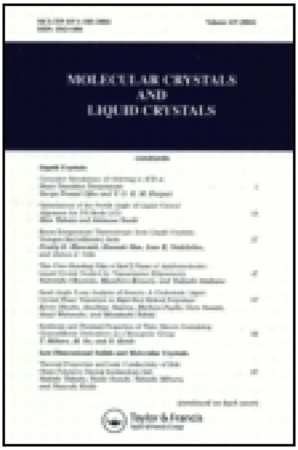

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Results from New Evaluation Models in the Dielectric Spectroscopy of Chiral Smectic Liquid Crystals

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Results from New Evaluation Models in the Dielectric Spectroscopy of Chiral Smectic Liquid Crystals

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The complex dielectric permittivity of the soft mode in the A^* phase and the Goldstone mode in the C^* phase has been studied as a function of temperature and frequency. Using simple evaluation models, the soft mode and the Goldstone mode rotational viscosities have been determined in the A^* and C^* phases respectively. The models enabled us to calculate values of the elastic constant of the Goldstone mode. A correction of the usually measured dielectric anisotropy in the C^* phase is also presented.

Keywords: dielectric spectroscopy, ferroelectric LC, Goldstone mode, soft mode

I. INTRODUCTION

Dielectric relaxation spectroscopy has proven to be a powerful technique not only to study molecular relaxations$^{1-3}$ but also to determine important material properties especially when investigating the chiral smectic liquid crystals.$^{4-6}$ The dielectric spectra of chiral systems (for example smectic A (A^*) and smectic C (C^*) phases) contain absorptions not appearing when studying the non-chiral systems. In particular, the dielectric spectra of the perpendicular component of the complex dielectric permittivity $\varepsilon_{\perp}^*$ in the chiral systems have their own "finger print" dispersions. In the A^* phase, there is an absorption with a strong temperature dependence due to the tilt fluctuation, this is the so called soft mode. This mode is observed in the frequency regime 10^3–10^6 Hz. In the C^* phase the spectra contain two additional absorptions.$^{7-11}$ One is due to the tilt fluctuation (soft mode) and one other predominant mode is due to the phase fluctuation (Goldstone mode). The relaxation frequency of the latter has a weak temperature dependence and lies in the frequency region 10–500 Hz.

When the system, in the A^* and C^* phases, is deformed and allowed to relax, it does so with a characteristic relaxation time to the unperturbed state driven by an elastic torque, and counteracted by a dissipative viscous torque, thus admitting the determination of the involved viscoelastic properties. These properties are of great importance for technical applications. Among the well known technically important material parameters which can be determined by dielectric measurements is the dielectric anisotropy $\Delta\varepsilon$. Due to the tilt and the helical structure in the C^* phase one usually measures a combination of the perpendicular $\varepsilon_\perp$ and parallel $\varepsilon_\parallel$ components of the dielectric permittivity. Thus, to obtain the correct value of $\Delta\varepsilon$, a correction due to the tilt angle is needed.

In the present paper, the contribution of the soft mode in the A^* phase and the Goldstone mode in the C^* phase to the dielectric permittivity and the corresponding values of the relaxation frequencies is measured at different temperatures. Using simple evaluation models the relevant viscosity coefficients of the soft mode and the Goldstone mode have been determined from the dielectric results. The frequency dependence of the dielectric anisotropy has been measured in the A^* and C^* phases, and a correction of $\Delta\varepsilon$ measured in the C^* phase is also presented.

