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## Liquid Crystals

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Online publication date: 06 August 2010

**To cite this Article** Hou, J. , Schacht, J. , GIEssELMANN, F. and Zugenmaier, P.(1997) 'Temperature and bias-field dependences of dielectric behaviour in the antiferroelectric liquid crystal, (R)-MHPOBC', *Liquid Crystals*, 22: 4, 409 – 417

**To link to this Article:** DOI: 10.1080/026782997209126

**URL:** <http://dx.doi.org/10.1080/026782997209126>

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# Temperature and bias-field dependences of dielectric behaviour in the antiferroelectric liquid crystal, (R)-MHPOBC

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(Received 21 August 1996; in final form 8 November 1996; accepted 5 December 1996)

Temperature and bias-field dependences of dielectric behaviour in the antiferroelectric liquid crystal, R-MHPOBC, were investigated (see also previous paper). There are mainly two relaxation modes in the  $\text{SmC}_\alpha^*$  and  $\text{SmC}^*$  phases: one behaves as the soft-mode, which shows significant slowing down in the  $\text{SmA}^*$  and  $\text{SmC}_\alpha^*$  phases; the other one appears at lower frequencies and changes the dielectric strength remarkably, especially in the  $\text{SmC}^*$  phase, which is considered to relate to the azimuthal phase-fluctuation of molecules in the parallel tilt sequences of the smectic layers. These two modes show different bias field dependences in different  $\text{C}^*$  subphases. In the  $\text{SmC}_A^*$  phase, two other types of relaxation mode were observed, which are probably due to the in-phase and anti-phase azimuthal angle fluctuations of molecules in the anti-tilt pairs.

## 1. Introduction

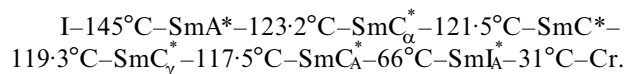
Antiferroelectric liquid crystal (AFLC) materials usually exhibit several types of chiral smectic  $\text{C}^*$  subphases, e.g. the ferro- ( $\text{SmC}^*$ ), ferri- ( $\text{SmC}_\gamma^*$ ) and antiferroelectric  $\text{C}^*$  ( $\text{SmC}_A^*$ ) phases [1, 2]. Although in each smectic layer the molecules are oriented similarly to that in ordinary ferroelectric liquid crystals (FLCs), the orientational correlation of molecules in different layers is supposed to be quite different in some  $\text{C}^*$  subphases. 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 among the molecules in the same and/or different layers.

In order to recognize and describe the structural features and the phase transition behaviour, it is necessary to accumulate more information about structural parameters, which may then be referred to as basic data for determining some models of free energy potentials. For this purpose, we have investigated the switching current behaviour and field-induced apparent tilt angle of the molecules in a previous paper [3], in comparison with some other results [4–7]. In addition to the direct structural analyses, the investigations of physical properties may also provide useful information about the structural features. In this work, the temperature and bias field dependences of the dielectric properties of the title compound [1, 4, 6–8] were investigated in detail. By means of a fitting operation, we were able separately

to evaluate the characteristic of each relaxation process. The structural changes in the different smectic phases and in the vicinities of phase transitions were also analysed, based on the dielectric behaviour.

## 2. Experimental

The compound (R)-MHPOBC was filled into a cell of 11  $\mu\text{m}$  thickness (E.H.C. Co. Ltd., Tokyo) with ITO layers and polyimide coating. In this cell, the sample adopts a planar alignment of the molecules and exhibits the following sequence of phase transitions on cooling:



The transition temperatures slightly differ from the values determined by DSC measurement. In this work, they were determined by careful observations of morphological changes, as well as by the changes in the dielectric properties under various bias fields.

Dielectric measurements were carried out in the frequency range from 10 Hz to 10 MHz, using a Hewlett-Packard 4192 impedance analyser. The measuring field was 0.11 Vpp, and the bias fields of various strengths were applied across the cell at several selected temperatures in each smectic phase.

## 3. Results and discussion

### 3.1. Temperature dependence

In figure 1, some dielectric absorption spectra for the  $\text{SmA}^*$  and  $\text{SmC}_\alpha^*$  phases are depicted. A relaxation mode appearing at several MHz relates to the resistance of the

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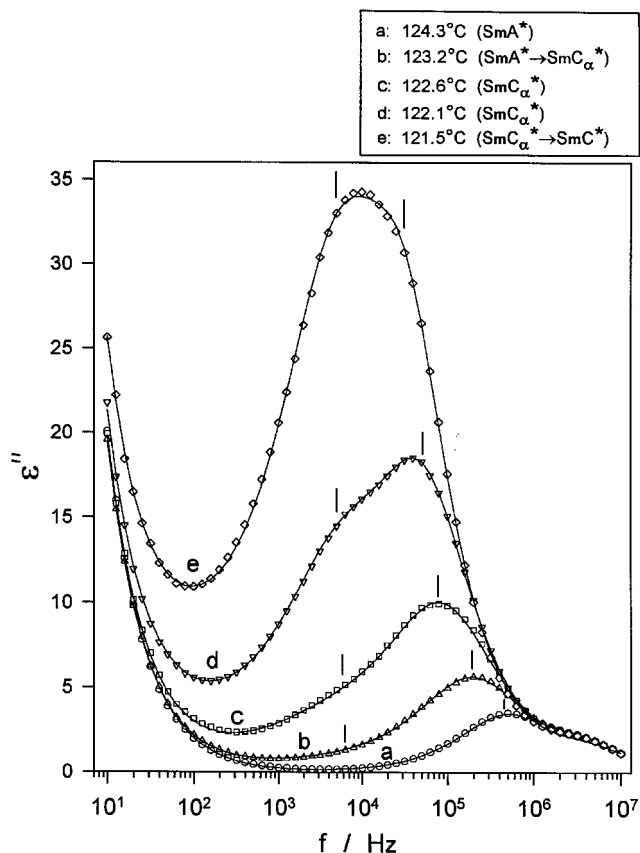


Figure 1. Temperature dependence of the dielectric absorption spectra in the SmA\* and SmC<sub>α</sub>\* phases.

