Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Online publication date: 06 August 2010

To cite this Article Hou, J. , Schacht, J. , GIEsSELMANN, F. and Zugenmaier, P.(1997) 'Investigations on the field-induced switching behaviour in an antiferroelectric liquid crystal', Liquid Crystals, 22: 4, 401 — 407
To link to this Article: DOI: 10.1080/026782997209117
URL: http://dx.doi.org/10.1080/026782997209117

LIQUID CRYSTALS, 1997, VOL. 22, NO. 4, 401–407

Investigations on the field-induced switching behaviour in an antiferroelectric liquid crystal

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(*Received 21 August 1996; in final form 25 November 1996; accepted 3 December 1996*)

The switching currents and field-induced apparent tilt angles in an antiferroelectric liquid crystal, (*R*)-MHPOBC, were measured. The structural differences among different smectic C* subphases may sensitively reflect the field or temperature dependence of the apparent tilt angle. In a thin cell, the apparent tilt angle was found to change in two steps as a function of field strength in the SmC_α^* and SmC* phases: a steep increase at lower fields and a small linear increase at higher fields. The steep increase in apparent tilt angle is divided into two parts via a plateau in the ferrielectric SmC_γ^* phase. Stepwise change with a plateau is also seen in the relation of apparent tilt angle versus temperature under various electric fields. Moreover, the apparent tilt angle in the vicinity of the plateau is almost temperature- and field-independent, implying a preferred orientation of the molecules in the ferrielectric state. The influence of the cell thickness on the structural changes was also investigated.

1. Introduction

An antiferroelectric liquid crystal (AFLC) is a special type of chiral liquid crystal which was first reported in 1989 for the compound 4-(1-methylheptyloxycarbonyl)phenyl 4′-octylbiphenyl-4-carboxylate, MHPOBC [1, 2]. Unlike simple ferroelectric liquid crystal (FLC) materials, AFLC compounds usually exhibit several types of chiral smectic C* subphases, e.g. ferro- (SmC*), ferri- (SmC_γ^*) and antiferroelectric (SmC_A^*) phases [1, 3]. Although in each smectic layer the molecules are oriented quite similarly as in ordinary FLCs, the orientational correlation between the neighbouring layers is supposed to be significantly different in the SmC_γ^* and SmC_A^* phases compared with that in SmC*; for example, the molecules in two adjacent layers are tilted in opposite directions with respect to the layer normal in the antiferroelectric state. Such differences may result from certain special and complicated interactions between the molecules in adjacent layers, which also lead to difficulties in the explanations of experimental results.

Landau type free energy expansion has been utilized in order to describe the structural changes during phase transitions, such as from the smectic A phase to the chiral smectic C phase of ordinary FLCs [4, 5]. Although some attempts have also been made by using modified Landau models to describe the AFLC systems [6–8], the proposed potential functions are too complicated and have only generalized forms, and therefore do not seem very suitable for rigidly describing the structural features. In such a situation, we are trying to determine some structural parameters and related potential functions, and to use them to describe the characteristics of ferro-, ferri- and antiferro-electric structures and phase transitions.

We chose the compound, (*R*)-MHPOBC, as the object of our investigation, a compound which to some extent has been studied before. However, some parameters of this compound need to be gathered again in more detail, for example, the temperature and/or field dependences of the spontaneous polarization and the apparent tilt angle of the molecules, as well as the dielectric properties in the various smectic C* subphases. It was also found that these parameters may sensitively depend on the cell property and measurement conditions. In this paper we will describe the switching current behaviour and the changes of apparent tilt angle while using only one cell. The results obtained from the dielectric measurements will be reported separately (cf. succeeding paper).

2. Experimental

The compound (*R*)-MHPOBC was filled into a 6·4 μm cell (E.H.C. Co. Ltd., Tokyo) with ITO layers and polyimide coating. In this cell, the sample showed an homogeneous alignment of the molecules and exhibited the following sequence of phase transitions on cooling:

$$\text{I–145°C–SmA*–123·2°C–}SmC_\alpha^*\text{–121·5°C–SmC*–119·3°C–}SmC_\gamma^*\text{–117·5°C–}SmC_A^*\text{–66°C–}SmI_A^*\text{–31°C–Cr.}$$

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The transition temperatures differed slightly from those determined on a sample by DSC measurement. In this study, they were determined by careful observation of morphological changes, as well as the changes in the switching behaviour under electric fields of various waveforms and strengths.

