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Molecular and collective modes in ferroelectric liquid crystals studied by dielectric spectroscopy

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The complex dielectric permittivity has been measured for a ferroelectric liquid crystal in the range 10^2 – 10^9 Hz. Six different relaxations have been obtained and characterized: soft mode (SmA^* and SmC^* phases), Goldstone mode (SmC^* phase), rotation around molecular long axis, rotation around molecular short axis, ferroelectric domain mode (SmC^* phase) and an internal motion associated with a polar group. Strengths and frequencies of these modes have been obtained for the different phases for different bias fields. Using these results together with spontaneous polarization and molecular tilt measurements we have also obtained the rotational viscosities associated with the soft mode and the Goldstone mode. We explain the results in the light of the so-called Landau extended model, concluding that the biquadratic coupling between polarization and tilt is quite important with regard to the bilinear coupling. This fact has been used to explain the noticeable increase of the activation energy of the frequency of the mode related to the rotation around the molecular long axis at the SmA^* – SmC^* phase transition.

1. Introduction

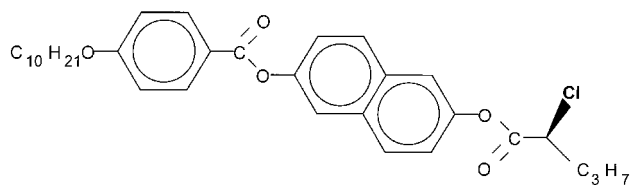
Ever since the existence of ferroelectricity in chiral smectic C^* (SmC^*) compounds was predicted by Meyer *et al.* [1], these materials have attracted great interest. The paraferroelectric SmA^* – SmC^* phase transition has been successfully described by means of two two-component order parameters, describing the director of the system and the in-plane polarization [2]. Then, there are two director modes: one is related to amplitude fluctuations and the other to azimuthal fluctuations of the director around the layer normal. They are called the soft mode and Goldstone mode, respectively. Due to the coupling with the spontaneous polarization, both are dielectrically active, giving relaxations in the low frequency regime (under MHz). Some years ago a free energy expansion with eleven terms was introduced to account for the observed temperature dependence of some of the measured properties for these materials: the ratio polarization/tilt, the helical pitch, the dielectric strength of the Goldstone mode and soft mode, etc. [3–6]. Also a theoretical calculation of the complex dielectric permittivity, based on the same generalized

Landau expansion, was presented. The main difference between this approach and earlier theories is the presence of a non-chiral biquadratic coupling between the two order parameters. In 1988 Zeks *et al.* [7] proposed a microscopic model in which the tilt causes a quadrupolar ordering of transverse molecular axes, showing that it is related to the biquadratic coupling. This microscopic model is not enough to describe all the observed temperature dependences of the spontaneous polarization, and the same authors and others have proposed an extension of this simple microscopic model [8, 9]. In any case, the essential point of the microscopic models is that the appearance of the spontaneous polarization in the SmC^* phase is related to the hindered rotation of the molecules around their long axes. The single particle potential consists of a chiral term (responsible for the polar ordering) and a non-chiral term (responsible for the quadrupolar ordering) and both are due to the molecular tilt. The point is that the frequency of the relaxation related to the rotation around the molecular long axis, as detected by dielectric spectroscopy, in general, does not show the change in its activation energy at the SmA^* – SmC^* phase transition, that one would expect from a significant change in the single particle potential. Except for temperatures very near the transition point,

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the non-chiral term is expected to be more important than the chiral term.

In the work presented here, we obtained the values of some of the coefficients in the free energy expansion from measurements of the complex dielectric permittivity, $\epsilon(\omega)$, the spontaneous polarization, P_S , and the tilt angle, θ . In particular, we deduced the β parameter. It measures the quite large relative importance of the biquadratic coupling with respect to the bilinear coupling. On the other hand, we obtained a noticeable change in the activation energy of the rotation around the molecular long axis, a fact that seems to be in accordance with the importance of the biquadratic coupling. The above mentioned study has been performed using the ferroelectric liquid crystal: 6-(2*S*-2-chloro-3-methylbutanoyloxy)-2-naphthyl 4-decyloxybenzoate which exhibits the phase sequence I-111.5°C-N*-103.5°C-SmA*-86.9°C-SmC*-60°C-Cr. The chemistry of this material together with results from calorimetric measurements have been published previously [10].



2. Experimental

Complex dielectric permittivity has been measured with two different impedance analysers, the HP4191A for the 10^6 – 10^9 Hz range and the HP4192A for the 10^2 – 10^6 Hz range. The former measures the impedance of the sample from the reflection coefficient at the end of the 50 Ohm coaxial transmission line; with this set-up, high conductivity electrodes must be used. In order to guarantee the same alignment conditions over the whole frequency range, the same cell must be used with both measuring systems. Thus, the cell consists of two gold plated brass electrodes (diameter 5 mm) separated by 50 μ m thick silica spacers, making a plane capacitor located at the end of the line. The alignment, although not perfect, was almost planar. This was checked by comparing the low frequency measurements with the results using commercially available cells with transparent ITO electrodes coated with polyimide. The spontaneous polarization was measured using the triangular wave method. The measurements were performed with both types of cells, and gave similar results. The apparent tilt angle of the molecules from the normal to the smectic layers was measured using a square wave.