II. EXPERIMENTAL

The capacitance and conductance measurements were made using the HP 4192 impedance analyzer (5 Hz-13 MHz). The cell consists of two conducting glass plates separated by two mylar spacers with a known thickness. For planar and homeotropic orientations, we have used spacers of 100 and 36 μm thickness, respectively. For $\varepsilon_\perp$ measurements, the planar orientation was obtained by shear and an ac field was applied simultaneously. For $\varepsilon_\parallel$ measurements, the glass plates of the cell were initially coated with surfactant (Quilon C) to achieve homeotropic orientation. A detailed discussion of dielectric measurements has been published elsewhere.[12]

The investigated substance is one of the BDH electroclinic mixtures. It is abbreviated 764E. It exhibits a significant field induced tilt angle in the A^* phase. The transition temperatures are

$$C^*(28°\mathrm{C})A^*(73°\mathrm{C})N^*(\approx 90°\mathrm{C})\ \text{Isotropic}$$

The soft mode dielectric behaviour in the A^* phase has been measured with the smectic layers aligned in a direction perpendicular to the glass plates. The measuring electric field was applied in a direction perpendicular to the director. The measured dielectric permittivity ε_S in this measuring geometry has a contribution due to the tilt fluctuation (soft mode), and a contribution which is connected with the molecular rotation around the long-molecular axis, and also a contribution due to the electronic polarizability. The second and third contributions have a characteristic relaxation frequency > 500 MHz, and they are incorporated into ε_∞. The experimental results have been analysed using Cole-Cole plots to determine values of the dielectric strength $\Delta\varepsilon_S$ ($\Delta\varepsilon_S = \varepsilon_S - \varepsilon_\infty$), and the soft mode relaxation frequency f_S.

Figure 1 shows the temperature dependence of the soft mode dielectric strength $\Delta\varepsilon_S$ in the A^* phase. Values of $\Delta\varepsilon_S$ are relatively large, (when compared with other compounds) and were measured up to 15°C in the A^* phase. For all other substances which we have investigated, the soft mode dielectric behaviour was studied up to 6°C above the transition temperature.

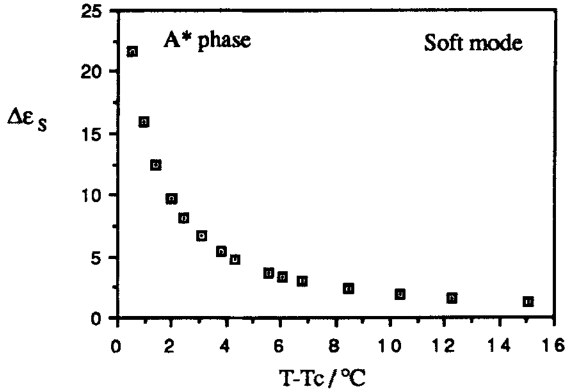

FIGURE 1 Temperature dependence of the soft mode dielectric strength in the A^* phase.

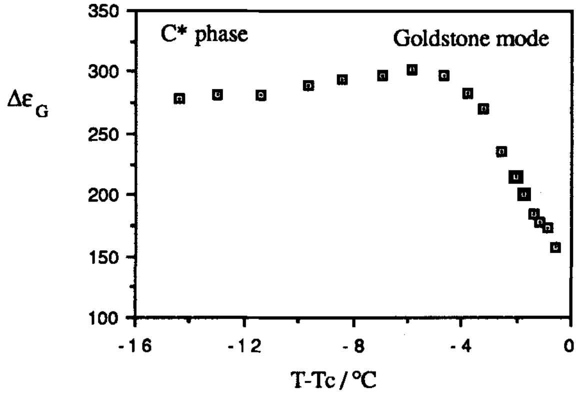

FIGURE 2 Temperature dependence of the Goldstone mode dielectric strength in the C^* phase.

In the C^* phase, the dielectric permittivity has an additional contribution (when compared with the A^* phase) due to the phase fluctuation of the director, the Goldstone mode. Figure 2 shows the dielectric contribution of the Goldstone mode $\Delta\varepsilon_G$ at different temperatures in the C^* phase. The Goldstone mode dielectric contribution increases rapidly below T_C, and reaches a maximum value ($\approx$300) at 5°C below T_C, and then it shows a slight decrease with decreasing temperature. It can be seen from Figures 1 and 2 that $\Delta\varepsilon_G$ is larger than $\Delta\varepsilon_S$ by two orders of magnitude.