Another cell of 11 μm thickness was also employed, in order to clarify the cell influence on the field-induced structural changes in some C* subphases.

Spontaneous polarization measurement was carried out by applying a triangular-wave electric field (4 MV m^{-1} and 20 Hz) which was generated by a pulse function generator (Hewlett-Packard 8116A) through a wide band amplifier (Krohn-Hite Mod. 7500). The signals of switching current were transferred to a two-channel digitizing oscilloscope (Hewlett-Packard 54200A) and then processed with a Hewlett-Packard 9000/382 work station.

Apparent tilt angles of the molecules were determined by an electro-optical method. The cell exhibited two stationary states of light transmission under a square-wave electric field (here 55 Hz and various strengths were used). The light intensities of these two transmission states were recorded as a function of the rotation angle of the cell, and then two curves of light transmittance versus rotation angle were obtained. The phase shift between the two curves equals twice the apparent tilt angle. Details of the measurement procedures are described elsewhere [9].

3. Results and discussion

3.1. *Spontaneous polarization*

The polarization reversal currents were measured using the 6·4 μm cell in a cooling process, and are represented in figure 1. The small bar above each curve denotes the position of the zero field. The curves show different shapes in the SmC$_\alpha^*$, SmC* and SmC$_A^*$ phases, whereas for SmC* and SmC$_\gamma^*$ they are similar.

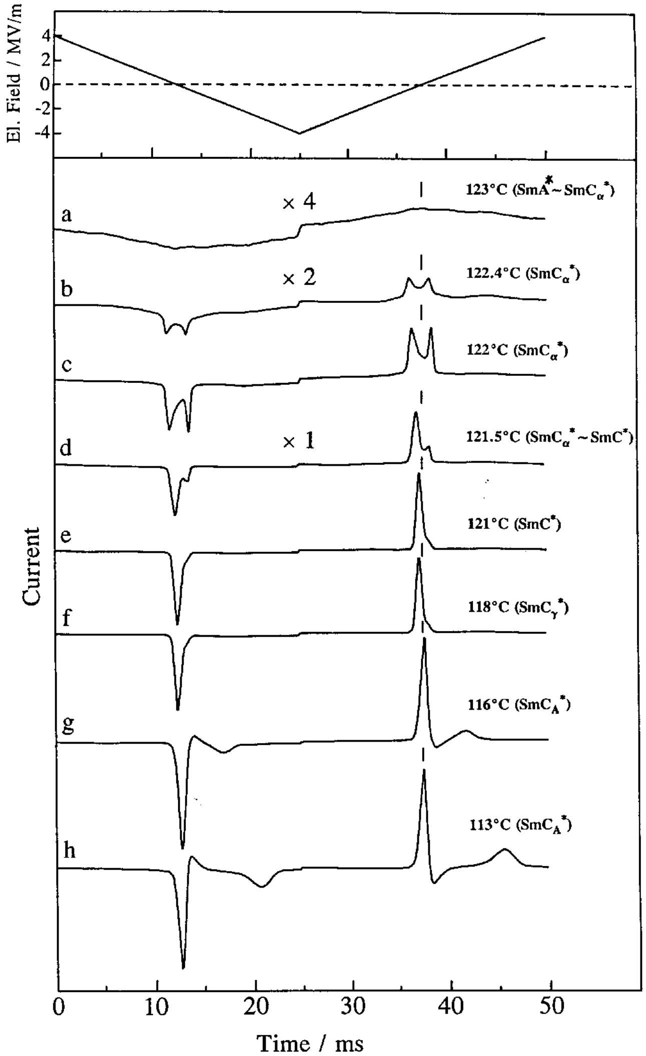

Figure 1. Switching current curves recorded for the 6·4 μm cell in the SmA*, SmC$_\alpha^*$, SmC*, SmC$_\gamma^*$ and SmC$_A^*$ phases. Curves (*a*) to (*c*) are given in larger magnifications as indicated.