3. Results

Figure 1 shows the dielectric permittivity at 125 Hz for zero (dots) and 0.4 V μ m⁻¹ (open circles) bias fields. Without a bias field, a sharp increase at the SmA*–SmC* transition, due to the helical structure, is observed. When the bias is on, this contribution is quenched and only a little cusp due to the soft mode remains. Figure 2 (open circles) shows the spontaneous polarization, P_S , versus temperature. The frequency of the triangular wave was 50 Hz and the maximum field value 3 V μ m⁻¹. The continuous line is the fit to the power law:

$$P_S(T) = P_0(T_h - T)^\delta \quad (1)$$

with $P_0 = 18.92$ nC cm⁻², $\delta = 0.5$ and $T_h = 86^\circ\text{C}$, in perfect agreement with the so-called mean field model. The

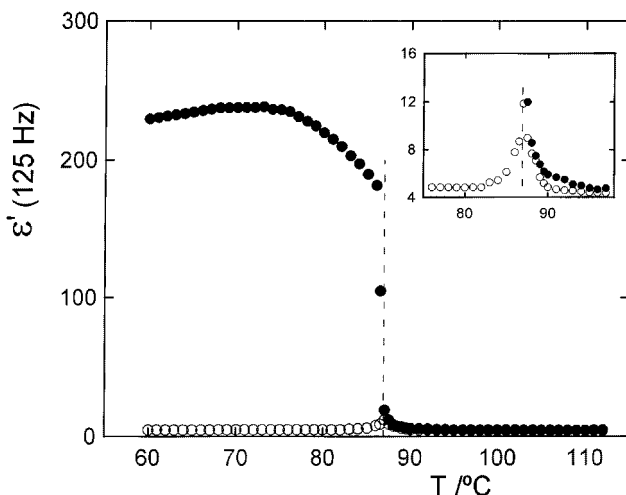


Figure 1. Real part of the dielectric permittivity at 125 Hz versus temperature: (●) bias field 0 V μ m⁻¹; (○) bias field 0.4 V μ m⁻¹.

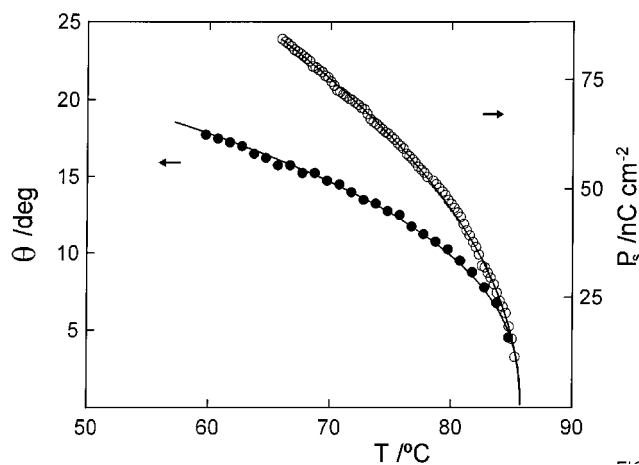


Figure 2. (●) Molecular tilt angle versus temperature; (○) spontaneous polarization versus temperature; continuous lines: fittings to equations (1) and (2).

apparent tilt angle of the molecules from the normal to the smectics layers, θ , was measured using a square wave of $\pm 3 \text{ V } \mu\text{m}^{-1}$. The whole temperature range could be fitted to the power law:

$$\theta(T) = \theta_0(T_h - T)^\delta \quad (2)$$

with $\theta_0 = 4.9^\circ$, $\delta = 0.39$ and $T_h = 86^\circ\text{C}$ (dots in figure 2). In both equations, T_h represents the transition temperature of the homogeneous sample (unwound). Although it should be different from the ‘true’ transition temperature, T_C , corresponding to the undisturbed helicoidal sample, they are practically equal [2, 4].

Now we will present the dielectric behaviour. When performing a frequency scan, dielectric spectroscopy is able to distinguish among possible molecular motions whenever they can be coupled with the electric field, and to separate their contributions to the dielectric permittivity, because of their different characteristic frequencies and, in general, important dipole moments. With this aim, the complex permittivity was measured between 10^2 and 10^9 Hz for all phases. The measurements were performed under two different bias field values, 0 and $0.4 \text{ V } \mu\text{m}^{-1}$. The measurements show that different separated relaxations with different strength, frequency and temperature behaviour are present from the isotropic to the SmC^* .

Dielectric data for liquid crystals are in general well described assuming the small step rotational diffusion model for the molecular dynamics [11]. In this theory each molecule is supposed to act independently of its neighbours which just contribute to mean potential. In the uniaxial mesophases (N, SmA or SmA*), this theory predicts for the planar alignment two modes that can be detected dielectrically. One is related to the rotation around the molecular long axis and then to the transverse dipole moment, and the other to the precession of the long axis around the director of the phase and then to the longitudinal dipole moment. If the order parameter of the molecular long axis is high (as is expected in the smectic mesophase), this last contribution should be very small. The frequencies of both modes are similar and the aspect of the relaxation is just a broad peak. Librations and also conformational changes could also contribute to this relaxation.