ITO electrodes coated with polyimide layers. Besides this, a mode with relaxation frequency about  $5 \times 10^5$  Hz is observed in the SmA\* phase, as marked by the small bar above the curve (a). On cooling, this mode increases in strength and shifts gradually towards lower frequencies. In the vicinity of the SmA\*–SmC<sub>α</sub>\* phase transition, another mode in the lower frequency range appears and increases on cooling. However, only small variations can be seen in its relaxation frequency, as indicated by the small bars above the curves (b) to (e). The dielectric strength of this mode further increases in the SmC\* phase, as seen in figure 2. In this phase, the mode located at higher frequencies reduces in strength and shifts in position closer to the strong mode. At lower temperatures in the SmC\* phase, the dielectric strength of the low frequency mode also decreases remarkably, as indicated by curves (b) and (c) in figure 2.

Usually, the complex dielectric permittivity  $\epsilon^*$  can be expressed by equation (1),

$$\epsilon^* = \frac{G}{i\omega} + \sum_{i=1}^n \frac{\Delta\epsilon_i}{1 + (i\omega\tau_i)^{1-\alpha_i}} \quad (1)$$

where  $G$  refers to the ionic conductivity in the cell, and

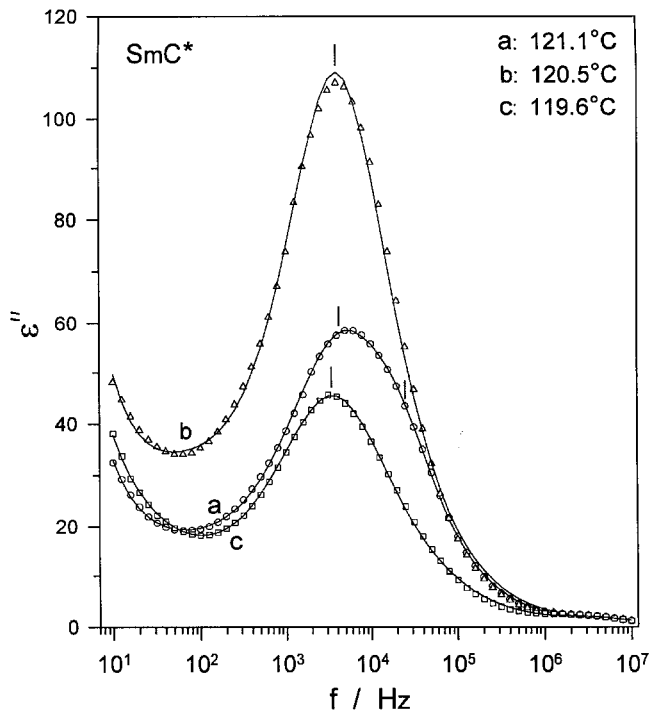


Figure 2. Temperature dependence of dielectric absorption spectrum in the SmC\* phase.

$\Delta\epsilon_i$ ,  $\tau_i$ ,  $\alpha_i$  to the dielectric strength, the relaxation time and the symmetric distribution parameter of the  $i$ th mode, respectively. The sum of  $\epsilon^*$  of all the modes was calculated by assuming the parameters in equation (1), and then it was fitted to the experimental data. The results of the fitting procedure are given by the solid lines in figures 1 and 2, which are in good agreement with the measured curves.

The Cole–Cole plots of individual relaxation modes at different temperatures in the SmC<sub>α</sub>\* and SmC\* phases are depicted in figure 3. Squares and triangles represent the two modes in the high and low frequency range (see figures 1 and 2), respectively. Notably, the dielectric strength of the low frequency mode increases significantly on cooling. In these curves, the mode in the very low frequency range, drawn by the symbol  $\diamond$ , is considered to originate from the migration of ionic impurities.

Some dielectric absorption spectra measured for the SmC<sub>γ</sub>\* and SmC<sub>α</sub>\* phases are depicted in figure 4. The mode at several KHz decreases in strength and shifts gradually towards lower frequencies (see curves (a) and (b), and finally vanishes in the vicinity of the SmC<sub>γ</sub>\*–SmC<sub>α</sub>\* phase transition, curve (c). It was also found that the small mode at  $\sim$  MHz undergoes stepwise changes in dielectric strength and relaxation frequency on passing through the SmC\*–SmC<sub>γ</sub>\* phase transition; it is the only mode in the SmC<sub>α</sub>\* phase, see curve (d).

Temperature dependences of the dielectric strength

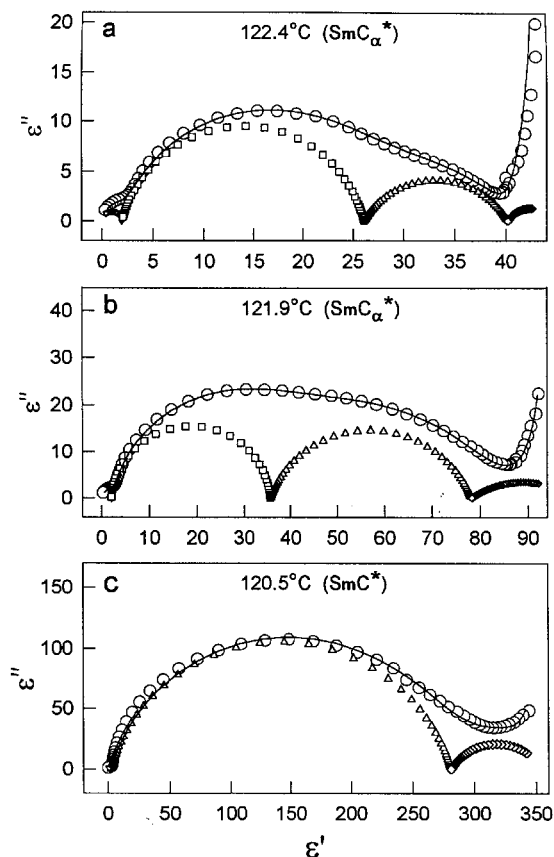


Figure 3. Cole-Cole plots of dielectric spectra in the  $\text{SmC}_\alpha^*$  (a), (b) and  $\text{SmC}^*$  (c) phases.