In the vicinity of the SmA*–SmC$_\alpha^*$ phase transition, a broad positive peak due to the spontaneous polarization begins to appear near the zero field (see curve (*a*)). This peak is split into two sharp peaks appearing on opposite sides of the zero field, and the strengths of these peaks increase greatly with lowering temperature (see curves (*b*) and (*c*)). The sharp peak at the left side shifts its position gradually toward the right, closer to the zero field, whereas the right side peak is almost unchanged in position. In the vicinity of the next phase transition, these two peaks, respectively, increase and decrease in strength remarkably (see curve (*d*)), and finally combine to one peak in the SmC* phase (curve (*e*)).

The SmC$_\alpha^*$ phase has been supposed to have a tilted structure of the molecules with respect to the layer normal: antiferroelectric-like and ferrielectric-like in the higher and lower temperature ranges, respectively [10]. A shoulder associated with the peak at the left side was previously observed and considered to be related to a ferrielectric-like structure [10]. However, such a shoulder is not detectable in this work, even for the same compound. The different types of cell, e.g. the rubbing condition of the cell surfaces, or the different measurement conditions (frequency, etc.) may have caused the slightly different switching behaviour.

The electro-optical switching behaviour in the ferrielectric SmC$_\gamma^*$ phase has previously been investigated on the same compound: a tetrastable switching feature was observed in the frequency range up to several tens of Hz [11]. However, in this study, the switching behaviour in SmC$_\gamma^*$ has been unexpectedly simple: only one peak appears, as depicted in curve (*f*), similar to that in the SmC* phase (curve (*e*)). The difference may originate from slightly different optical purities of the samples used, although both are considered to be optically pure (the optical purity has been found sensitively to influence the stability and the temperature range of the SmC_γ^* phase [12]). For the present sample, the structural difference between the SmC_γ^* and SmC* phases can be detected by measurement of the apparent tilt angle, as described later.

The switching current curves in the SmC_A^* phase are quite complicated (see curves (*g*) and (*h*)). Mainly two peaks appear: the one around zero field is related to the field-induced transition from one of the ferroelectric states to the antiferroelectric structure; the other at higher field arises from the further transition to the other ferroelectric state. The position of the second peak shifts gradually towards higher fields as the temperature decreases, suggesting an increase in stability of the antiferroelectric structure.

In this phase, however, the strong peak near the zero field is always followed by a small backward current flow at higher field side. This small peak only appears on application of electric fields with frequency up to several tens of Hz. The strength of this peak relative to that of the sharp peak and the frequency range within which it appears were found to change with temperature. Such a peak has been detected in previous work on the same compound and in other AFLC systems [11, 13, 14]. Based on the textural changes of the sample during a switching process, the appearance of this peak was interpreted as being caused by a spatial inhomogeneity of the mesophase domains. A direct switching process from one ferroelectric state to the other, followed by a backward transition to the antiferroelectric structure has been suggested as taking place in some regions of the cell [13]. At this stage, however, it is still difficult to clarify the mechanism of this overshooting switching behaviour at the molecular level, due to the complexities of the structures and molecular interactions in the antiferroelectric state, as well as of some influences from outside.

The values of the spontaneous polarization (P_S), calculated as the total integrated area of the current peaks, by taking into account the directions or polarities of these peaks with respect to the baseline, are plotted in figure 2, which shows a similar temperature dependence to that in some FLC systems. The P_S appears and its value increases steeply in the vicinity of the SmA*–SmC_α^* phase transition, which corresponds to the SmA*–SmC* phase transition in some ordinary FLCs. After that, the P_S increases gradually, and no discontinuous change can be seen on passing through the other phase transitions.

3.2. *Apparent tilt angle*

The structural differences among the different smectic C* subphases are considered to be reflected in the different behaviour of their molecular movement under electric fields. The necessary information can be gathered to some extent from the temperature and field dependences of the apparent tilt angle of the molecules with respect to the smectic layer normal.