In all cases, dielectric data have been analysed from the fitting of the complex dielectric permittivity to:

$$\varepsilon(\omega) = \sum_k \Delta\varepsilon_k(\omega) + \varepsilon_\infty - i\sigma_{\text{DC}}/\omega\varepsilon_0 \quad (3)$$

where $\Delta\varepsilon_k(\omega)$ accounts for the contribution of each mode, σ_{DC} for the d.c. conductivity, and ε_∞ for the high frequency permittivity. For $\Delta\varepsilon_k(\omega)$ we use the Havriliak–

Negami function:

$$\Delta\varepsilon_k(\omega) = \Delta\varepsilon_k \frac{1}{[1 + (i\omega\tau)^{\alpha_{\text{HN}}}]^{\beta_{\text{HN}}}} \quad (4)$$

where $\Delta\varepsilon_k$ is the dielectric strength, τ the relaxation time and α_{HN} , β_{HN} control the shape of the relaxation. $\alpha_{\text{HN}} = \beta_{\text{HN}} = 1$ is the Debye function; $\beta_{\text{HN}} = 1$, $0 < \alpha_{\text{HN}} \leq 1$ is the Cole–Cole function; $\alpha_{\text{HN}} = 1$, $0 < \beta_{\text{HN}} \leq 1$ is the Cole–Davidson function. In general all these parameters are temperature dependent.

3.1. I and N* phases

In the I and N* phases we observed two relaxations. The high frequency one (hereafter called t, where t means transverse dipole moment) is related mainly to the rotation around the molecular long axis and the low frequency one (hereafter called l, where l means longitudinal dipole moment) to the reorientation of the molecular long axis around the short axis [12]. However, the frequency of mode t is out of our frequency window and we could not characterize it. Mode l follows the Debye law.

3.2. Smectic mesophases

In the smectic mesophases with planar alignment, the relaxational pattern changes [13]: more relaxations are present. These additional relaxations are director modes. In the SmA* phase, the soft mode, related to collective tilt fluctuations, that is, amplitude changes of the director, appears on the low frequency side. On the high frequency side, we observe a very broad relaxation. Two Havriliak–Negami functions are needed to account for its shape. The one with the lower frequency is mode t and we will call mode x the high frequency relaxation. In the tilted smectic mesophase, SmC^* , the spectrum is a little more complicated. Together with the modes in the orthogonal smectic mesophase, there is a contribution related to the helical structure, the Goldstone mode, whose strength hides the soft mode. Because of this, it is usual to study the dielectric response under a bias field high enough to unwind the helical structure and quench the Goldstone mode.

Figure 3 shows a typical plot of the complex permittivity versus the logarithm of the frequency for a temperature in the SmC^* phase. The figure shows the three relaxations above mentioned, mode G (Goldstone), mode t and mode x. The inset shows (on another scale) the imaginary part, in order to see the Goldstone mode strength; the real part is out of scale. The solid lines are the fittings: modes G and x are Debye and mode t Havriliak–Negami with $\alpha_{\text{HN}} \approx 0.9$ and $\beta \approx 0.4$. Figure 4 shows the complex permittivity for the same temperature as figure 3, but with a $0.4 \text{ V } \mu\text{m}^{-1}$ bias field. The

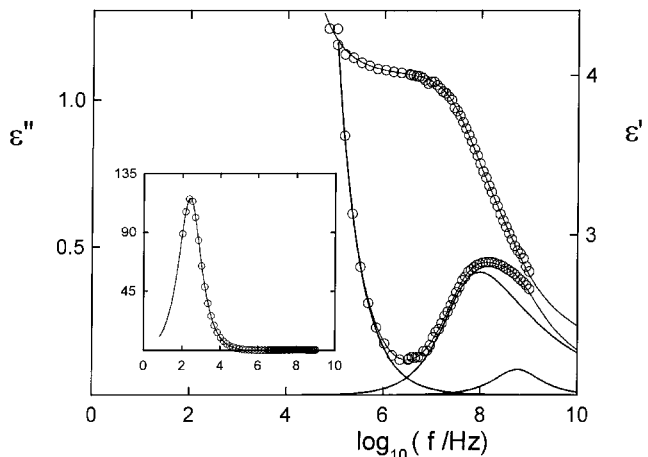


Figure 3. (○) Complex dielectric permittivity in the SmC* phase; continuous line: fitting to equations (3) and (4) showing modes x , t and Goldstone. The inset shows on an enlarged scale the Goldstone mode contribution (only the imaginary component; the real component is out of scale).

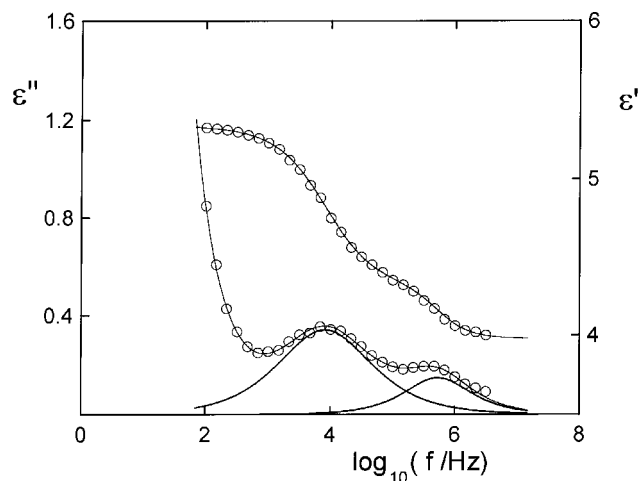


Figure 4. (○) Complex dielectric permittivity in the SmC* phase at $0.4 \text{ V } \mu\text{m}^{-1}$ bias field; continuous line: fitting to equations (3) and (4) showing the soft mode and the domain mode.

