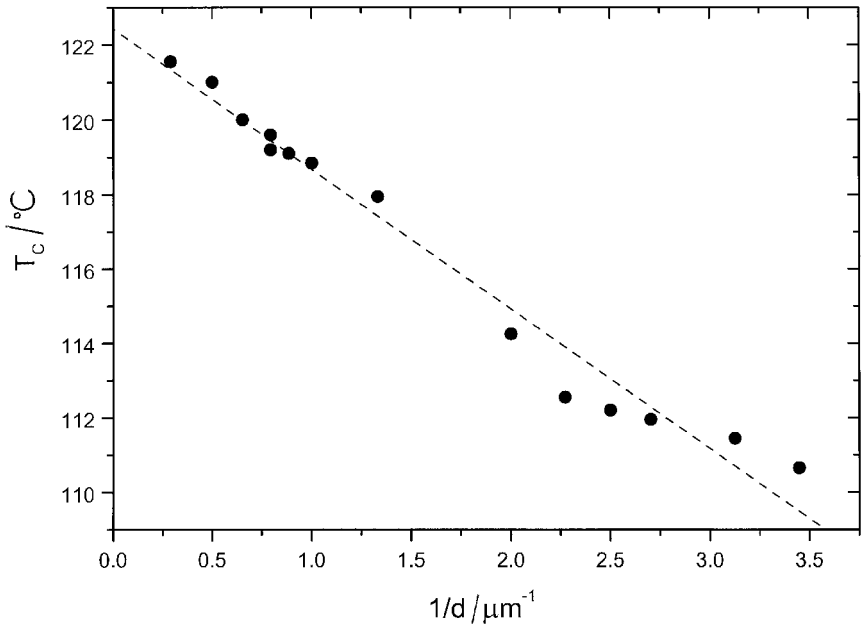

Figure 3. Thickness dependence of the smectic A–smectic C^*_α phase transition temperature in planar ITO cells of MHPOBC. No polymer is applied to the ITO electrodes.

the electro-optic strength, as shown in figure 4 for four different thicknesses. This is a clear indication that the nature of the smectic C^*_α–smectic C* phase transition changes from first order in the bulk to second order in a submicron confined geometry. The nearly divergent behaviour at the transition is very probably a result of the divergence of the helical period due to the unwinding action of the surfaces.

In the smectic C* phase we observe a polar phase mode and the relaxation rate τ^{-1} of this mode increases strongly with falling thickness. It is approximately proportional to the inverse cell thickness, which is characteristic of a 'thickness' mode. Most importantly, we observe that the ferroelectric phase is very favourable in the confined geometry. This indicates that ITO surfaces are polar and induce significant ferroelectric order at the surfaces. This polar order then propagates into the interior of the cell. When the temperature of the cell is in the range of a bulk smectic C^*_γ phase, this phase is highly unstable in the proximity of this surface polar perturbation and disappears for thicknesses lower than 4 μm.

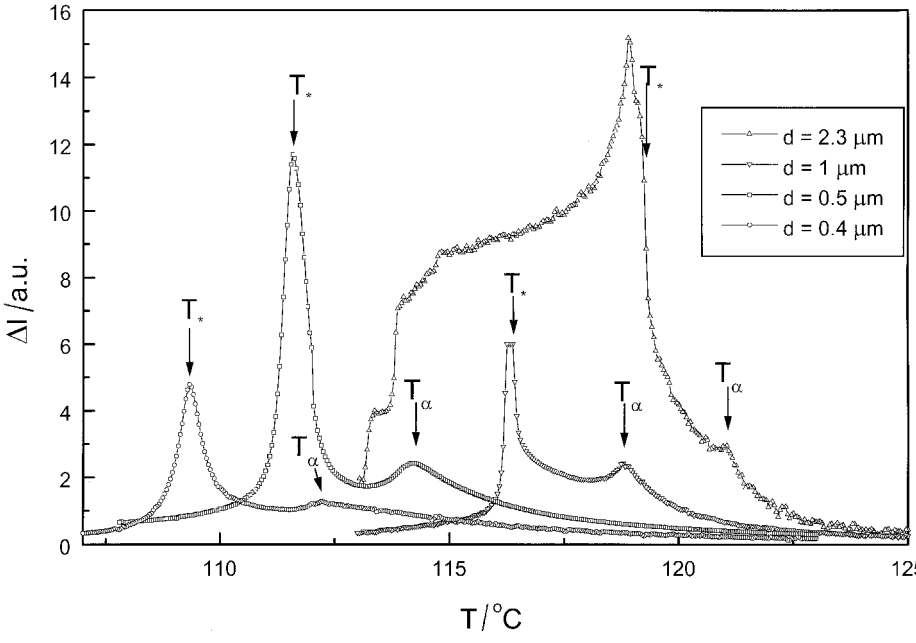

Figure 4. Temperature dependence of the electro-optic strength ΔI for four different thicknesses of homogeneously aligned MHPOBC. T_α and T_* denote transition temperatures to the smectic C^*_α and smectic C* phases, respectively.

