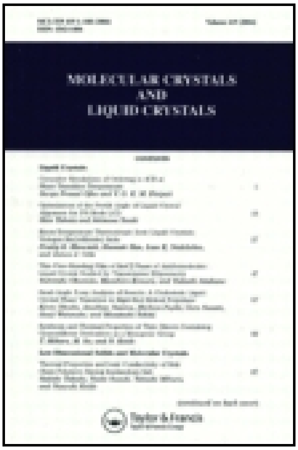

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Dielectric Dispersion in the $S^*_{C\alpha}$ Phase of an Antiferroelectric Liquid Crystal

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Dielectric Dispersion in the $S^*_{C\alpha}$ Phase of an Antiferroelectric Liquid Crystal

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We have performed dielectric measurements in the $S^*_{C\alpha}$ phase of an antiferroelectric liquid crystal. Without superimposition of a DC bias, one relaxation process is detected in this phase. This process goes continuously from the S_A soft mode to the S^*_C Goldstone mode, with linear temperature dependence of the reversed dielectric strength and of the critical frequency. The $S^*_{C\alpha}$ phase is clearly detected since a break in slopes is observed at the S_A – $S^*_{C\alpha}$ and the $S^*_{C\alpha}$-S^*_C phase transitions. This relaxation process is connected with the helicity of the $S^*_{C\alpha}$ phase since it is strongly modified under bias. At high bias, one relaxation process is also observed which behavior is similar to that of the soft mode at a S_A-S^*_C phase transition.

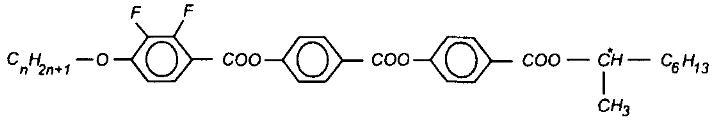
Keywords: Dielectric constant; phase transitions; relaxation process; ferroelectrics; liquid crystals

1. INTRODUCTION

The discovery of the $S^*_{C\alpha}$ phase and of the ferrielectric S^*_{CFI1}, S^*_{CFI2} phases [1] followed this of the chiral smectic C antiferroelectric S^*_{CA} phase [2, 3]. Although they have been intensively studied (DSC [1], X-ray diffraction [4, 5], electro-optical response [6], optical [7, 8] and dielectric [9, 10] measurements and Raman scattering [11]), the molecular arrangements of these phases and the relevant intermolecular interactions are not yet completely known [12, 13]. Experimental studies and development of theoretical models of these phases are still of interest. Here, we present experimental results on the dielectric characterization of the $S^*_{C\alpha}$ phase of an antiferroelectric liquid crystal. The neighboring S_A and S^*_C phases and the effect of a DC bias are also studied.

2. EXPERIMENTAL

We have studied the homologous n=11 of the following benzoate series :



This compound exhibits the $S^*_{C_A}$, S^*_{CFI} and $S^*_{C\alpha}$ phases with the following phase sequence :

$$K\ 58.8\ S^*_{CA}\ 70.5\ S^*_{CFI1}\ 71.4\ S^*_{CFI2}\ 80.5\ S^*_{C}\ 108.6\ S^*_{C\alpha}\ 109.5\ S_A\ 127.7\ I$$

The transition temperatures were determined on cooling (except for the K - $S^*_{C_A}$ phase transition) from DSC measurements and optical observations [14]. Let's notice that the $S^*_{C\alpha}$ phase exists over about 1°C. For this study, an original measuring cell has been developed. This cell consists of a planar capacitor made of two ITO coated glass plates (5Ω□, 13mm×14mm). The ITO layers have been chemically etched to obtain 5mm width strip-lines. The cell thickness was fixed to 22μm with mica spacers. After superimposition of the glass plates, the active part sizes are 5mm×5mm. In this configuration, the sample on the plates sides, which is not correctly orientated, is not taken into account in the measurement. The sample is introduced by capillarity in the S_A phase or in the isotropic phase. A planar orientation of the sample is obtained with PVA coating and rubbing. This orientation is checked with a polarizing microscope. The electrical contact on the ITO layers is made with coaxial connectors (SMA standard). The temperature of the sample is stabilized much better than 0.1°C using a temperature controller (Oxford Instrument ITC601 with a platinum sensor) and anticalorific filters. Dielectric measurements were performed in the frequency range 20Hz - 1MHz with HP4284A impedance analyzer. The real and imaginary parts of the complex permittivity are calculated from the measured capacitance C_m and conductance G_m :

$$\varepsilon' = \frac{C_m}{C_0} \quad (1) \qquad\qquad \varepsilon'' = \frac{G_m}{2\pi F C_0} \quad (2)$$

where F is the frequency and C_0 is the empty cell capacitance measured before cell filling. The measuring AC voltage was fixed to $0.1V_{rms}$. A DC bias up to 40V can be superimposed to the AC voltage. The experimental set-up is completely controlled via a PC computer equipped with HPVEE software.