Goldstone mode is suppressed; the high frequency relaxation (about 500 kHz) is the soft mode and the low frequency one (about 10 kHz) should be related to the domain mode [14, 15].

Figures 5 and 6 show the strengths and frequencies of all modes (excluding the strength of the soft mode).

4. Discussion

4.1. The extended Landau model

In this section we will analyse the temperature dependences of the frequency and strength of the Goldstone

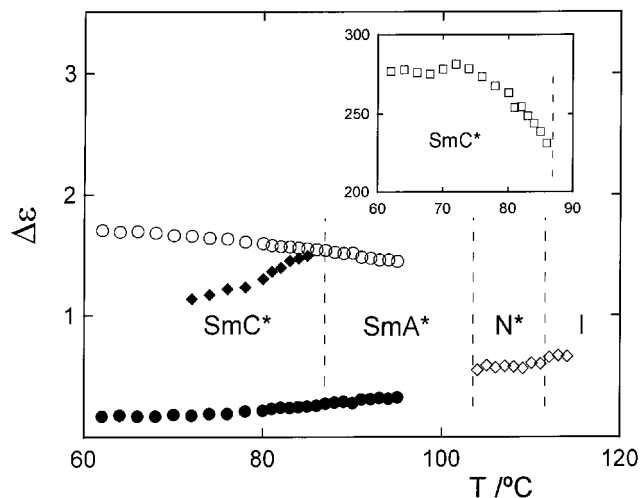


Figure 5. Dielectric strength of the different modes (deduced from the fittings) versus temperature. (□) Goldstone mode; (◆) domain mode; (◇) mode I; (○) mode t ; (●) mode x .

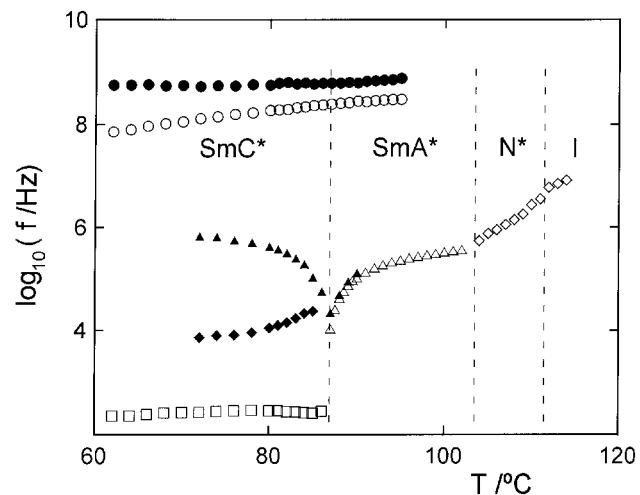


Figure 6. Frequency of the different modes (deduced from the fittings) versus temperature. (□) Goldstone mode; (◆) domain mode; (◇) mode I; (○) mode t ; (●) mode x ; (△) soft mode; (▲) soft mode at $0.4 \text{ V } \mu\text{m}^{-1}$ bias field.

and soft modes. The results will be explained in the light of the extended Landau mean field model for the SmA*–SmC* phase transition. Making use also of polarization and tilt measurements, we will be able to obtain the rotational viscosities associated with the collective modes and some parameters involved in the free energy expansion. First we will mention some results of the generalized Landau model.

The generalized Landau model for the free energy density describing the SmA*–SmC* transition can be

expressed as:

$$G = \frac{1}{2}\alpha(T - T_0)\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 - \Lambda q\theta^2 + \frac{1}{2}K_{33}q^2\theta^2 + \frac{1}{2\varepsilon}\mathbf{P}_S^2 - \mu q\mathbf{P}_S\theta - C\mathbf{P}_S\theta - dq\theta^4 + \frac{1}{4}\eta\mathbf{P}_S^4 - \frac{1}{2}\Omega\mathbf{P}_S^2\theta^2 \quad (5)$$

where we use the same notation as in references [3–6]. In particular Ω is the coefficient of the above mentioned biquadratic coupling, C is that of the piezoelectric bilinear coupling, \mathbf{q} is the wave-vector of the helix, ε denotes the high temperature dielectric permittivity and T_0 corresponds to the phase transition temperature of the corresponding racemic mixture ($\Lambda = C = d = 0$). This temperature is different from T_C but practically equal [2, 4].

The spontaneous polarization and the spontaneous tilt are usually determined experimentally for unwound systems ($\mathbf{q} = 0$). Minimizing equation (5) with respect to the polarization, one obtains the following relation between \mathbf{P}_S and θ [2]:

$$\left(\frac{1}{\varepsilon} - \Omega\theta^2\right)\mathbf{P}_S + \eta\mathbf{P}_S^3 - C\theta = 0 \quad (6)$$

Close to T_C , where θ is small, \mathbf{P}_S is also small and proportional to θ :

$$\mathbf{P}_S = \varepsilon C\theta \quad (7)$$

a relation predicted by earlier theories for the whole temperature range.