Figure 3 shows the apparent tilt angles induced by electric fields of various strengths in the 6·4 μm cell. The apparent tilt angle increases linearly with the field in the SmA* phase (see curve (*a*)), due to the electroclinic effect. In the SmC_α^* and SmC* phases, it essentially shows changes in two parts: the steep field-induced increase at lower fields and the small linear increase at higher fields; in the second part the molecules are fully switched and the small change in the apparent tilt angle is caused

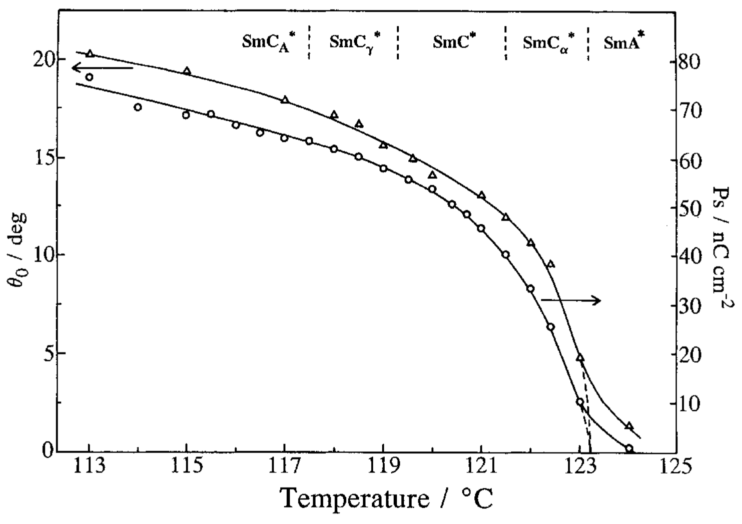

Figure 2. Temperature dependences of spontaneous polarization (P_S) and molecular tilt angle (θ_0 in the 6·4 μm cell.

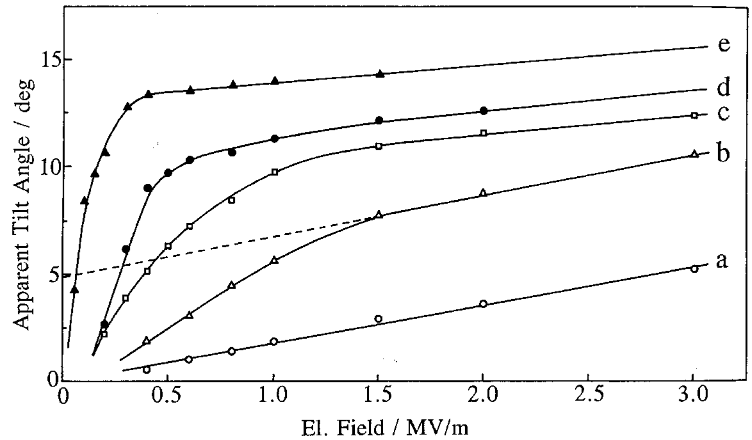

Figure 3. Field dependence of apparent tilt angle in the 6·4 μm cell measured for the SmA* [(*a*) 125°C], SmC_{α}^{*} [(*b*) 123°C, (*c*) 122·4°C, (*d*) 122°C] and SmC* [(*e*) 121°C] phases.

only by the electroclinic effect. It is also seen that the slope of the first part increases greatly on lowering the temperature in the SmC_{α}^{*} phase.

Results of apparent tilt angle versus field strength have been reported on the same compound inserted in a 16 μm cell [15]. Several intermediate states induced by electric fields were observed in the vicinity of the SmC*–SmC_{α}^{*} phase transition (the measurement was executed on a heating process), but the results are different from those obtained in this work. To clarify the origin of the difference, more detailed measurements were repeated in the corresponding temperature range, by using an 11 μm cell. The results, shown in figure 4, are similar to those previously reported [15]. The apparent tilt angle changes in several steps at a temperature slightly higher than the SmC_{α}^{*}–SmC* transition (see curve (*a*)): at first, the angle increases linearly with field strength and then increases steeply; after that, it shows a stepwise change and finally reaches a saturated state. The multi-step changes in the apparent tilt angle in the SmC_{α}^{*} phase may be associated with the structural changes involved in starting from a ferrielectric-like orientation state of the molecules in a helical structure [15].

