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DIELECTRIC RELAXATION PROCESSES IN A MODEL FERROELECTRIC LIQUID CRYSTAL

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Abstract: The soft mode, Goldstone mode and a new ferroelectric mode have been detected in the Sm C* phase of a fluorinated compound. The dielectric increment of the Goldstone mode found in the Sm G* phase is by about one order of magnitude lower in comparison with that found in the Sm C* phase. In addition to collective processes, in both chiral phases a biased reorientation of molecules around their long axes contributes to the dielectric increment.

Keywords: dielectric relaxatin, ferroelectric

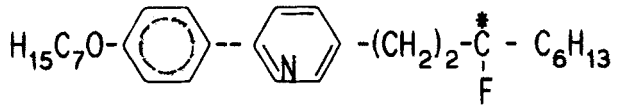
INTRODUCTION

Up to now many ferroelectric liquid crystal (FLC) materials have been studied by the dielectric spectroscopy[1-14]. The substances studied are in some cases mixtures[8] for which the intensities of relaxation processes coming from the chiral molecules are distinctly reduced. On the other hand some single component systems[4,10,12] show a deficient soft mode due to a weak coupling between the chiral centers and the permanent dipole moments. In such cases it is difficult to discuss the results in terms of the theories[15-17] predicting the dielectric spectrum for the Sm A* and Sm C* phases. Dielectric measurements on highly ordered smectic phases are also very rare[12,18]. Recently, new substances have been synthetized [18] showing both the strong dipole moments attached to the chiral centers and highly ordered phases as well. As it is known from the recent studies on some FLC- mixtures[13,22,23] and on single component FLCs [10,19b] as well, in the Sm C* phase - in addition to the soft mode (SM) and Goldstone mode (GM) - a new relaxation process shows up, which is called in this paper a new ferroelectric mode (NFM). Recently, we have performed di-

electric studies on the highly polar fluorinated compound in the case of which this mode is exceptionally strong.

EXPERIMENTAL

In this paper the newest results concerning dielectric properties of the fluorinated compound,



(Cr. - 67°C- Sm G*- 71°C - Sm C*- 80°C - Sm A* - 87°C - Is.) are presented. The substance studied shows two chiral and tilted smectic phases, namely, the Sm C* and Sm G*[12] ones. The substance has also been investigated dielectrically quite recently [11,18b] , but this study reveals some additional effects which seem to be important in the physics of liquid crystals. By using the HP impedance analyzer[8,10] one was able to perform precise measurements of the perpendicular component of the complex electric permittivity ($\varepsilon^*_\perp = \varepsilon'_\perp - i\,\varepsilon''_\perp$) in the frequency range between 5 Hz and 13 MHz. The capacitor consited of two gold-coated electrodes separated by 10 μm-thick spacers. The cell was callibrated using toluene as a reference.

The sample being in the isotropic phase filled up the capillary gap between the electrodes kept under vacuum in the temperature controlled sample-holder. A planar alignment has been obtained by slow cooling of the sample (-4K/h) in the magnetic field of 1.2 T on going from the isotropic phase to the Sm A* and then to the Sm C* phase. In the Sm C* phase the dielectric measurements were performed without the magnetic field and an A.C. electric field was used to recover [22b] the Goldstone mode suppressed by the alignning magnetic field or by the bias field. The measuring electric field was chosen to be 0.1 V_{pp} so as to ensure the linearity between the polarization and the oscillating field. Temperature was controlled by means of an oil temperature controller with some extra thermal isolation. In such circumstances the relative temperature was measured with the accuracy of ± 0.02K. The measurements have been repeated 3 times to find the best experimental conditions and the reproduction of the data was quite good. More than 10 points per decade were taken to improve the resolution and data processing. The bias voltages up to 35 V have successfully been used in the Sm C* phase but they were insufficient to suppress the Goldstone mode in the Sm G* phase using 10μm cells.

RESULTS AND DISCUSSION

Sm A^* and Sm C^* phases

Fig. 1 presents the dielectric spectrum obtained in the Sm C^* phase of the fluorinated substance. Such kind of a spectrum is exhibited up to 4 K below the Sm A^* - Sm C^* transition. A sum of four Cole-Cole functions was used to describe the $\varepsilon_\perp^*$ component:

$$\varepsilon_\perp^* = \varepsilon_{\perp\infty} + \sum_{j=1}^{4} \frac{\Delta\varepsilon_{\perp j}}{1 + (i\omega\tau_j)^{1-\alpha_j}} \qquad (1)$$

where $\Delta\varepsilon_{\perp j} = \varepsilon_{\perp 0 j} - \varepsilon_{\perp\infty j}$ are the respective dielectric increments for the following relaxation processes: 1) the molecular mode (MM), 2) the soft mode (SM), 3) the new ferroelectric mode (NFM), and 4) the Goldstone mode (GM). $\varepsilon_{\perp\infty}$ is the high frequency limit of the electric permittivity connected with the electronic and atomic polarization. τ_j and α_j are the relaxation times and the distribution parameters, respectively.