In the planar alignment, to obtain the complex dielectric permittivity, a harmonic external field, parallel to the smectic layers, is applied to the sample. If this field is low enough to consider the linear response, the dielectric behaviour of the director modes can be obtained from equation (5) (adding the energy associated with the measuring field, and an extra term due to the changes of the order parameters) and the Landau–Kalatnikov equations. The expressions we will use in the following paragraphs for the frequencies and strengths of the soft and Goldstone modes correspond to these assumptions [5].

4.1.1. The Goldstone mode in the SmC^* phase

As shown in figures 5 and 6, we have obtained the frequency and strength of the Goldstone mode. From these data and with the \mathbf{P}_S and θ values we obtain the Goldstone mode rotational viscosity making use of the

relation [5, 6]:

$$\gamma_G = \frac{1}{4\pi\varepsilon_0} \left(\frac{\mathbf{P}_S}{\theta}\right)^2 \left(\frac{1}{\Delta\varepsilon_G f_G}\right) \quad (8)$$

In figure 7 we have plotted (Arrhenius diagram) γ_G deduced from equation (8) (dots) and deduced from the polarization reversal (open circles). This last method allows determination of the rotational viscosity of the c-director, γ_C . Both viscosities are related through: $\gamma_G = \gamma_C/\sin^2\theta$. The agreement between both series, although not very good, is similar to that obtained by other authors [16]. A fitting to the Arrhenius law of the Goldstone mode rotational viscosity deduced from equation (8) gives an activation energy of 32 kJ mol⁻¹, which is similar to the activation energies found for other compounds [6, 17, 18]. The deviation near T_C may be due to the electroclinic effect.

4.1.2. The soft mode in the SmA^* phase

As was shown in figures 5 and 6, we have also obtained the frequency and strength of the soft mode in the SmA^* phase at 0 V μm^{-1} and in both SmA^* and SmC^* phases at 0.4 V μm^{-1} . Both the frequency and $1/\Delta\varepsilon_S$ have the typical V-shape as temperature functions. In the SmA^* phase $\Delta\varepsilon_S$ has been fitted to the modified Curie law [4, 5]:

$$\varepsilon_0\Delta\varepsilon_S = \frac{\varepsilon^2 C^2}{\alpha(T - T_C) + (K_{33} - \varepsilon\mu^2)\mathbf{q}_0^2} \quad (9)$$

where \mathbf{q}_0 is the wave vector of the helix at $T = T_C$. From the fitting, which is represented by a solid line in figure 8,

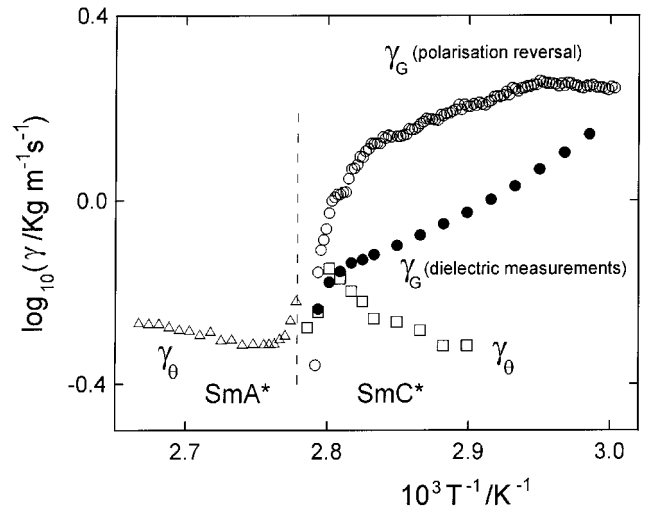


Figure 7. Arrhenius plot of the rotational viscosities. (○) Goldstone mode, from the reversal of the spontaneous polarization; (●) Goldstone mode, from equation (8); (□) soft mode, from equation (13); (△) soft mode, from equation (11).

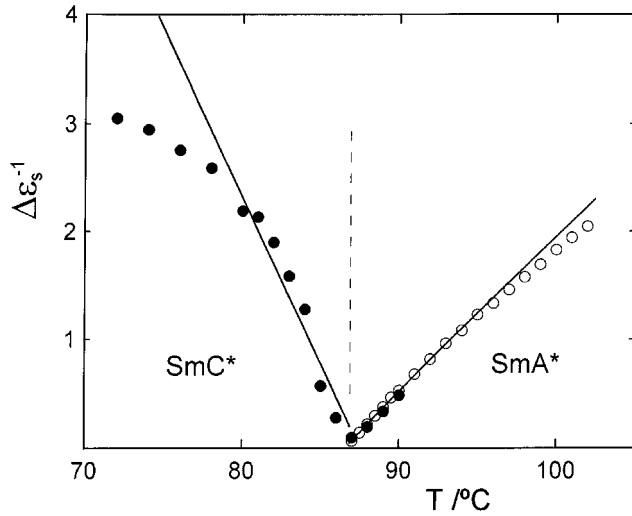


Figure 8. Inverse of the soft mode strength. (○) At $0 \text{ V } \mu\text{m}^{-1}$ bias field; (●) at $0.4 \text{ V } \mu\text{m}^{-1}$ bias field; continuous line: fitting to equations (9) and (12).

we deduced:

$$\frac{\varepsilon^2 C^2}{\varepsilon_0 \alpha} = 6.37 \text{ K}$$

$$\frac{(K_{33} - \varepsilon\mu^2) \mathbf{q}_0^2}{\alpha} = 0.28 \text{ K}$$

$$T_C = 86.9^\circ\text{C}.$$

When the bias is on, near the SmA*–SmC* phase transition, some changes in the soft mode behaviour are expected. However, they are only noticeable very near the SmA*–SmC* phase transition as can be seen in figures 6 and 8, and this was also verified by other authors [19].

