

THE DEPENDENCE ON THE HELICAL PITCH OF THE ANTIFERROELECTRIC DIELECTRIC MODES

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In an attempt to determine the physical nature of the low-frequency dielectric mode in antiferroelectric liquid crystals, we have studied the dielectric response in thick planar-oriented samples of Smectic C_A* compounds undergoing a helix inversion. If the mode is collective there ought to be a minimum in the dielectric absorption due to the mode, at the temperature at which the helical pitch diverges. Although the effect is not large, we find minima for both antiferroelectric modes at this point, indicating that both modes are related to the helical director structure. A corresponding experiment has also been performed on a binary mixture which shows a helix inversion for a certain mixing ratio. However, because the effect in this case is overshadowed by unavoidable variations in other parameters, no minimum was detected.

Keywords: antiferroelectric; Smectic C_A*; liquid crystal; helix inversion; dielectric spectroscopy

INTRODUCTION

The dielectrically active modes typical of antiferroelectric liquid crystals are still not completely understood, and it is an important task to elucidate their physical nature. The two modes are observed in planar-oriented cells and are usually distinguished by their respective critical (relaxation) frequencies f_c . The high-frequency antiferroelectric mode (in this paper

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referred to as AF_{high}) has only a weak temperature dependence of f_c , usually with a maximum somewhere within the SmC_A^* phase. This mode was first attributed to a soft mode [1, 2], but inconsistencies with this explanation have been pointed out and it has instead been explained as an anti-phase motion of molecules in adjacent layers [3].

The low-frequency antiferroelectric mode (here called AF_{low}) is still subject to much discussion. There is some evidence, like the Arrhenius behavior of f_c , for interpreting this as a *non-collective* molecular mode, and in many papers it is concluded that the mode is due to rotation of the molecules around their short axes [e.g. 1, 2, 4] which can only be the case if the sample alignment is not perfectly planar [5]. The permittivity contribution, ϵ , of the mode would then be expected to decrease on applying a DC-bias field over the sample, and a decrease in temperature (accompanied by an increase in tilt angle) should lead to an increase in ϵ . However, in [3] exactly the opposite behavior has been observed. Furthermore, the critical frequency of the short axis rotation mode seen in homeotropic orientation (here denoted f_{hom}) has often failed to coincide perfectly with the corresponding frequency of the AF_{low} mode measured in a planar sample (f_c of AF_{low} is typically two to five times higher than f_{hom}) [3-4]. These observations are difficult to explain in the frame of a non-collective mode, and therefore it seems reasonable that the AF_{low} mode could be collective in character.

In the model proposed by Buivydas *et al.* [3] the AF_{low} mode corresponds to a collective reorientation of the molecules in the same direction around the cone (in-phase motion), where the coupling to the electric field is made possible by the helical superstructure and the corresponding small shift in the local polarization directions. Because of the helix there is a small deviation from the 180° angle between the directors in adjacent layers (see figure 1). Hence, the polarizations do not cancel completely and a small net polarization appears. This mesoscopic polarization allows us to study the motion with dielectric spectroscopy.

In a material featuring a helix inversion this deviation from a perfect anti-tilt structure should diminish when we approach the inversion point, since here the pitch diverges and the helical superstructure disappears. The polarizations of neighboring layers should then really cancel, and the permittivity contribution due to the mode should tend to a minimum.

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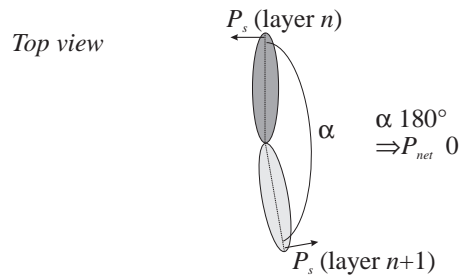


FIGURE 1. Due to the helical superstructure the molecules in adjacent layers are not at exactly 180° angle to each other. Therefore the polarizations in adjacent layers do not cancel totally and a small net mesoscopic polarization appears.

In this work we have studied the modes in two antiferroelectric liquid crystalline systems featuring helix inversions. We have investigated a pure liquid crystal compound with a temperature-induced helix inversion within the SmC_A^* -phase (EHPOCBC, *cf.* figure 2), and we have also prepared and studied a mixture system where the two pure components ((S)-EHPnCBC-12 & (S)-TFMHPnBC-11) have different helical handedness but the same sign of the spontaneous polarization P_s . At a certain mixing ratio a helix inversion is thus induced and, as the spontaneous polarizations of the two mixture components do not cancel, one might hope to see mainly the effect of the pitch change on the antiferroelectric mode in a sequence of such mixtures.