3. RESULTS AND DISCUSSION

Measurements without DC bias

We have performed dielectric measurements in the S_A, $S^*_{C\alpha}$ and S^*_C phases by cooling and by heating with a temperature step of 0.1°C. For these phases, similar results are obtained on cooling and on heating. For this reason, we will present only experimental data on cooling. Dielectric spectra in the different phases are given in figure 1. In a first approximation, the frequency dependence of ε' and ε'' shows the existence of only one relaxation process in these phases.

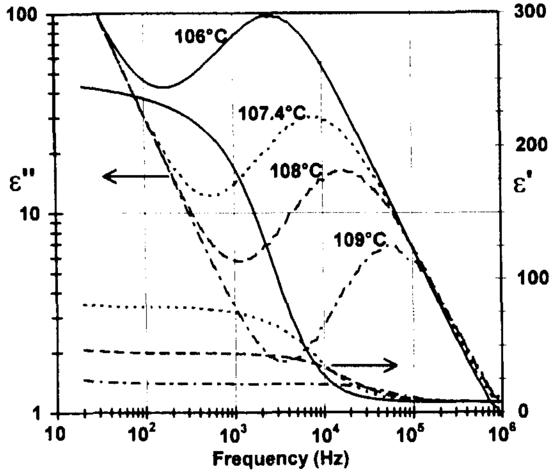


Figure 1 : Dielectric spectra in the different phases without DC bias : S_A (109°C), $S^*_{C\alpha}$ (108°C), $S^*_{C\alpha}$ (107.4°C), S^*_C (106°C).

To analyze the results, the dielectric spectra were fitted with the following formula [15] using Mathcad software :

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + j\left(\dfrac{F}{F_C}\right)^{1-\alpha}} - j\frac{\sigma}{2\pi F\varepsilon_0} \qquad (3)$$

where ε_∞ is the permittivity at a high frequency, $\Delta\varepsilon$, F_C and α are respectively the dielectric strength, the critical frequency and the distribution factor of the relaxation process, σ and ε_0 are the conductivity and the vacuum permittivity. Figure 2 shows the temperature evolutions of $\Delta\varepsilon$, $1/\Delta\varepsilon$ and F_C in the different phases. In this temperature range, the distribution factor is lower than 0.15 which is in agreement with dielectric spectra dominated by one relaxation process. In the S_A and S_C^* phases, we find again the dielectric behaviors connected respectively with the classical soft mode and Goldstone mode [16, 17]. In the S_A phase, at 110°C,

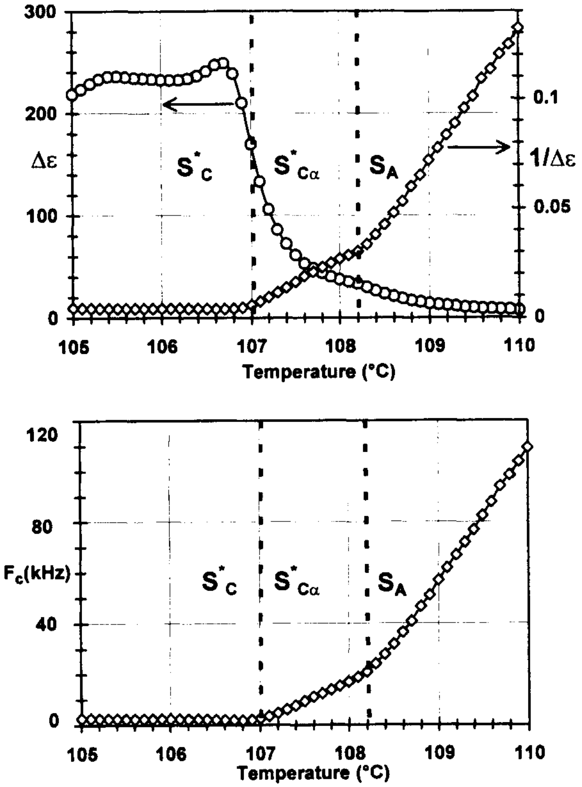


Figure 2 : Temperature evolution of Δε, 1/Δε and F_c in the different phases without DC bias.