In order to obtain the soft mode rotational viscosity, one additional measurement is needed. If one measures the field dependence of the induced tilt angle in the SmA* phase due to the electroclinic effect, εC could be obtained [20, 21]; this has been done at 90°C for the SmA* phase. At this temperature the behaviour of the induced tilt versus field is linear at least till $\mathbf{E} = 3 \text{ V } \mu\text{m}^{-1}$, allowing neglect of the higher order terms in the equation governing the equilibrium value of the tilt in the presence of a bias field [21]. Figure 9 shows the induced tilt versus the applied field with the fitting to:

$$\theta_{\text{incl}} = \frac{\varepsilon C}{\alpha(T - T_C) + (K_{33} - \varepsilon\mu^2) \mathbf{q}_0^2} \mathbf{E} \quad (10)$$

resulting in $\varepsilon C / \varepsilon_0 = 2.4 \times 10^8 \text{ V m}^{-1}$ and $\alpha = 8.2 \times 10^4 \text{ N m}^{-2} \text{ K}^{-1}$. These values are similar to those in references [4, 16, 22]. We checked them by obtaining the spontaneous polarization from the tilt value near T_C using equation (7). Although this relation is not valid

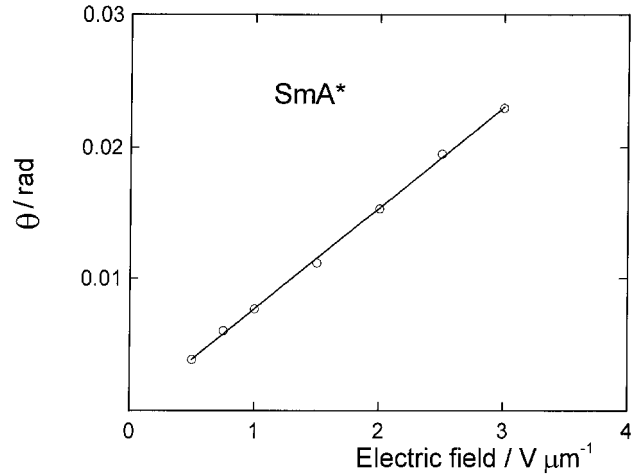


Figure 9. Induced tilt versus field at 90°C in the SmA* phase; continuous line: fitting to equation (10).

because, as we shall see later, polarization and tilt are not proportional, it gives useful results, at least not far from T_C . The experimental value of \mathbf{P}_S at 85°C is 15.5 nC cm^{-2} and the calculated value using equation (7) is 18.3 nC cm^{-2} . Now one can obtain the soft mode rotational viscosity in the SmA* phase from [5, 6]:

$$\gamma_\theta = \frac{\varepsilon^2 C^2}{2\pi\varepsilon_0 \Delta\varepsilon_S f_S} \quad (11)$$

this is plotted in figure 7 using triangles.

4.1.3. The soft mode in the SmC* phase

Due to the large dielectric strength of the Goldstone mode, to study the soft mode in the SmC* phase it is necessary to apply a bias field to suppress the helical structure.

This field will modify above all the soft mode behaviour near the phase transition. In our case we have obtained the frequency and strength of the soft mode in the SmC* phase at $0.4 \text{ V } \mu\text{m}^{-1}$. The strength has been fitted to [5] (see figure 8):

$$\Delta\varepsilon_S = \frac{(b_3/b_7)^2}{4\alpha\varepsilon_0(T_C - T) + A} \quad (12)$$

where A is a cut off term and b_3, b_7 are related, among others, to the biquadratic coupling between tilt and polarization. This term reflects a quadrupolar order of the short axes of lath-like molecules. Although equation (12) was obtained for undisturbed systems with a helix, we will assume its validity when the sample is unwound by a bias field [19]. We obtained the following values: $b_3/b_7 = 3.3 \times 10^{-3} \text{ C m}^{-2}$, $A = 2.25 \times 10^{-6} \text{ C}^2 \text{ m}^{-4}$.

Now one can obtain the soft mode rotational viscosity

in the SmC* phase from [5, 6]:

$$\gamma_\theta = \frac{(b_3/b_7)^2}{4\pi\Delta\epsilon_S f_S} \quad (13)$$

as plotted in figure 7 by squares.

Figure 7 shows that the values of γ_G and γ_θ are similar near T_C (in this case on both sides of the critical temperature), as predicted for symmetry reasons [23]. Although other authors have obtained for the SmC* phase $\gamma_G \ll \gamma_\theta$ [16], in our case we have just the contrary.