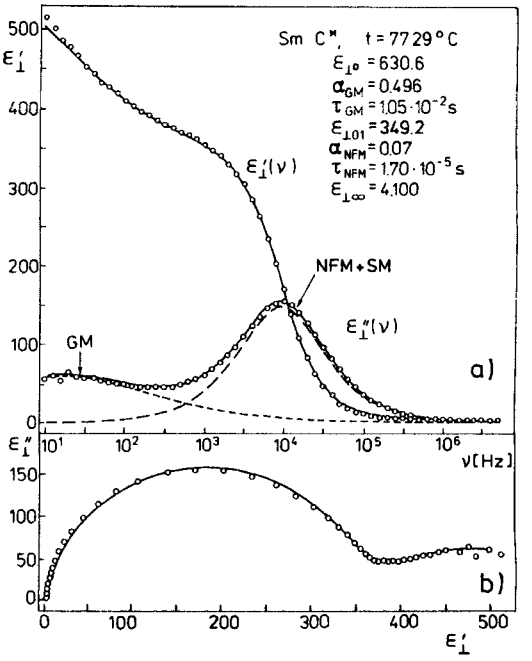


FIGURE 1 a) Goldstone mode and soft mode dielectric spectrum in the Sm C^* phase of the substance studied. b) Cole-Cole representation of the dielectric spectrum (no bias field was applied). Open circles (o) denote experimental points. Solid lines are model fits of eq. (1) to the experimental points. Dashed lines denote the absorption curves obtained by the fitting. The scale is the same for both $\varepsilon'_\perp$ and $\varepsilon''_\perp$.

As is seen in Fig.1 a) and b) there is an overlapping of the SM, NFM and GM, however, at this temperature the latter shows up in the Hz region

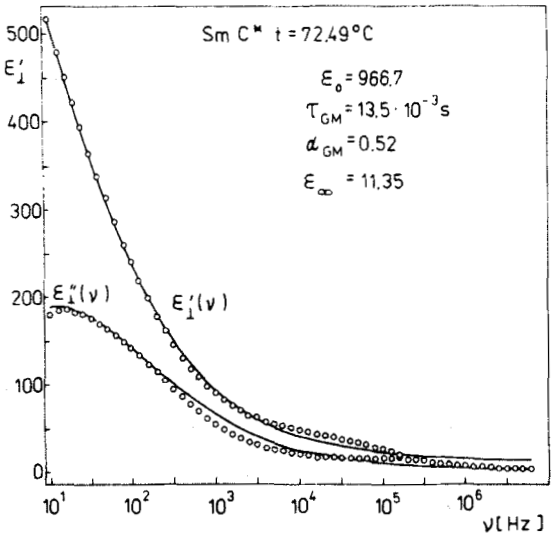


FIGURE 2 Goldstone mode dielectric spectrum obtained in the low temperature range of the Sm C* phase (V_B = 0.0).