and relaxation frequency of some modes described above are summarized in figure 5. It is seen in figure 5 (b) that the mode on the higher relaxation side (plotted by black squares) shows significant and continuous slowing down on cooling. The strength of this mode (white squares) increases only slightly in the  $\text{SmA}^*$  and  $\text{SmC}_\alpha^*$  phases. This mode is not plotted at lower temperatures because of the difficulty in separating the two overlapped modes, see curves in figure 1 (e) and in figure 2 (b). A relaxation mode showing significant slowing down in the same frequency range is commonly observed in either FLC or AFLC systems, and is assigned as the soft-mode [8–13], due to the collective tilt fluctuation. In some AFLCs, the characteristic of the soft-mode can be more distinctly observed when the compounds only exhibit simple phase transitions, such as a direct transition from  $\text{SmA}^*$  to  $\text{SmC}_\alpha^*$  or via the  $\text{SmC}^*$  phase [11]. From the temperature dependence of the relaxation modes shown in figure 5, we would also prefer to ascribe the high frequency mode of this compound to the soft-mode, although the strength, etc. of this mode is difficult to evaluate clearly in the vicinity of the  $\text{SmC}_\alpha^*$ – $\text{SmC}^*$  phase transition. As shown later, this mode can be clearly seen

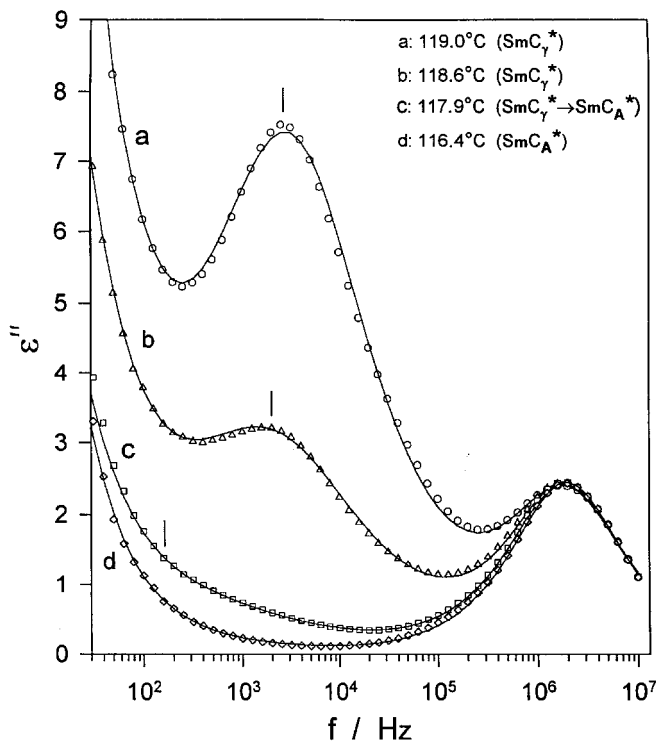


Figure 4. Temperature dependence of the dielectric absorption spectra in the  $\text{SmC}_\gamma^*$  and  $\text{SmC}_\alpha^*$  phases.

when the mode on the lower frequency side is heavily suppressed by an electric bias field.

As mentioned above, the low frequency mode begins to appear in the vicinity of the  $\text{SmA}^*$ – $\text{SmC}_\alpha^*$  phase transition; its strength (white triangles) undergoes significant changes in the  $\text{SmC}^*$  phase. However, only small variations can be seen in its relaxation frequency (black triangles) in the  $\text{SmC}_\alpha^*$  and  $\text{SmC}^*$  phases. On further cooling, this mode shifts remarkably towards lower frequencies in the  $\text{SmC}_\gamma^*$  phase and vanishes near the transition to the  $\text{SmC}_\alpha$  phase. For AFLCs, several models have been proposed so far to describe the behaviour of a relaxation mode in the same frequency range. One of the explanations is to ascribe this relaxation to the so-called Goldstone-mode [8, 10, 11], originating from collective azimuthal angle fluctuations along the smectic cone. For liquid crystals, the Goldstone-mode is usually detectable in the  $\text{SmC}^*$  phase of ordinary FLCs. In the  $\text{SmC}_\alpha^*$  and  $\text{SmC}_\gamma^*$  phases of AFLCs, however, the molecules may not always fluctuate continuously in the same azimuthal direction on a larger scale, and in some places, other types of molecular tilting with a large phase difference, such as the anti-tilt pairs, may also exist in neighbouring layers. Locally, the director configuration can be approximately described by the parallel-tilt and anti-tilt pairs. The azimuthal angle fluctuation of the anti-tilt pairs usually does not