Unexpectedly, the ferrielectric-like structural feature or stepwise change of apparent tilt angle was observed over the whole temperature range of the SmC* phase, as depicted in curve (*b*) of figure 4. Such a change cannot be clearly seen in a thin cell (curve (*e*) of figure 3), and also not in ordinary FLC systems. That is to say, the structural feature of this phase is not the same as that shown by the ordinary SmC* phase, but is more or less ferrielectric-like, similar to that in the SmC_{γ}^{*} phase at lower temperatures (cf. curve (*c*) in figure 4). The non-stepwise change in the apparent tilt angle in a thin cell is probably due to the less regular helical structure (a texture characteristic of the helical structure cannot be clearly seen). For such a structure, an external electric field is considered mainly or only to cause the rotations

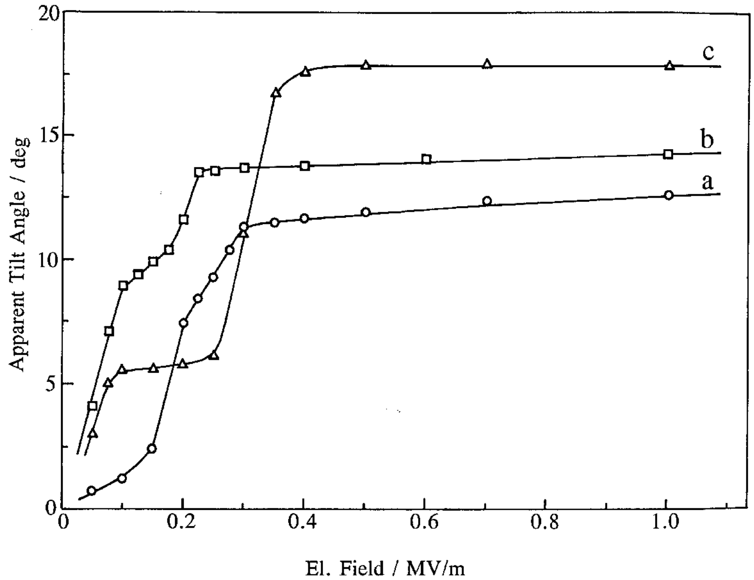

Figure 4. Field dependence of apparent tilt angle in the 11 μm cell measured for the SmC_{α}^{*} [(*a*) 122°C], SmC* [(*b*) 121°C] and SmC_{γ}^{*} [(*c*) 119°C] phases.

of the molecules along the smectic cone, and hence, the stepwise change as seen in the thick cell, resulting from the unwinding of the ferrielectric helical structure, will not be obvious.

The field dependence of the apparent tilt angle in the SmC*, SmC_{γ}^{*} and SmC_{A}^{*} phases in the 6·4 μm cell is given in figure 5. The monotonous rapid increase as in SmC* (curve (*a*)) is divided into two parts by a small plateau in the vicinity of the SmC*–SmC_{γ}^{*} phase transition (see curve (*b*)). The plateau grows with lowering temperature (curve (*c*)) and then becomes smaller (curve (*d*)) and vanishes at temperatures slightly below the SmC_{γ}^{*}–SmC_{A}^{*} transition (curve (*e*)). As the temperature further decreases in the SmC_{A}^{*} phase, the apparent tilt angle increases more steeply with field strength (see curve (*f*)).

The results for SmC_{γ}^{*} in the cells of different thickness are similar, as seen from curves (*c*) in figures 4 and 5. The slight difference can be found in the values of the apparent tilt angles in the fully switched state: those in the thick cell are slightly larger. Additionally, at each stage, the apparent tilt angle in the thick cell could be made to increase by lower fields, implying easier movement of the molecules which are less restrained by the cell surfaces.