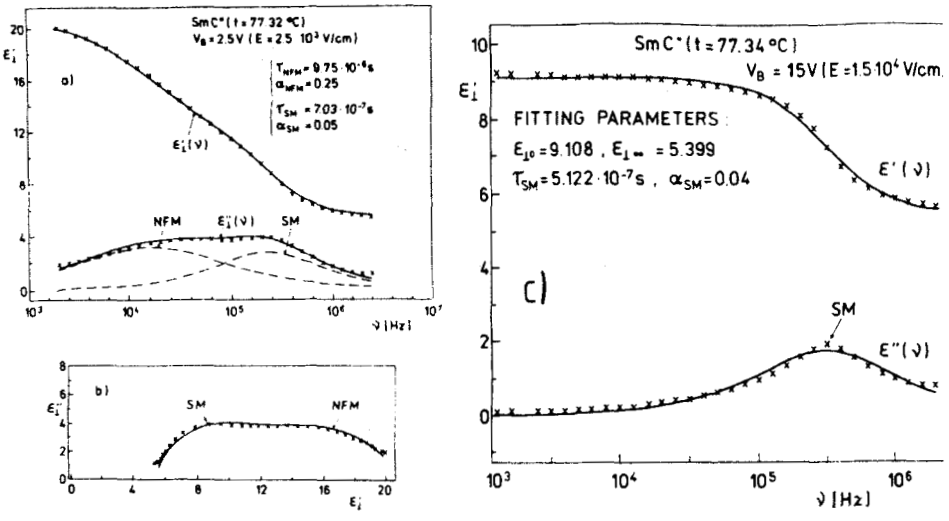


FIGURE 3 a) Soft mode and a new ferroelectric mode after suppressing the GM by a bias voltage of 2.5 V. b) Cole-Cole representation of SM and NFM. c) Soft mode dielectric spectrum after suppressing NFM. Crosses (x) are experimental values of $\varepsilon'_\perp$ and $\varepsilon''_\perp$. Solid lines and dashed lines are curve fits of eq. (1) by considering two terms.

as a separate broade peak ($\alpha_{GM} = 0.496$). This part of the spectrum agrees quite well with the data presented recently by Vallerien et al.[11]. Thus we deal here with rather complex dielectric spectrum in spite of the fact that the substance studied is a single component system.

The highest peak in ε'' showing up at 10 kHz seems to be a new ferroelectric mode (NFM). At the zero bias field SM is completely covered by NFM. In Fig. 3a one can see them resolved under a bias voltage of 2.5 V. One should add that at higher temperatures, i.e. closer to the Sm C*-Sm A* transition, the SM is completely covered by the GM as it was found before for the ZLI-3654 mixture[8,13] and for other systems.

In the lower temperature range of the Sm C* phase the GM shows up in the Hz region (Fig. 2) and its dielectric increment reaches almost a value of 1000. By using bias fields one can easily suppress the GM in the Sm C* phase. However, the 10 kHz-frequency component called in this paper NFM strongly overlapps to the soft mode (Fig. 1b, 3a and 3b). One should add the following: 1) the non-identified mode, reported in[13,19] , has the same physical nature as NFM and 2) the NFM is connected with the formation of a special kind of modulated structure (ferroelectric domains) which are being formed due to the tendency of the macroscopic spontaneous polarization of smectic layers to compensate each other. Thus we shall call NFM as "domain mode"[22] as well.

The doublet seen in Fig. 3a) was acquired at 10 temperatures inside the Sm C* phase. It was found that the "critical" field needed to suppress the GM is exponentially temperature dependent[20]. In Fig. 3c) one can see pure soft mode spectrum after suppressing the GM completely. In the Sm C* phase a D.C. electric field of $1.5 \cdot 10^4$ V/cm was sufficient to suppress both the GM and NFM. The dielectric increments of the SM obtained in the pretransition region are seen in Fig. 4. In the "paraelectric" Sm A* and in the ferroelectric Sm C* phase the $\Delta\varepsilon_{SM}$ (as well as ν_S) obey a Curie-Weiss like law[15,16]:

$$\Delta\varepsilon_{SM}^{-1} = a(T - T_c) + b \qquad (2)$$

with $T_c = 80^{\circ}C$ which coincides with the transition temperature. Most probably one has to do here with the second order phase transition. Fig.4b presents the ν_S critical frequency versus T. As one can notice the values of ν_S are rather high in comparison with those found for other substances[1-9]. However, the values reported in this paper were obtained at 15 kV/cm

bias field. One should add that the slope ratio predicted by the theories[15,16] is found to be -2. Whereas the values calculated from Fig. 4 can be between -0.4 and -0.6 but such values are typical for ferroelectric liquid crystals[13,14].

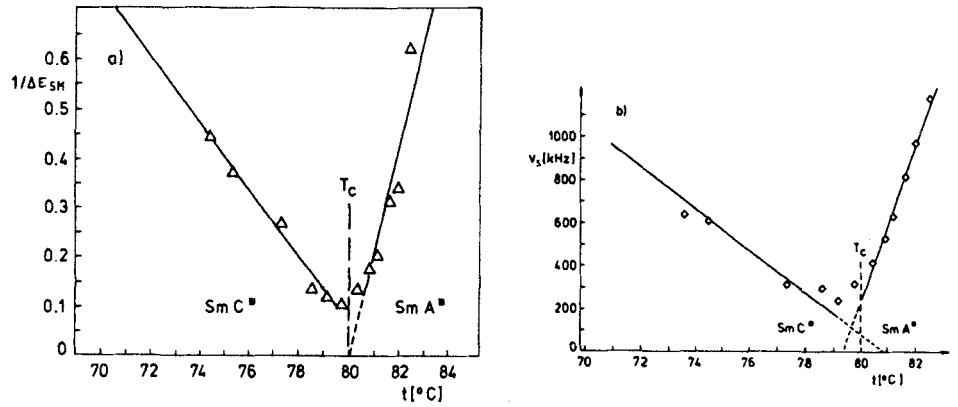


FIGURE 4 Curie-Weiss plot for the SM dielectric increment (a) and SM critical frequency (b) in the vicinity of the Sm C*-Sm A* transition. (V_B = 15 V).