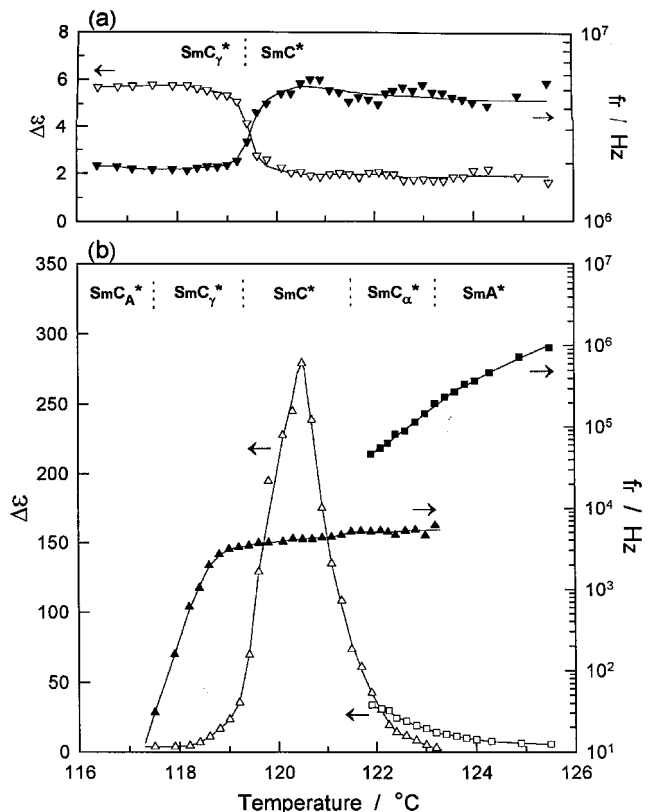


Figure 5. Temperature dependences of dielectric strength and relaxation frequency of some relaxation modes.

induce or only induces very small local polarization [13]. Hence, its contribution to the dielectric property is small. As a plausible explanation, the low frequency mode mentioned above may originate from the azimuthal angle fluctuation of directors in the parallel tilted molecular sequences.

Another mode at several MHz may originate from the resistance of the ITO electrodes, as well as the high frequency permittivity,  $\epsilon_\infty$  of the liquid crystal material. In ordinary LC systems, the absorption in this range is less temperature dependent. It is also seen that the mode strength of  $\sim 2.0$  remains almost unchanged in the  $SmA^*$ ,  $SmC_\alpha^*$  and  $SmC^*$  phases of the current compound (see Figure 5(a)). However, in the vicinity of the  $SmC^*$ – $SmC_\gamma^*$  phase transition, this mode even becomes much stronger and simultaneously shifts towards lower frequencies. As discussed later, a contribution from the structural characteristics of the  $SmC_\gamma^*$  and  $SmC_A^*$  phases may be contained in this dielectric absorption.

### 3.2. Bias field dependence

#### 3.2.1. In the $SmA^*$ and $SmC_\alpha^*$ phases

In  $SmA^*$ , the soft-mode is only slightly affected by the electric bias field. The situation is different in the  $SmC_\alpha^*$  and in the other  $C^*$  subphases at lower

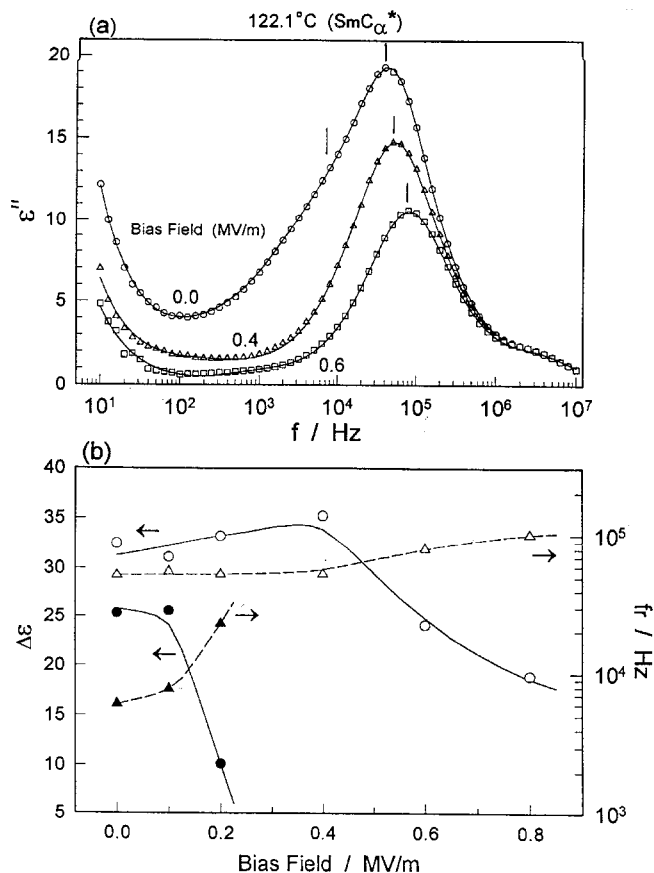


Figure 6. Bias field dependences of (a) the dielectric absorption spectrum and (b) the dielectric strength and relaxation frequency of some modes in the  $SmC_\alpha^*$  (122.1 °C) phase.

temperatures; in these phases the molecules are tilted from the smectic layer normal and form a helical structure [14]. Figure 6(a) shows the changes in the dielectric absorption spectrum under bias fields of various strengths in the  $SmC_\alpha^*$  phase. The changes of dielectric strength and relaxation frequency are plotted in figure 6(b). At zero field, the observed strong peak and a shoulder attached to it on the low frequency side belong to the soft-mode and the mode due to the azimuthal angle fluctuation of the molecules in the parallel tilt sequences (for convenience, named ‘low-mode’), respectively. With increase of the bias field, the low-mode decreases in strength (black circles) remarkably and shifts closer to the position of the soft-mode (black triangles), as can be seen in figure 6(b). This mode could not be detected under bias fields higher than about  $0.3 \text{ MV m}^{-1}$ , when the molecules are probably fully switched, as can be understood from our previous investigation on the apparent tilt angle of the molecules [3]. At low bias fields, a small increase is observed in the strength of the soft-mode (white circles). This mode