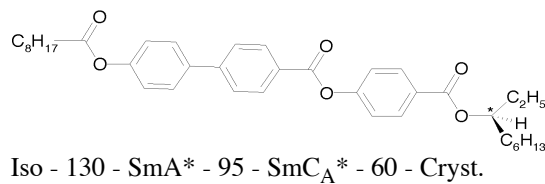


FIGURE 2. Structure and phase sequence, as observed in bulk on cooling, of EHPOCBC. Temperatures are in $^\circ\text{C}$.

As the pitch is long on either side of the divergence point, $p \rightarrow \infty$, one has to expect strong hysteretic and quenching effects from the cell surfaces in general. We would therefore have to go to unusually thick samples in order to detect the effect, if any. As such thick cells are hard to align, we would also sooner or later run into homogeneity problems.

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EXPERIMENTAL

We have performed dielectric spectroscopy investigations in the range 100 Hz to 13 MHz using the dielectric bridge HP4192A. All compounds have been studied in a wide temperature interval ($\Delta T \approx 20^\circ\text{C}$) in the SmC_A^* phase, as well as in the phases lying above this in temperature. As temperature controller we used the Linkam TMS 91 and the whole setup was controlled by an HP 9133 computer. The Cole-Cole equation [6] was fitted to the experimental data using the program ProFit.

As measurement cells we have used commercially available EHC cells with a rubbed polyimide layer giving planar alignment, and self-made shear cells for the homeotropically aligned samples. The cells were filled by capillary action in atmospheric pressure for the EHC cells and in vacuum for the shear cells. The planar samples were uniformly aligned by applying a 100 Hz, 200 V_{pp} square wave electric field while heating or cooling the sample slowly through the liquid crystalline phase transitions, or from the isotropic phase into the SmA^* phase. By applying a quick shear with high amplitude over the self-made cell a very good homeotropic alignment was obtained. These homeotropic samples were used for detection of the short axis rotation.

Measurements were performed both on heating and on cooling at a very slow rate (0.05-0.3°C/minute). At intervals of 0.1°C dielectric spectroscopy scans were performed with a measuring voltage varying between 0.1V and 1V depending on cell thickness.

As expected, because the influence of the boundaries for a given cell becomes larger the longer the helix, we had to perform our measurements in fairly thick cells to see a clear effect from the helix inversion. Varying the thickness in the range up to 25 μm did not give any conclusive results. Most further measurements were therefore made on 25 μm cells, but twice we opened EHC cells in order to insert thicker spacers (glass fiber or mylar). The cells were then glued together under pressure. In this way we constructed two cells with 50 μm and 140 μm cell gap, respectively.

RESULTS AND DISCUSSION

Behavior at a Temperature-Induced Helix Inversion

In order to experimentally verify the pitch dependence of f_c and ϵ of the AF modes, we studied the dielectric behavior of S-EHPOCBC. The helix inversion takes place 12°C below the $\text{SmA}^* \rightarrow \text{SmC}_A^*$ transition.

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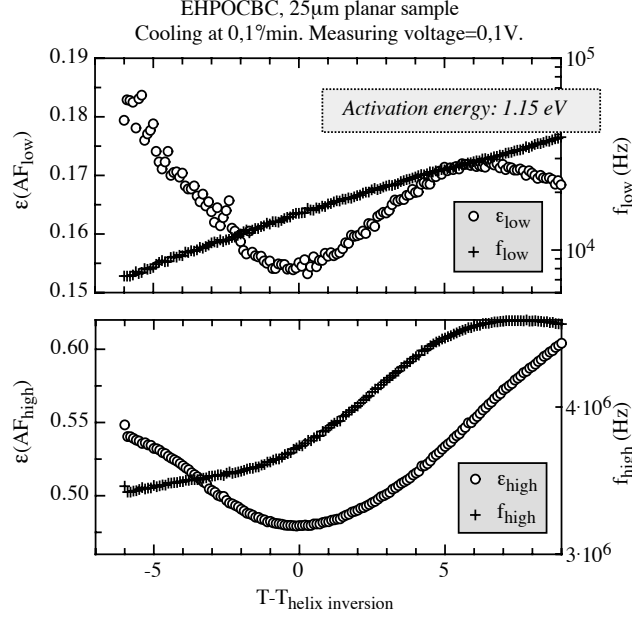


FIGURE 3. The permittivity contributions (left y-axes) and critical frequencies (right y-axes) of the low- and high-frequency AF modes in the vicinity of the helix inversion, as measured in a $25\ \mu\text{m}$ planar sample. The effect on the permittivity contributions of both modes from the pitch divergence is clearly seen.