the dielectric strength and the critical frequency are respectively 7.5 (1/Δε ≈ 0.13) and 110 kHz. The dielectric strength increases up to 30 at the S_A-$S_{C\alpha}^*$ phase transition whereas the critical frequency decreases up to 20 kHz. The reversed dielectric strength and the critical frequency linearly depend on temperature with slopes of respectively 0.05/°C and 50 kHz/°C. In the S_C^* phase, the relaxation process presents a high dielectric strength ($\Delta\varepsilon \geq 200$) and a relatively low critical frequency ($F_C \approx 2$kHz), which slightly depend on temperature. The $S_{C\alpha}^*$ phase is clearly detected with dielectric measurements over a temperature range about 1.2°C in agreement with that previously mentioned and detected from DSC measurements and optical observations [14]. Contrary to other results [9, 18], no discontinuity of the dielectric strength and of the critical frequency are observed at the S_A-$S_{C\alpha}^*$ and $S_{C\alpha}^*$-S_C^* phase transitions. The process observed without bias goes continuously from the S_A soft mode to the S_C^* Goldstone mode. In the $S_{C\alpha}^*$ phase, we obtain linear temperature dependencies of the reversed dielectric strength and of the critical frequency. The slopes are different of those observed in the S_A phase : 0.02/°C for $1/\Delta\varepsilon$ and 15kHz/°C for F_C. These results are similar to those obtained for the mode labeled RP2 in an other compound [19] for which a polydispersive behavior is observed in the $S_{C\alpha}^*$ phase.

Measurements with DC bias

To have a better understanding of the origin of the relaxation process observed in the $S_{C\alpha}^*$ phase, we have studied the effect of a DC bias on dielectric properties at different temperatures. In figure 3, as an example, we give the dielectric spectra in the $S_{C\alpha}^*$ phase at 105.4°C and for a DC bias varying from 0V to 40V. Up to 11V (0.5V/µm electric field), the dielectric spectra are slightly modified. At higher bias values, the relaxation process shifts at high frequency and its dielectric strength is strongly lowered. This behavior is confirmed in figure 4 where the bias dependence of these parameters in the $S_{C\alpha}^*$ and S_A phases is reported. We can notice the weak variations in the S_A phase. In a compound with similar chemical formula, only slight effect of the bias on the mode contribution

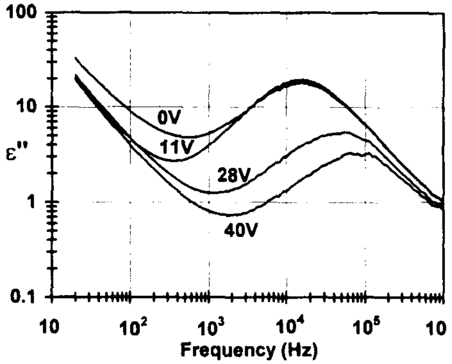


Figure 3 : DC bias effect in the $S^*_{C\alpha}$ phase (105.4°C)

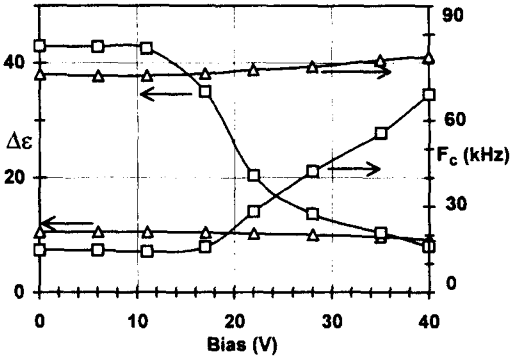


Figure 4 : Influence of DC bias on the dielectric strength and the critical frequency in the $S^*_{C\alpha}$ phase (□, 105.4°C) and in the S_A phase (Δ, 107°C).

in the $S^*_{C\alpha}$ phase was observed [20]. Our results show that the relaxation process observed in the $S^*_{C\alpha}$ phase without bias is connected with the helicity of this phase (Goldstone mode). The temperature dependence of Δε and F_C without and with bias in the $S^*_{C\alpha}$ and S_A phases is reported in figures 5 and 6. Without DC bias, we find again the previously described behavior (figure 2). Under DC bias, the dielectric strength and the critical frequency are respectively maximum and minimum at the transition $S_A - S^*_{C\alpha}$ phase transition. Linear temperature dependencies of the reversed dielectric strength and of the critical frequency are also observed from one part to the other of this transition. This behavior [17, 21] is characteristic of the soft mode at the $S_A - S^*_C$ phase