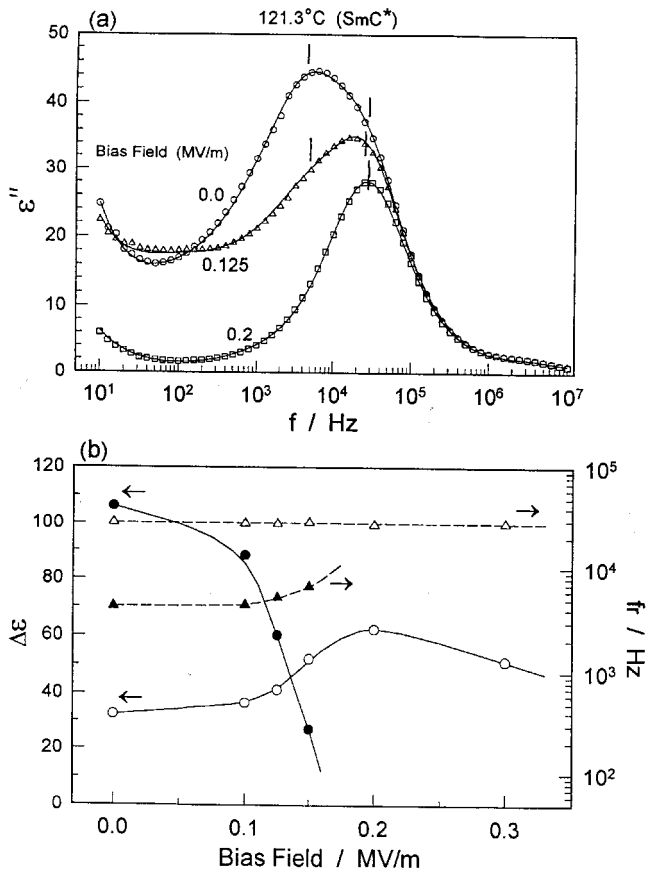


Figure 7. Bias field dependences of (a) the dielectric absorption spectrum and (b) the dielectric strength and relaxation frequency of some modes in the SmC\* (121.3°C) phase.

is gradually suppressed and shifts to higher frequencies (white triangles) with further increase of the bias field.

### 3.2.2. In the SmC\* phase

Figure 7 shows the bias field dependences of the soft- and the low-modes at 121.3°C, a temperature just below the SmC<sub>α</sub>\*–SmC\* transition. In this phase, the low-mode, at zero field, is much stronger compared with the soft-mode. In addition, the unwinding of the helical structure was found to be induced in the range of lower electric fields [7, 3]. Accordingly, the low-mode (black circles and triangles) is suppressed at smaller fields; at the same time, the strength of the soft-mode (white circles) is increased.

The soft-mode cannot be clearly seen in the lower temperature range of SmC\* (see curves (b) and (c) in figure 2). This mode is only detectable when the low-mode is heavily suppressed by the electric field, as indicated by the bottom curve in figure 8 (the mode strength and relaxation frequency are not given, because of difficulty in separating the two modes). The suppression of the low-mode by the electric field may correspond

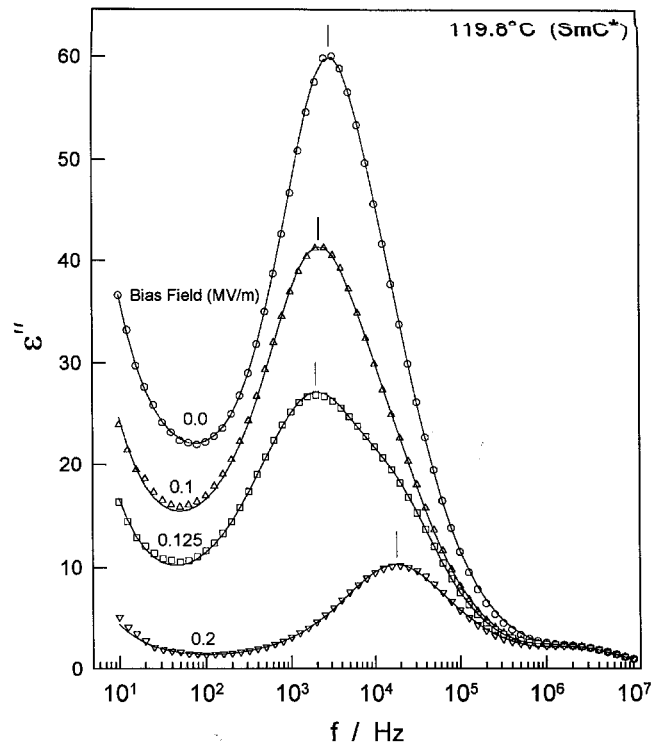


Figure 8. Bias field dependence of the dielectric absorption spectrum in the SmC\* (119.8°C) phase.

to the distortion of the molecular orientations or the unwinding process of the helical structure. During this structural change, however, the low-mode may even shift to lower frequencies, different from the positional changes of the same mode at higher temperatures (see figures 6 and 7).

### 3.2.3. In the SmC<sub>γ</sub>\* phase

Only the low-mode can be observed in the ferroelectric SmC<sub>γ</sub>\* phase, as shown in figure 9, and its changes under bias fields are quite different from those in the other C\* subphases at higher temperatures. The mode strength is at once increased at very low bias fields, and then suppressed gradually on further increase of the field. The relaxation frequency of this mode is almost unchanged at low bias fields, and begins to increase at a field of about 0.15 MV m<sup>-1</sup>.