As illustrated by the broken lines in figures 3 and 5 (curves (*b*)), the values of the apparent tilt angle in the fully switched state were extrapolated to the zero-field coordinate. Assuming that the smectic layers are in or nearly in a bookshelf geometry, the value obtained may correspond to the tilt angle, θ_0, of the molecular directors along the smectic tilt cone. As shown in figure 2, θ_0 increases smoothly with lowering temperature, similar to the temperature dependence of $\mathbf{P}_S$. The SmA*–SmC_{α}^{*} transition occurs at about 123·2°C; this temperature was estimated from the results of the extrapolations indicated by the broken lines in figure 2.

Results for the apparent tilt angle in the SmC_{γ}^{*} phase of the same compound have also been reported [15]. It was suggested that the first stage of the increase in apparent tilt angle is due to the field-induced unwinding process of a ferrielectric helical structure (a structural model of SmC_{γ}^{*} has been proposed [16]), and the second part is associated with the further transition to the ferroelectric state. Differences from those results are that the maximum broadness of the plateau is much smaller and the steep increase in the apparent tilt angle starts in the range of higher fields as the temperature decreases, but not always from the zero field (it does seem to start from the zero field in the 11 μm cell). Moreover, the apparent tilt angle in the fully switched state in both the thin and thick cells may increase reasonably with lowering temperature, whereas the reported values of the angle in the corresponding state were almost the same even at different temperatures and in the different phases [15]. The above-mentioned differences may originate from the different types of cell (a 16 μm cell was used [15]) or from the different techniques and conditions of measurement (waveform and frequency of a.c. field, etc.). In a thin cell, as used in this work, the helical structure is considered to be less complete, and in addition, the molecular orientations may be more strongly influenced by the cell surfaces; hence, a field of higher strength will be required to cause the reorientations of molecules. Also, in the present experiments, the waiting time before a measurement after changing the field strength or temperature was long enough to achieve a stationary state of molecular orientation. It is intended in further work to clarify how the helix-unwinding process occurs, for example, the

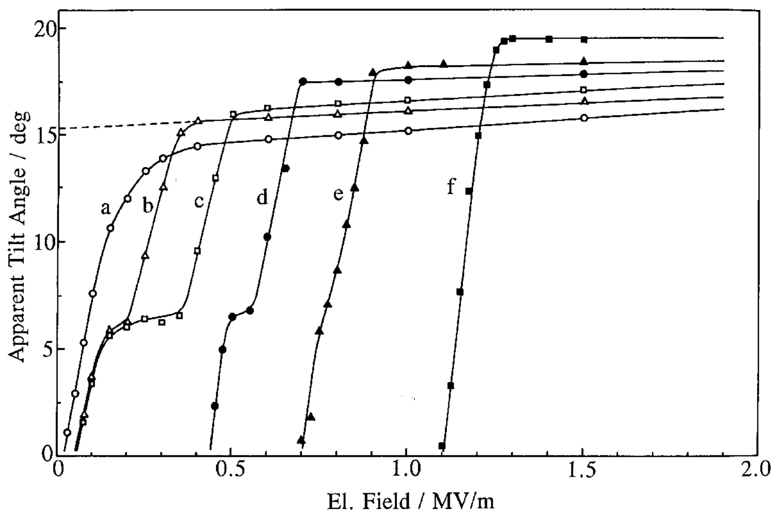

Figure 5. Field dependence of apparent tilt angle in the 6·4 μm cell measured for the SmC* [(*a*) 120°C], SmC_{γ}^{*} [(*b*) 119·3°C, (*c*) 119°C, (*d*) 118°C] and SmC_{A}^{*} [(*e*) 117°C, (*f*) 115°C] phases.

changing manner of the helicoidal pitch under applied fields, and the switching behaviour in a very thin cell where no helical structure can be formed.