This means that the extended mean-field approximation describes the dielectric properties even in the pretransition region only qualitatively.

The fluorinated substance seems to be a model compound for dielectric investigations of liquid crystals. Both the soft mode and Goldstone mode exhibit very high dielectric increments leading to well defined dielectric spectra even in the Sm A* phase where a very strong soft mode relaxation is present. Additionally, SM and NFM show up nearly in the whole temperature range of the Sm C* phase.

Results for the Sm G* phase

Fig. 5 shows the dielectric spectrum obtained in the Sm G* phase which seems to be a ferroelectric one with much weaker dielectric increment (by about factor 10) of the GM. The peak showing up at 10 kHz can be NFM, however, its bias field dependence is weaker than in the Sm C* phase. Such spectra have been taken at two temperatures below the Sm C*-Sm G* transition. In the Sm G* phase the spontaneous polarization vector splits up into 6 components which are arranged on the hexagonal lattice due to the long range in-plane correlations[24]. Additionally, the interlayer correlations of AAA type lead to suppressing of the helix. The same effect was found for the Sm J* phase of 8OSI[12], in which case the intensity of the dielectric spectrum is drastically reduced.

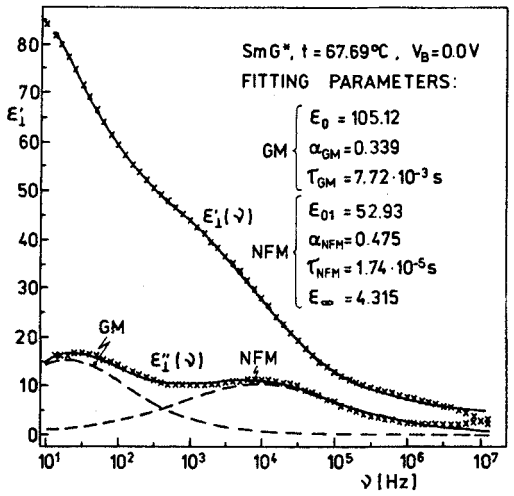


FIGURE 5 Goldstone mode and NFM spectrum in the Sm G* phase.

Molecular dynamics

Highly ordered smectic phases (Sm J, Sm G , Sm K and Sm H) differ from crystalline solids in molecular dynamics. Namely, the molecules in these smectics undergo rapid reorientational motion around their long molecular axes with the correlation time of 10^{-10} - 10^{-11}s [25]. Such reorientational motion gives contribution to the dielectric increment. In the case of the fluorinated compound there is a pronounced difference between the extrapolated value of ε_∞ and the typical value of $\varepsilon_\infty \approx 3.0$ for liquid crystals. In all smectic phases studied here there is a difference of about 1.2 between these two values. This contribution to the dielectric increment originates from the fast and biased molecular reorientations around the long axes. However, in the highly ordered Sm G* phase and in the low temperature range of the Sm C* phase a dispersion process starts above 1 MHz. Our data have been processed (including the highly ordered Sm G* phase) and a new paper is in preparation [20].

CONCLUSIONS

1.The dielectric spectrum of the Sm C^* phase of the fluorinated compound consists of four main contributions: GM, NFM, SM and MM. Two of them (GM and NFM) can be suppressed by applying a D.C. bias field.

2. Up to 4^o below the Sm A^*-Sm C^* transition temperature the GM overlapps to NFM and SM as well. In the low temperature range of the Sm C^* phase the GM shows up in the Hz region giving a broad dielectric spectrum with the dielectric increment of the order of 10^3.

3. In the Sm G^* phase the GM has lower dielectric increment (by factor 10) due to the in-plane two-dimensional order and inter-layer correlations. The 10 kHz-process (NFM) observed in the Sm G^* phase seems to be a domain mode.

4. In the vicinity of the Sm A^*- Sm C^* transition its parameters fulfill the Curie-Weiss law. The slope ratios, calculated from the temperature dependences of $\Delta\varepsilon_S^{-1}$ and ν_S as well, can be between -0.4 to -0.6 which is in discrepancy with the mean-field theory.

5. The ε_∞ values found for the Sm C^* and Sm G^* phases show that there is a high frequency relaxation process connected with a biased reorientation of chiral molecules around their long axes.

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