The results in figure 9 were obtained at 118.9°C, a temperature slightly below the SmC\*–SmC<sub>γ</sub>\* transition. In the corresponding temperature range, the field-induced apparent tilt angles of the molecules of the same compound were also measured using cells of different thicknesses [3, 7]. The results are similar: with increasing electric field over a critical strength, the apparent tilt angle begins to increase steeply but in two parts via a small plateau. The first part is induced under electric fields of about 0.05 to 0.12 MV m<sup>-1</sup> and the second part

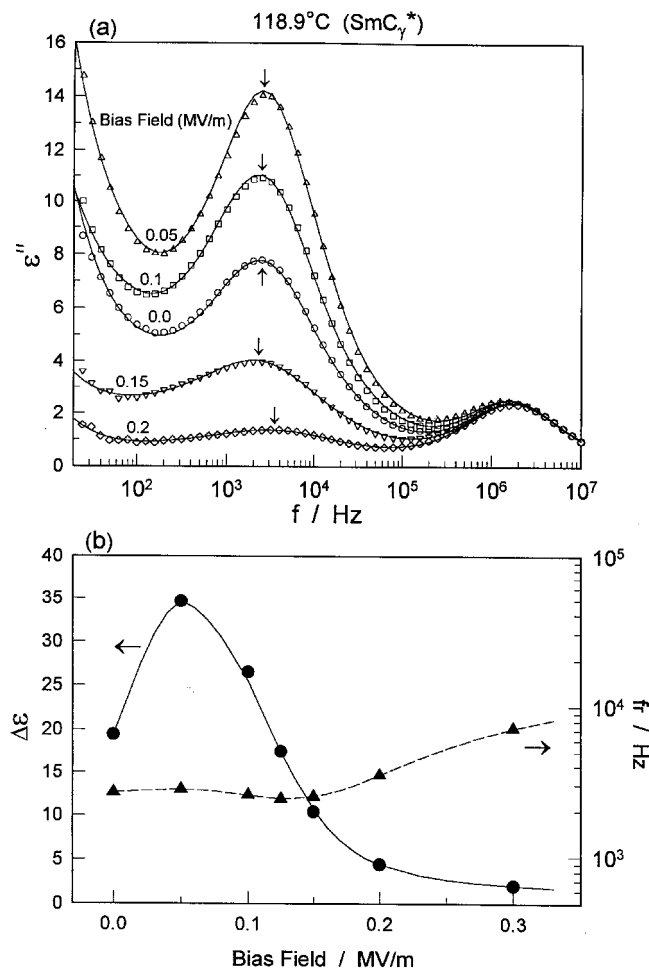


Figure 9. Bias field dependences of (a) the dielectric absorption spectrum and (b) the dielectric strength and relaxation frequency of some modes in the  $\text{SmC}_\gamma^*$  ( $118.9^\circ\text{C}$ ) phase.

is in the range of  $0.2$  to  $0.3 \text{ MV m}^{-1}$ . These two stages of increase in apparent tilt angle are associated with the field-induced unwinding process of a ferroelectric helical structure and the further transition to the ferroelectric state, respectively [7].

From the comparison of the apparent tilt angle with dielectric behaviour, we can see that some structural orderings may even become more stable at very low electric fields, while the induced apparent tilt angle is very small. The structural changes or molecular reorientational behaviour under higher electric fields are envisaged as follows, based on a proposed structural model of the  $\text{SmC}_\gamma^*$  phase [15]. In figure 10(a), a scheme representing the molecular orientations in different smectic  $\text{C}_\gamma^*$  layer, at zero field, is given. Some sequences of molecules with the same tilt direction are drawn, they are connected by pairs of molecules tilted in the opposite directions. However, the details about the spatial correlation of molecular orientations might not be so simple;

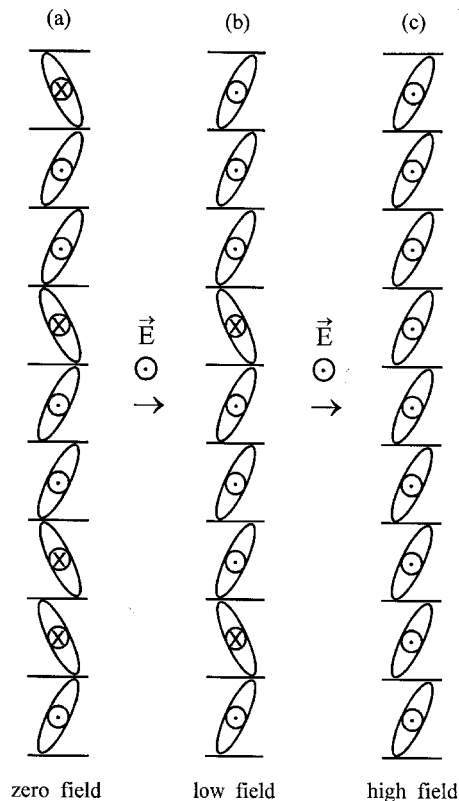


Figure 10. Schematic representation of structural models of  $\text{SmC}_\gamma^*$  under different bias fields.

some pairs of molecules with non-parallel or non-anti-tilt orientations may also be introduced from place to place. On a macroscopic scale, the apparent tilt angle of the molecules cannot be detected, due to the cancellation by the helical structure. As mentioned above, the macroscopic structural orderings could not be heavily distorted by very low bias fields. The changes in the dielectric strength are probably due only to some structural variations at the microscopic level — for example, the molecular reorientations occurring in some smectic layers, where the molecules tend to move along the smectic cones and make more preferred orientational correlation with the molecules in neighbouring layers. Consequently, some sequences of smectic layers with parallel or nearly parallel molecular orientations will be longer, as illustrated in figure 10(b), and therefore, the dielectric strength of the low-mode due to the azimuthal angle fluctuation in the parallel tilt sequences will be increased, see figure 9(b). Besides, structural changes may also be caused in some defect points, where the molecular orientations are not regular and more easily distorted by an electric bias field.