The measurement results for a $25\ \mu\text{m}$ cell are shown in figure 3. In the vicinity of the inversion temperature a dip in ϵ of AF_{low} is apparent, whereas the critical frequency does not show any sign of being affected. The activation energy was determined by fitting an Arrhenius function to f_c as a function of temperature. The high-frequency mode exhibits a clear decrease in ϵ as well as f_c at the inversion point. In cells thinner than $25\ \mu\text{m}$ neither mode shows any sign of being affected by the helix inversion.

An interesting observation is that in runs in which a DC-bias was occasionally applied, no minimum could be seen at the temperature of the helix inversion, even in the scans performed with zero DC-bias. This indicates that the modes are related to the helical structure of the material and that, due to pinning at the cell surfaces, the relaxation time back to this structure after application of a strong electric field, is quite long.

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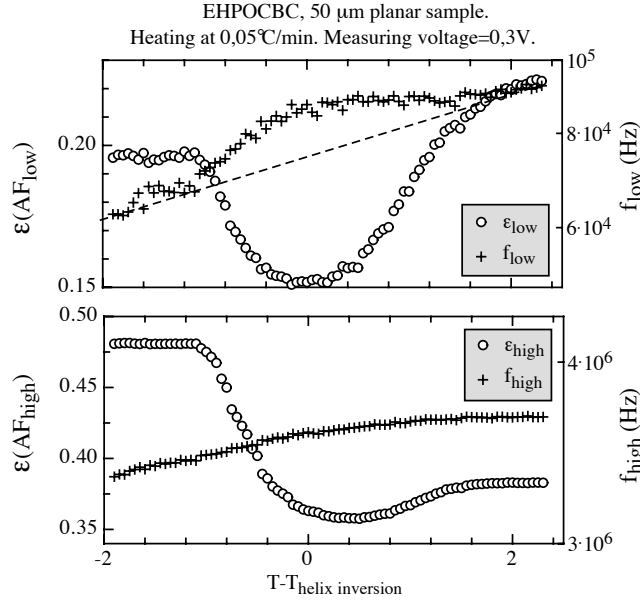


FIGURE 4. The permittivity contributions (left y-axes) and critical frequencies (right y-axes) of the low- and high-frequency AF modes in the vicinity of the helix inversion, as measured in a 50 μm planar sample. The dashed line is drawn to indicate the expected Arrhenius-like temperature dependence of the critical frequency.

To get yet clearer results we prepared a 50 μm cell with EHPOCBC, the results of which are shown in figure 4. The lowering of the permittivity contribution at the helix inversion is now confirmed. However, a surprising result is that for AF_{low} this seems to be accompanied by an *increase* in critical frequency. The expected effect, if any, would be a lowering in f_c at diverging pitch p [7]. It seems that for $p \rightarrow \infty$ even a 50 μm thick cell starts to behave as thin, scaled as d/p , such that the surfaces contribute to a small increase in the helical elasticity. AF_{high} also showed a distinct decrease in ϵ , while the effect on f_c was not as clear.

Novotná *et. al.* have reported studies on SmC^* materials featuring helix inversions [8], giving evidence that the confinement of the compound in a cell has a large effect on the helix near an inversion point. The temperature of the inversion can be much shifted, and often the helix does not reform after the divergence of the pitch. Lately, people from the same group have performed a most interesting extension to this work [9], in which dielectric spectroscopy measurements have been carried out on a helix-inverting SmC^* compound, both in a cell and on a

free-standing film. While the free-standing film measurements look like one would expect from a SmC^* phase with diverging pitch, the cell measurements are radically different, which is a very clear sign of the great influence from the cell surfaces on the behavior near a helix inversion. Hence, it is most likely that the weak effect from the helix inversion on the antiferroelectric modes found in the present work, may be an effect of the cell confinement of the material.