A stepwise change was also observed in the curves of apparent tilt angle versus temperature under electric fields of various strengths (results in figure 6 were obtained for the 6·4 μm cell). Under fields high enough to cause full switching, the apparent tilt angle begins to fall at temperatures near to or lower than the SmC*–SmC_γ^* transition (see curves (*b*) to (*e*)), whereas it may drop in the range of higher temperatures under a small field (curve (*a*)). A plateau can be clearly seen in curves (*a*) to (*e*) in the temperature range of SmC_γ^* and partially of the SmC* and SmC_A^* phases. As the temperature further decreases in SmC_A^*, the plateau becomes less distinct and finally disappears, as seen in curves (*e*) and (*f*) of figures 5 and 6.

Moreover, hysteresis was observed in both the curves of apparent tilt angle as functions of field strength (figure 7) and of temperature (figure 8). In SmC* and in the temperature range much lower than the SmC_γ^*–SmC_A^* transition, the apparent tilt angle only changes monotonously and shows a small hysteresis between the two curves obtained during the processes of increasing and decreasing the field strength, as illustrated in curves (*a*) and (*d*) of figure 7. As indicated by the other curves in these figures, the hysteresis is strong in the temperature range of SmC_γ^* and near the SmC_γ^*–SmC_A^* transition. It is also seen that the plateau obtained with decreasing field strength (figure 7, curves (*b*) and (*c*)) and with decreasing temperature (figure 8, curves (*a*) and (*b*)) is larger than those in the corresponding reverse processes. Therefore, the hysteresis is larger in the range of small apparent tilt angles than at larger angles. The appearance of the plateau may result from a structural feature of the ferrielectric phase. It is also characteristic that the apparent tilt angle in the vicinity of the plateau is almost temperature- and field-independent. This may imply a

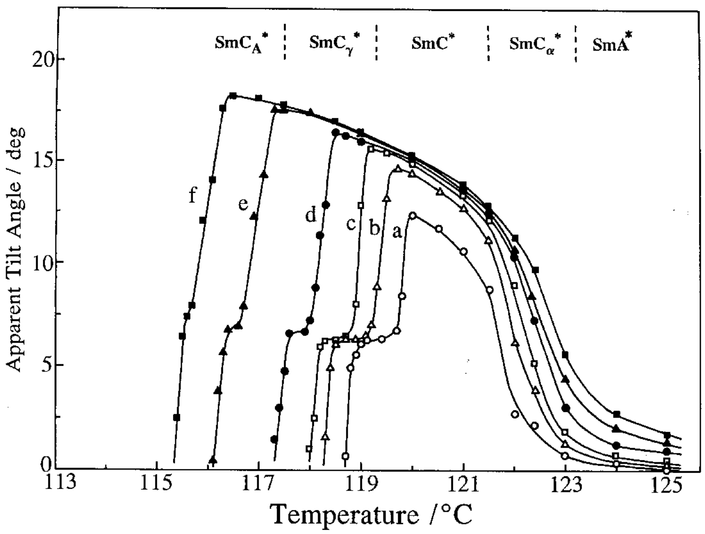

Figure 6. Temperature dependence of apparent tilt angle in the 6·4 μm cell measured on cooling under square-wave electric fields of (*a*) 0·2, (*b*) 0·3, (*c*) 0·4, (*d*) 0·6, (*e*) 0·8 and (*f*) 1·0 MV m^{-1}.

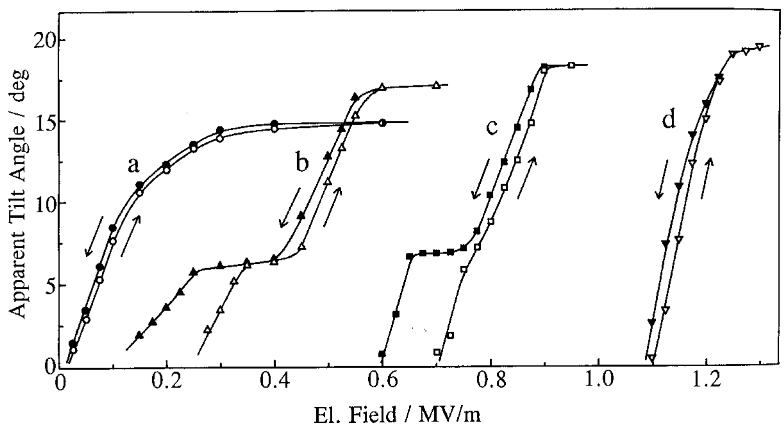

Figure 7. Field dependence of apparent tilt angle in the 6·4 μm cell obtained during the processes of increasing and decreasing the field strength in the SmC* [(*a*) 120°C], SmC_γ^* [(*b*) 118·5°C] and SmC_A^* [(*c*) 117°C, (*d*) 115°C] phases.