4.2. Microscopic model: Relation between the microscopic and the Landau model

As we have mentioned above, some years ago Zeks *et al.* [7, 24] proposed a mean-field microscopic model to account for the origin of spontaneous polarization in the ferroelectric SmC* phase. They also showed that this model is compatible with the extended Landau model. In this model it is assumed that the ordering of the transverse electric dipoles, μ_t , is induced by the tilt via a chiral (a_1) and a non-chiral (a_2) interaction represented by the potential:

$$U(\psi) = -a_1\theta\cos\psi - a_2\theta^2\cos 2\psi \quad (14)$$

Assuming that the order parameter of the molecular long axis is 1, the angle ψ describes the orientation of μ_t in the plane perpendicular to the molecular long axis, being $\psi=0$ when μ_t points parallel to the direction of \mathbf{P}_S . The chiral term tends to align the transverse dipoles in the direction where $\psi=0$, producing a polar order. The non-chiral term has two minima, $\psi=0$ and $\psi=\pi$ producing a quadrupolar order and it is expected to be much more important than the polar order.

We have followed the procedure of Buka *et al.* [25] to obtain the coefficients a_1 and a_2 from the values of \mathbf{P}_S and θ . Taking into account the relationships between a_1 , a_2 and the parameters of the Landau model [7], we tried to fit the experimental values of \mathbf{P}_S/θ as a function of θ^2 using equation (6) with the $C, \Omega, \epsilon, \eta$ values calculated from the microscopic model, but it was not possible. In particular the dimensionless β parameter, given by $\beta = \epsilon\eta^{1/2}C/|\Omega|^{1/2}$, that measures the relative importance of the chiral interaction (C) and the non-chiral one (Ω) was too small, $\beta = 0.014$. This fact shows that the extended Landau model is not in perfect agreement with the microscopic model presented before. Meister and Stegemeyer [9] and also Urbanc and Zeks [8] have proposed another microscopic model, including as a particular case the above mentioned model, to account for more complex temperature behaviour of the spontaneous polarization, in particular the case when \mathbf{P}_S suffers sign-reversal. This model predicts some variations in the relationships among the microscopic parameters and the parameters of the Landau model. Maybe, using this new

microscopic model, the agreement would be better. Figure 10 shows the experimental values of \mathbf{P}_S/θ as a function of θ^2 and the corresponding fit to equation (6). Assuming $\epsilon/\epsilon_0 = 4$, that is the value deduced from the dielectric relaxation study and which corresponds, in the SmA phase, to the value of the permittivity after the relaxation of the soft mode, we obtained: $C = 4.9 \times 10^7 \text{ V m}^{-1}$, $\eta = 9 \times 10^{16} \text{ N m}^6 \text{ C}^{-4}$ and $\Omega = 9.3 \times 10^{11} \text{ N m}^2 \text{ C}^{-2}$.

With these values, $\beta = 0.54$, very far from the value obtained from the microscopic model. These values are similar to the values obtained for other compounds [4, 22, 25], and the discrepancy with the fitting to the microscopic model is above all in the η parameter. Note that there is also a difference in C with respect to the value deduced from the soft mode dielectric contribution ($6.1 \times 10^7 \text{ V m}^{-1}$). Despite the discrepancies, one can roughly estimate the strength of the chiral and non-chiral terms in equation (14). Assuming for the effective transverse dipole moment a value $\mu_t \approx 2D$ and the relationship $a_1 = C\mu_t$, one obtains $a_1 = 3.2 \times 10^{-22} \text{ J}$. Assuming for the particle density a value $\rho \approx 10^{27} \text{ m}^{-3}$ and the relationship $a_2 = \Omega\rho\mu_t$, one obtains $a_2 = 4.1 \times 10^{-20} \text{ J}$. For $\theta = 0.25 \text{ rad}$, $a_1\theta = 8 \times 10^{-23} \text{ J}$, which is roughly one order of magnitude lower than kT in the temperature range of the SmC* phase and $a_2\theta^2 = 2.6 \times 10^{-21} \text{ J}$, which is of the order of kT , as expected.

4.3. Molecular modes and domain mode

Now we shall discuss the dielectric relaxation study. This study is summarized in figures 5 and 6, where we have plotted, as temperature functions, the dielectric strengths and the relaxation frequencies, respectively.

The relaxation related to the reorientation of the molecular long axis around the short axis was observed

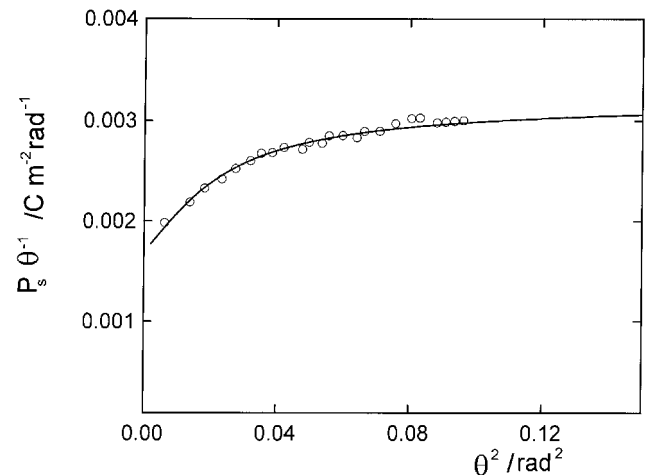


Figure 10. Temperature dependence of the \mathbf{P}_S/θ rate versus θ^2 ; continuous line: fitting to equation (6).

in the isotropic and N^* phases. Figure 11 shows its frequency versus temperature in an Arrhenius plot. It shows a jump at the $I-N^*$ transition due to the onset of the nematic order. The high value of the activation energy, 195 kJ mol^{-1} in the isotropic phase and 294 kJ mol^{-1} in the N^* phase is noteworthy; similar values were obtained for a related compound [13]. Its strength shows a small but continuous decrease when going from the isotropic to the N^* phase (due to the somewhat partial planar alignment).