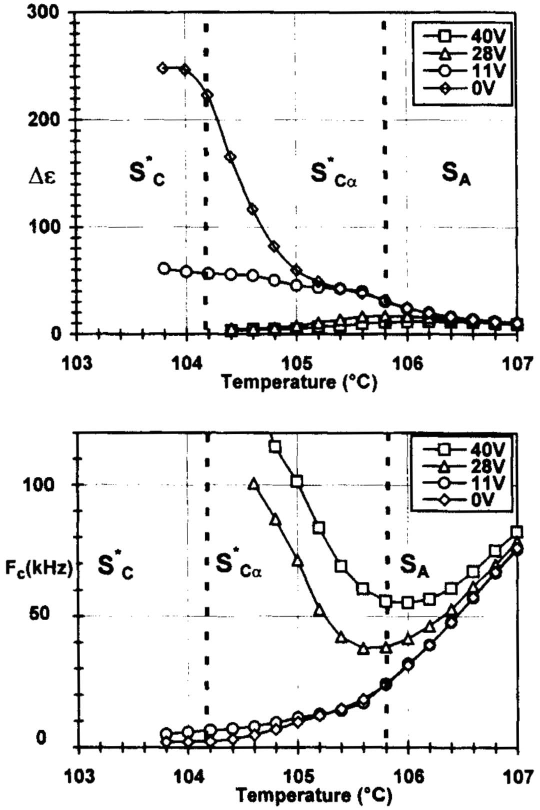


Figure 5 : Temperature dependencies of Δε and Fc without and with DC bias.

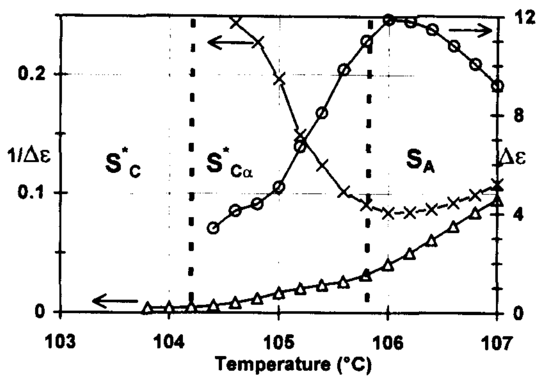


Figure 6 : Temperature dependencies of Δε with a DC bias of 40V (o), and of 1/Δε without (Δ) and with a DC bias of 40V (X) in the S*$_{C\alpha}$ phase and in the S$_A$ phase.

transition, usually evidenced with measurements under bias. The relaxation process under bias could be attributed to the soft mode at the S_A-$S^*_{C\alpha}$ phase transition. At the vicinity of the S_A-$S^*_{C\alpha}$ phase transition, the dielectric strength and the critical frequency of this process (Δε ≈ 10, Fc ≈ 60 kHz at bias = 40V) are of the same order of magnitude than that observed without bias (Δε ≈ 30, Fc ≈ 20 kHz). It is well known that the soft mode is modified by the application of a bias (Δε decrease, Fc increase) [21]. For this reason, the process observed without bias near the S_A-$S^*_{C\alpha}$ phase transition could be attributed to the soft mode. Such an interpretation of a soft mode at high temperatures and a Goldstone mode at low temperatures is in agreement with models prediction of an antiferroelectric behavior near the S_A-$S^*_{C\alpha}$ phase transition and a ferrielectric behavior near the $S^*_{C\alpha}$-S^*_C phase transition [12, 13]. The low dielectric strength and the high critical frequency of the Goldstone

mode in the $S^*_{C\alpha}$ phase is connected with the very short helical pitch in this phase [8].

4. CONCLUSION

We have performed dielectric measurements in the $S^*_{C\alpha}$ phase with and without DC bias. Two different dielectric behaviors are brought out in this phase depending on a DC bias being superimposed to the measuring electric field or not. Without DC bias, one relaxation process connected with the helicity of the $S^*_{C\alpha}$ phase is observed. This process goes continuously from the S_A soft mode to the S^*_C Goldstone mode. The relaxation process observed under bias has the same behavior as that of the soft mode at a S_A-S^*_C phase transition. Other dielectric measurements are in progress on other homologous of this series with larger $S^*_{C\alpha}$ temperature ranges (for example, ΔT=5.2°C for n=9) to complete these data. This work is complementary of other studies on the $S^*_{C\alpha}$ phase and contribute to a better understanding of the structure of this phase.

Acknowledgments

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