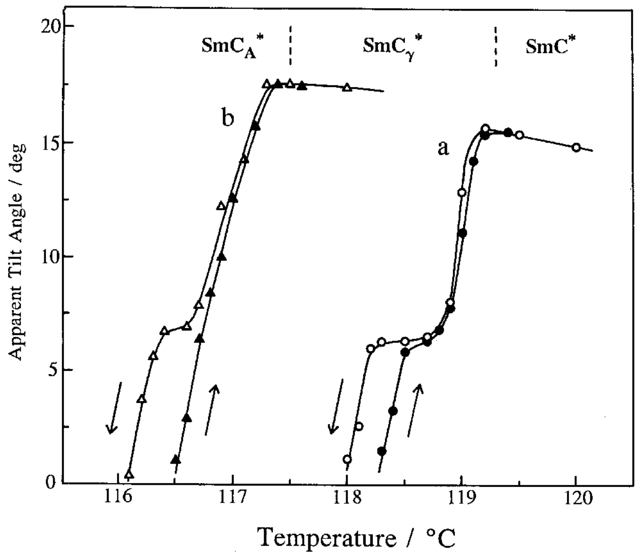

Figure 8. Apparent tilt angles in the 6·4 μm cell obtained on heating and cooling under electric fields of (*a*) 0·4 and (*b*) 0·8 MV m^{-1}.

preferred orientational structure of the molecules in the ferrielectric state.

4. Conclusions

The polarization reversal currents and the field-induced apparent tilt angles of the molecular directors were measured, and will be referred to as a part of the primary structural parameters adopted in a future investigation concerning the free energy of the AFLC system. The principal results are as follows:

(i) The structural differences among the different smectic C* subphases may sensitively reflect the field or temperature dependence of the apparent tilt angle, especially in the case of the SmC* and SmC_γ^* phases, which, however, exhibit almost the same switching current behaviour.

(ii) In a thin cell, the apparent tilt angle shows an ordinary electric field dependence in the SmA*, SmC_α^* and SmC* phases. It increases linearly in SmA* due to the electroclinic effect, but in two parts in the SmC_α^* and SmC* phases: a steep field-induced increase at lower fields and a small linear increase at higher fields, where the molecules are fully switched.

(iii) The field dependence of apparent tilt angle is abnormal in a thick cell; in particular, a stepwise change due to the ferrielectric-like structural ordering is observed even in the SmC* phase.

(iv) The apparent tilt angle changes in a complicated manner in SmC_γ^* and in the vicinity of the SmC_γ^*–SmC_A^* phase transition: two stages of steep increase via a plateau were observed. Such a stepwise change is also seen in the relation of the apparent tilt angle versus temperature under electric fields of various strengths. Moreover, hysteresis is found between the two curves of apparent tilt angle obtained by increasing and decreasing the field strength or the temperature; this is more pronounced in the range of small apparent tilt angles below the plateau. It is also characteristic that the apparent tilt angle in the vicinity of the plateau is almost temperature- and field-independent, implying a preferred orientational structure of the molecules in the ferrielectric state.

(v) In the lower temperature region in the SmC_A^* phase, the plateau disappears and the apparent tilt angle changes more steeply with field strength.

We thank Prof. Dr. A. Saupe (Max-Planck-Arbeitsgruppe Flüssigkristalline Systeme an der Martin-Luther-Universität Halle) for helpful discussions. One of the authors, Jianan Hou, is grateful to the Alexander von Humboldt Foundation for a fellowship.

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