In homogeneous cells with thickness less than 4 μm, we did not observe the smectic C^*_γ phase. Instead, we observed a ferroelectric phase mode extending over the temperature interval of the bulk smectic C^*_γ and smectic C* phases.

In thick homeotropic cells the transition to the smectic C^*_A phase occurs very sharply at a temperature 2.5 K below the smectic C^*_α–smectic C* transition. In homogenous cells with thickness of a micron or less, we observed the ferroelectric phase mode even 5–10 K below this transition. This is a strong indication of a coexistence of ferroelectric and antiferroelectric domains, which is reflected in the electro-optic spectrum. The inset to figure 5 shows a frequency sweep 5 K below this transition and one can see three modes there. The highest with measuring frequency $\nu \approx 300$ kHz is an antiferroelectric mode, a ferroelectric mode has $\nu \approx 5$ kHz and the slow mode with $\nu \approx 10$ Hz represents the 'switching' mode, which was described recently [11]. The coexistence of ferroelectric and antiferroelectric order in thin cells can also be clearly observed in the temperature dependence of the electro-optic strength, shown in figure 5. One can clearly see the 'step-like' decrease of the electro-optic strength with decreasing temperature. These jumps are due to vanishing of the ferroelectric domains with decreasing temperature. In addition, we have observed strong hysteresis in the temperature dependence of the electro-optic strength upon cooling and heating (see figure 5). We conclude that decreasing the thickness causes coexistence of the ferroelectric smectic C* and the antiferroelectric smectic C^*_A phase over a very wide temperature range; this has already been observed in some other antiferroelectric materials [4–6]. The smectic C* phase is metastable in this temperature range, as we have observed that after a short pulse of a strong measuring electric field ($\mathbf{E} > 0.5$ V μm^{-1}), the liquid crystal undergoes transition into the antiferroelectric phase. We have observed this coexistence in some samples even 15 K below the transition to the ferroelectric phase. This coexistence appears over a much wider temperature range on cooling.

As previously discussed by various authors [7, 11], we have also observed additional modes in the electro-optic response, the amplitudes of which typically increased non-linearly with increasing measuring voltage. Although the nature of these modes is not quite clear, they may be attributed either to the motion of structural defects or they may even give rise to soliton-like switching of a ferroelectric cell as a whole [11]. On the basis of these observations, it is clear that one should analyse the electro-optic response of thin cells of a polar smectic material with great care. Detailed temperature and field dependence studies of these modes in very thin cells enabled us additionally to determine the phase transition temperatures between the smectic C^*_α and smectic C* phase. As an example, we show in figure 6 the temperature dependence of the critical electric fields $\mathbf{E}_c$ which are necessary to induce additional non-linear modes in planar samples of MHPOBC with thickness 0.5 μm. In the smectic A phase we always obtain a single mode in the electro-optic response up to the maximum applied measuring a.c. field of $\mathbf{E} = 2.5$ V μm^{-1}. However, exactly at the transition to the smectic C^*_α phase we observed an additional mode with relaxation frequency of a few

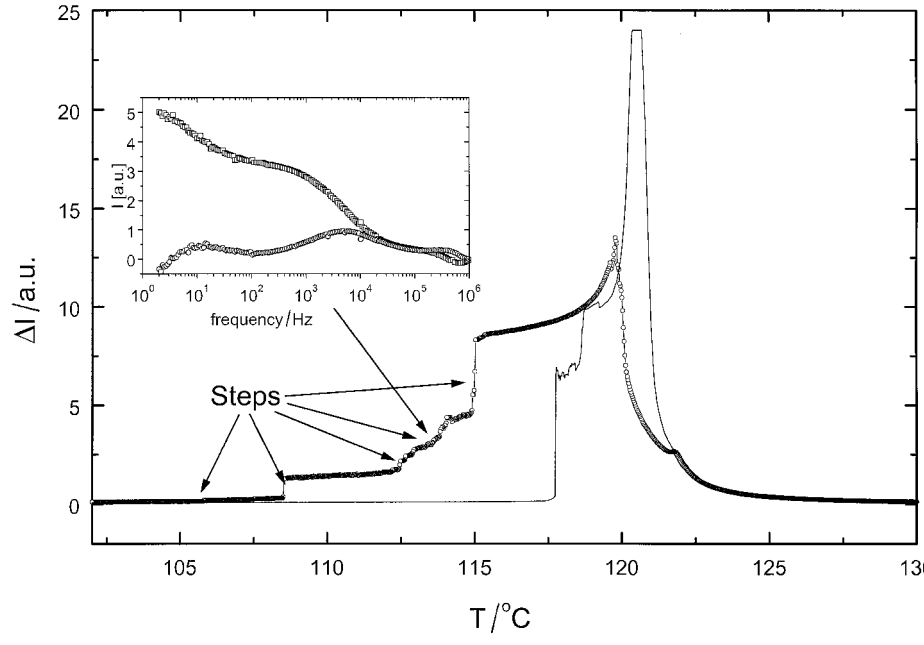

Figure 5. Temperature dependence of the electro-optic strength on cooling (open circles) and heating (full line) in homogeneously aligned MHPOBC with thickness 2.3 μm. The inset gives the linear electro-optic response in the coexistence region which is a combination of the smectic C* phase and the smectic C^*_A phase.