The helical structure is unwound under bias fields higher than about  $0.05 \text{ MV m}^{-1}$ . Accordingly, the strength of the low-mode is greatly decreased, (see

figure 9(b), and the apparent tilt angle increases steeply. However, this increase ceases only at a value of the apparent tilt angle much smaller than that in the fully switched state, where the tilt angle of the molecules on the smectic cone can be found. This implies that the local correlation of molecular orientations may not be changed very much during helix unwinding, different from the situation in the ferroelectric  $\text{SmC}^*$  phase. The discontinuous change in the apparent tilt angle or the appearance of a plateau on further increase of the electric field might be due to a stable feature of the ferroelectric structure in the helix-unwound state. The field range of this stable structure was found to change with temperature in  $\text{SmC}_\gamma^*$  [3, 7]. However, as shown in figure 9, no special or discontinuous changes can be seen in the dielectric property of this stable structure in the range of 0.12 to 0.2  $\text{MV m}^{-1}$ . On increasing the electric field over another critical strength of about 0.2  $\text{MV m}^{-1}$ , the apparent tilt angle will markedly increase again and reach a fully switched state or the field-induced ferroelectric state illustrated in figure 10(c). Along with this structural change, the dielectric constant changes only slightly, but the relaxation frequency increases significantly, see figure 9(b).

### 3.2.4. In the $\text{SmC}_A^*$ phase

Temperature and bias field dependences of the dielectric properties in the antiferroelectric  $\text{SmC}_A^*$  phase have been investigated on various types of AFLC compounds. However, the interpretations or assignments for some dielectric modes showing similar behaviour were not the same [11, 13]. The field-induced dielectric behaviour in the  $\text{SmC}_A^*$  phase of this sample is also different, as compared with other compounds.

In figure 11, the changes of the dielectric absorption spectrum under various bias fields and the related relaxation parameters are given. Essentially, only one absorption peak is observed near 1 MHz at zero bias field; its strength (white circles) is about 6.0. This absorption has been observed in the  $\text{SmC}_\gamma^*$  phase: it was sharpened from a dielectric strength of about 2.0 and shifted to lower frequencies in the vicinity of the  $\text{SmC}^*-\text{SmC}_\gamma^*$  phase transition, as shown in figure 5(a). From the bias field dependence in figure 11, we can see that this mode will decrease in strength and shift to higher frequencies gradually, when the bias field is higher than a critical strength. This implies that a contribution from the liquid crystal structure, with its position very close to that of an absorption peak, related to the low pass effect of the cell, may also be contained in this strong absorption. Actually, for the same compound, an absorption in the same frequency range (not discussed in detail) was also observed, where its position was far from that of the low-pass-effect mode [8].

With increase of the bias field, another absorption appears at several KHz, as marked by the arrow in figure 11(a). It grows in strength (white triangles) and gradually increases the relaxation frequency (black triangles). The growth of this mode ceases at a bias field of about 1.3  $\text{MV m}^{-1}$ ; after that, it decreases and reaches a constant value at higher bias fields.

The dielectric properties in the same frequency ranges in  $\text{SmC}_A^*$  have also been analysed for some AFLC systems. In one of the investigations, the absorptions at  $\sim$  MHz and  $\sim$  KHz were associated with the soft-mode and a mode due to the director fluctuation around the molecular short axis, respectively [11]. However, in the other cases, the corresponding two modes were considered to be caused by the so-called anti-phase and in-phase azimuthal angle fluctuations of the directors in the anti-tilted molecular pairs, respectively (see figure 8 in reference [13]). The anti-phase-fluctuation at  $\sim$  MHz can cause changes in local polarization and hence is dielectrically detectable, whereas the in-phase-fluctuation could be observed only when the anti-tilt pairs are distorted. Also, the modes related to the in-phase-fluctuation and to the fluctuation around the molecular short axis were analysed by using two types of the cell with planar and homeotropic alignments of the smectic layers, respectively [13]. These two modes appeared at different relaxation frequencies at the same temperatures, and also showed different temperature and bias field dependences.

In this work, we prefer to explain the results obtained from the homogeneously aligned molecules according to the models in reference [13]. It was found in previous studies [3, 7] that in the same temperature range in  $\text{SmC}_A^*$ , the apparent tilt angle of the molecules may experience a steep increase under electric fields of about 1.1–1.3  $\text{MV m}^{-1}$ . Before this increase, the apparent tilt angle was only induced for very small values at lower electric fields. In this range of bias field, the dielectric absorption at about 1 MHz, due to the anti-phase-fluctuation, is almost unchanged, as seen in figure 11(b), whereas the mode due to the in-phase-fluctuation is induced and increased in strength. This may result from a gradual distortion of the molecular orientations in the anti-tilt pairs. With further increase of the electric field, the apparent tilt angle increases remarkably and then reaches a saturated value; this change may correspond to the field-induced transition from the antiferroelectric to the ferroelectric state. Accordingly, the high frequency mode is suppressed and saturated at a strength of about 4.8, which may be the dielectric strength of the compound at very high frequencies,  $\epsilon_\infty$ . The mode at lower frequency also decreases in strength (white triangles), but it does not disappear completely in the induced ferroelectric state. Such behaviour under a bias field was