Figure 12 shows the frequency of the mode related to the overall rotation around the molecular long axis. The behaviour of this mode at the $\text{SmA}^*-\text{SmC}^*$ phase transition has been studied for many other ferroelectric liquid crystals [12, 13, 26, 27]. In nearly all cases, no jumps,

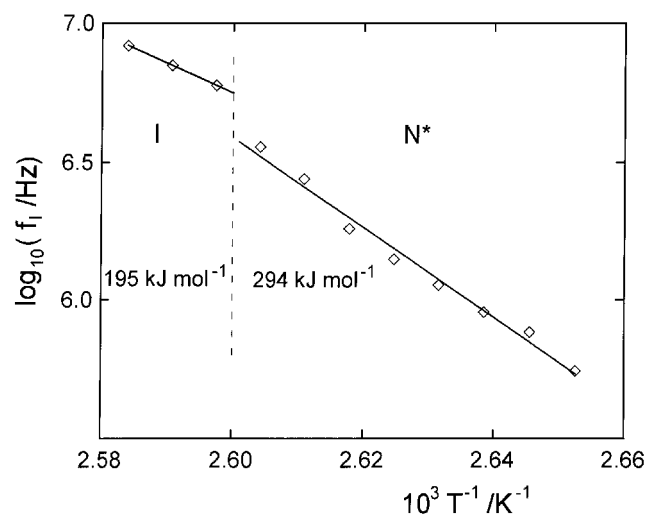


Figure 11. Arrhenius plot of the frequency of the mode related to rotation around the molecular short axis.

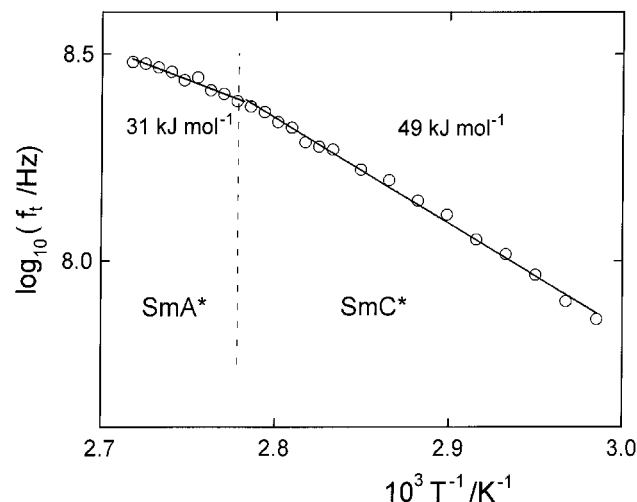


Figure 12. Arrhenius plot of the frequency of the mode related to rotation around the molecular long axis.

no significant changes in the activation energy were observed at the transition. In our compound a noticeable change in the activation energy has been observed from 31 kJ mol^{-1} in the SmA^* phase to 49 kJ mol^{-1} in the SmC^* phase. This fact could be explained in the context of the microscopic model mentioned above as being due to a significant increase in the quadrupolar order of the transverse axes when the molecules are tilted. Some authors have proposed [28] that this mode should split into two at the $\text{SmA}^*-\text{SmC}^*$ phase transition due to the biaxial nature of the tilted smectic mesophases. The larger the quadrupolar ordering, the larger the splitting. We did not observe this effect either in our measurements at $0 \text{ V } \mu\text{m}^{-1}$ or at $0.4 \text{ V } \mu\text{m}^{-1}$. We think that this effect would only be observable under extreme conditions for several reasons. This mode has a Havriliak–Negami shape. A splitting will appear as a broadening of this shape, it being impossible to decide between one or two processes. In our case, it is even more difficult because we have another relaxation with only a slightly larger frequency. The dielectric strength of this mode is very small (dots in figure 5) and its frequency has little thermal activation (see dots in figure 6). This mode could be related to some internal degree of freedom of the molecule associated with a polar group or also a librational motion [29].

To conclude, we have performed a broad band dielectric study (10^2 and 10^9 Hz) of a ferroelectric liquid crystal. The collective modes, Goldstone (in the SmC^* phase) and soft mode (in the SmA^* and SmC^* phases), have been characterized. These results, together with measurements of molecular tilt and spontaneous polarization in the SmC^* phase and induced tilt in the SmA^* phase, allowed us to obtain the Goldstone and soft mode rotational viscosities. All these results were interpreted in the light of the so-called extended Landau model. Molecular modes, mainly related to the overall rotations around the molecular long and short axes, have also been characterized; the latter occur only in the I and N^* phases. It shows a quite high thermal activation, but its behaviour is normal. The former rotation was characterized in the SmA^* and SmC^* phases. The thermal activation is smaller with values in the usual range. However, we observed an increase on going from the paraelectric to the ferroelectric mesophase that could be explained as an increase in the quadrupolar order [30, 31]. Additionally we observed a domain mode in the SmC^* phase, when measuring under a bias field, and a high frequency mode (SmA^* and SmC^* phases) that could be related to some internal degree of freedom associated with a polar group.

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