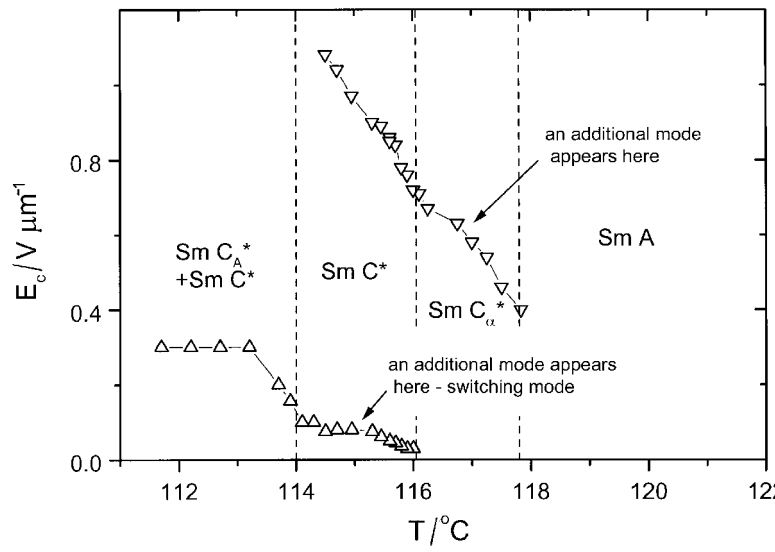

Figure 6. Temperature dependence of the two critical values of the applied measuring electric field $\mathbf{E}_C$ which induce additional, non-linear modes in the thin planar sample of MHPOBC. These modes appear in the region above the line of the measuring critical values.

Hertz which appears when the measuring a.c. electric field exceeds $\mathbf{E}_C = 0.4\ \mathrm{V\ \mu m^{-1}}$. The magnitude of the electric field necessary to induce the second mode in the response of the smectic C^*_α phase increases linearly with decreasing temperature, while the relaxation frequency of this additional mode remains around 10 Hz. Furthermore, exactly at the transition into the smectic C* phase, we have observed three modes for sufficiently large a.c. electric fields. For small values of the measuring voltage we obtain a single mode. By increasing the magnitude of the measuring voltage, we observe an additional slow mode with a relaxation frequency in the Hertz region at an electric field of $\mathbf{E}_C = 0.03\ \mathrm{V\ \mu m^{-1}}$.

We have observed a similar mode in the smectic C* phase of a ferroelectric liquid crystal [11] with the same electric field dependence. By increasing the measuring electric field, the amplitude of this mode first grows linearly with field, whereas the relaxation frequency remains unchanged. By increasing the field, the relaxation frequency of this mode starts to increase linearly above $\mathbf{E} > 0.08\ \mathrm{V\ \mu m^{-1}}$ and finally, in the limit of very strong fields, this mode represents a switching of the polarization over the entire cell. Upon further increasing the measuring field, the third mode appears at some critical value of the applied measuring field, $\mathbf{E}_C = 0.8\ \mathrm{V\ \mu m^{-1}}$. By carefully measuring the temperature dependence, we observe that this third mode is just the continuation of the 'second' mode observed in smectic C^*_α phase, as shown in figure 6.

Let us briefly comment on the possible origin of these additional, non-linear modes. The additional mode in the smectic C^*_α phase is obviously related to the tilt angle, as it is absent in the paraelectric smectic A phase. In view of the extremely large values of the electric field necessary to induce this mode, we conjecture that it represents switching of the director at the two surfaces. By decreasing the temperature, the surface coupling increases due to increased tilt, and has to be balanced by the electric energy **PE**, which leads to an increase of the critical electric field. As far as the additional mode in the smectic C* phase is concerned, it is related to the appearance of spontaneous polarization in this phase. In view of its characteristic field-dependence, we conclude that it represents soliton-like switching of the cell as a whole, as discussed earlier [11].

4. Conclusion

In conclusion, the effects of planar confined geometry on the tilted smectic phases of MHPOBC are the following. (i) The smectic C^*_γ phase does not exist in planar aligned cells with thickness less than 4 μm. Instead of this phase, we have observed coexistence of the ferroelectric smectic C* phase and the antiferroelectric smectic C^*_A phase over a very wide temperature range. (ii) The smectic C^*_α phase is stable at all measured thicknesses down to 0.3 μm. (iii) The discontinuous phase transition smectic C^*_α—smectic C* becomes continuous below a critical thickness of 1.5 μm. (iv) The decrease of the smectic A–smectic C^*_α phase transition temperature is proportional to the inverse of the cell thickness.

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