In order to compare the activation energy of AF_{low} with that of the molecular reorientation around the short axis, we prepared a homeotropic cell with EHPOCBC. The activation energy for the short axis rotation was in this way measured to be 1.13 eV which should be compared to the value 1.15 eV obtained for AF_{low} (*cf.* figure 3). The values are thus more or less identical; the difference is within experimental error. This supports the short axis reorientation model for AF_{low} .

Behavior in a helix-compensated mixture

A helix inversion can also be provoked by mixing two compounds in a certain ratio. As a first preliminary study we mixed (S)-EHPnCBC-12 (right-handed SmC_A^* helix) with (S)-TFMHPnBC-11 (left-handed SmC_A^* helix) in different proportions. However, a binary mixture is a much more complicated system than a single compound. For different mixing ratios not only the pitch varies, but also P_s and the tilt angle, as well as the phase transition temperatures, or even phase sequences. Furthermore, a different cell has to be prepared for each chosen ratio, which results in non-identical alignment for different measurements.

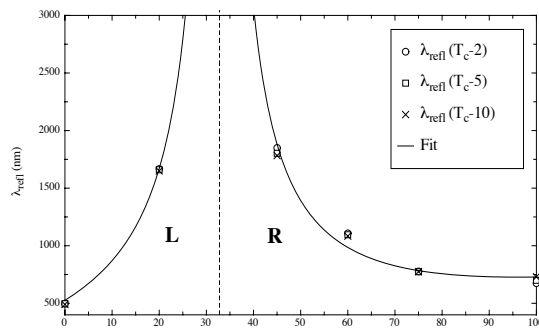


FIGURE 5. Central wavelength for selective reflection peak as a function of mixing ratio of the left- and righthanded SmC_A^* compounds (S)-TFMHPnBC-11 and (S)-EHPnCBC-12. Helix inversion takes place at a mixing ratio of 2:1.

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The pitch as a function of mixing ratio was obtained by measuring the light transmission as a function of wavelength in a spectrophotometer (figure 5). From the location of the transmission dip due to Bragg reflection the helical pitch can be calculated. By doing a simple fit (displayed as a continuous line in the figure) to the experimental results we found that the mixing ratio for a helix inversion corresponds to approximately 33% (S)-EHPhCBC-12.

The different mixtures were measured in EHC cells of $25\mu\text{m}$ thickness. The obtained data does unfortunately not give a coherent picture. Figure 6 shows a summary of our results for AF_{low} obtained from heating runs only. The values of f_c and ϵ , as obtained by fitting to experimental data, are plotted as a function of mixing ratio. Far from the point of the helix inversion a clear trend is generally seen, but in the region of interest we have obtained contradictory results from different measurements.

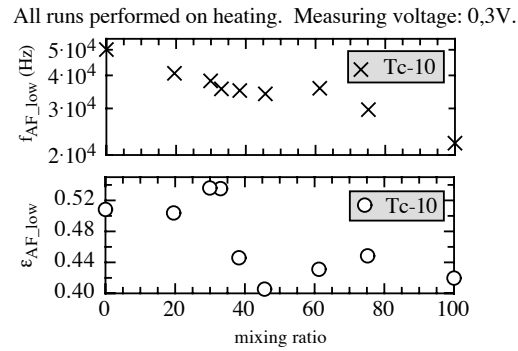


FIGURE 6. Values of critical frequency f_c and permittivity contribution ϵ of AF_{low} , taken 10°C below the upper SmC_A^* border, as a function of mixing ratio.

CONCLUSIONS

The studies on EHPOCBC give unambiguous evidence that both antiferroelectric modes are related to the helicoidal structure of the SmC_A^* phase. The permittivity contributions from both modes clearly diminish when the pitch diverges. While the observed decrease is not very dramatic, it must be pointed out that the present work is based on measurements in cells, where the diverging helix may be strongly affected by surfaces. A natural extension would therefore be to perform similar mea-

measurements on a free-standing film of the material, if such a sample can be obtained. The helix-compensated mixture is a complex system where many parameters influence the measurements, and the results obtained do not allow any clear conclusions in the matter of interest.

The decrease in the AF_{low} permittivity contribution at the helix inversion supports the *collective* model for the mode. On the other hand, the strong resemblance in critical frequency between AF_{low} and the short axis reorientation, seen in the comparison between homeotropic and planar measurements, lends support to the idea that the antiferroelectric mode is indeed identical to the *non-collective* molecular reorientation process. In summary, therefore, the question of the AF_{low} mode can still not be considered as permanently settled.

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