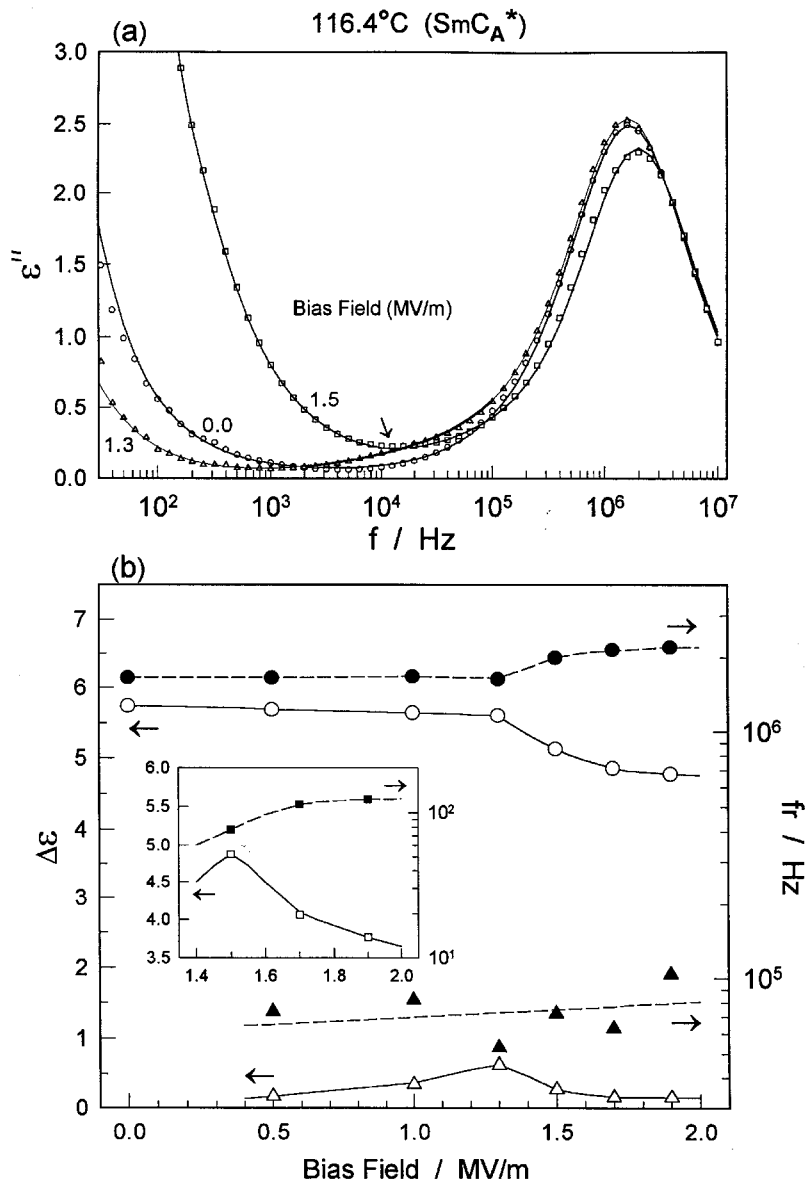


Figure 11. Bias field dependences of (a) the dielectric absorption spectrum and (b) the dielectric strength and relaxation frequency of some modes in the  $\text{SmC}_A^*$  ( $116.4^\circ\text{C}$ ) phase.

also observed on a mode in the corresponding frequency range [13]. The appearance of the mode in the ferroelectric state was thus interpreted by proposing that the in-phase-fluctuation motion is changed to a motion also of the in-phase-fluctuation type, but essentially in a parallel correlation of the molecular orientations. The induced ferroelectric state may not be quite ordered or probably has a heavily distorted helical structure. Therefore, the in-phase-fluctuation might still be detectable by dielectric means [13]. The existence of the distorted structural orderings might also be the reason why the dielectric strength ( $\sim 4.8$ ) and the relaxation frequency ( $\sim 2.0$  MHz) related to the high frequency permittivity  $\epsilon_\infty$ , cannot be consistent with the values

measured in the  $\text{SmC}^*$  phase at higher temperatures, see figure 5(a) and 11(b).

In figure 11(a), a remarkable increase of the dielectric absorption in the frequency range below 10 KHz can also be seen. The related relaxation mode has a strength (white squares in figure 11(b)) and relaxation frequency (black squares) of about 5.0 and 100 Hz, respectively. With further increase of the bias field, this mode becomes smaller and shifts towards higher frequencies. As mentioned above, the dielectric absorption in this frequency range may originate from the migration of ionic impurities. However, as also shown in figures 6–9, this absorption may always change, following the field-induced structural changes in the liquid crystal compound—for

example, helix-unwinding or the transition from the ferroelectric (or antiferroelectric) to the ferroelectric states.

#### 4. Conclusions

Temperature and bias-field dependences of the dielectric behaviour in the compound, (R)-MHPOBC, were investigated.

There are mainly two relaxation modes in the  $\text{SmC}_\alpha^*$  and  $\text{SmC}^*$  phases. One at higher frequencies behaves as the soft-mode, which shows significant slowing down in the  $\text{SmA}^*$  and  $\text{SmC}_\alpha^*$  phases. The other one begins to appear at lower frequencies in  $\text{SmC}_\alpha^*$  and grows significantly on cooling, but it shows only a small variation in the relaxation frequency. This mode, named low-mode, is considered to relate to the azimuthal angle fluctuation of the molecules in the parallel tilt sequences of the smectic layers. In the lower temperature range in  $\text{SmC}^*$ , the low-mode is reduced remarkably in strength and becomes the only mode in  $\text{SmC}_\gamma^*$ , and finally disappears in the vicinity of the  $\text{SmC}_\gamma^*-\text{SmCA}^*$  phase transition. These two modes show various bias field dependences in the different phases. According to the field-induced helix-unwinding or molecular reorientation, the low-mode was found to experience remarkable changes, especially in the  $\text{SmC}_\gamma^*$  phase.

There are two other types of relaxation mode in the antiferroelectric  $\text{SmCA}^*$  phase: the one at about 1 MHz is almost unchanged by small bias fields; the other one at 60~100 KHz only appears when a bias field is applied, and increases gradually with bias field strength. These two modes are considered to relate to the anti-phase and in-phase azimuthal angle fluctuations of the molecules in the anti-tilt pairs, respectively. They are significantly suppressed at bias fields higher than a critical

strength, where the transition from the antiferroelectric to the ferroelectric structure is induced by the bias field.

One of the authors, Jianan Hou, is grateful to the Alexander von Humboldt Foundation for a fellowship.

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