The temperature dependence of the relaxation frequency of the soft mode f_S in the A^* phase, and the Goldstone mode f_G in the C^* phase is shown in Figure 3. Values of f_S vary between $\approx$100 kHz and $\approx$20 kHz, with a strong temperature dependence. These values are higher by two orders of magnitude than values of f_G found to be equal 200 Hz, with a weak temperature dependence.

Measurements of spontaneous polarization P were performed in a thin cell (2 μm) using the ac bridge technique. The variation of P with temperature is shown in Figure 4. The temperature dependence of the spontaneous and the induced tilt is shown in Figure 5.

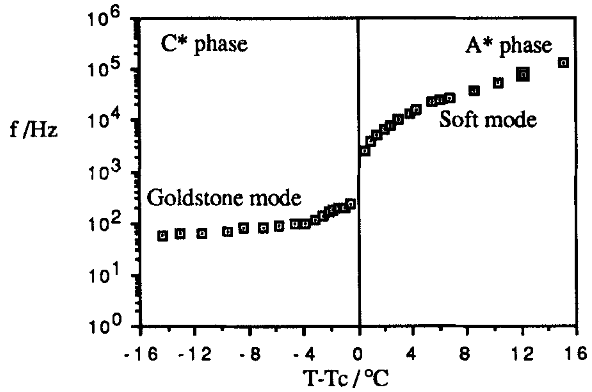

FIGURE 3 Temperature dependence of the soft mode and the Goldstone mode relaxation frequencies in the A^* and C^* phases.

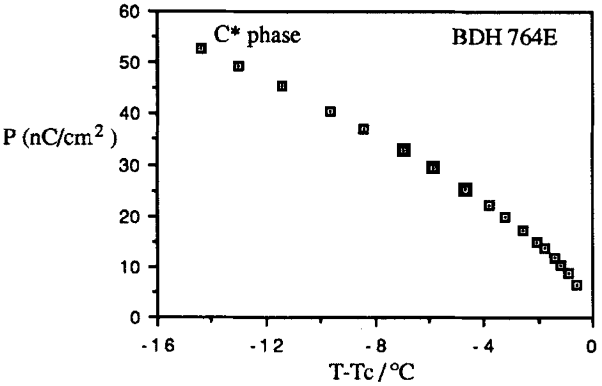

FIGURE 4 Temperature dependence of the spontaneous polarization the C^* phase.

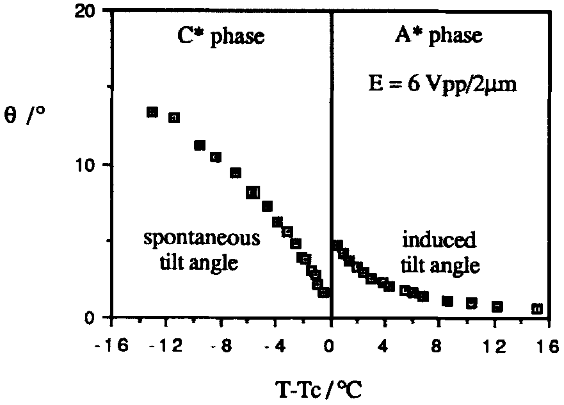

FIGURE 5 Temperature dependence of the induced tilt angle in the A^* phase, and the spontaneous tilt angle in the C^* phase, with 6 V peak to peak applied to a 2 μm thick cell.

III. EVALUATION MODELS

Soft Mode Rotational Viscosity in the *A** Phase

Using a simple Landau expansion,[13] the soft mode dielectric contribution $\Delta\varepsilon_S$ and the relaxation frequency f_S can be written as

$$\Delta\varepsilon_S = \frac{\varepsilon^2 C^2}{\varepsilon_0 \alpha (T - T_C)} \tag{1}$$

$$f_S = \frac{\alpha (T - T_C)}{2\pi\gamma_\theta} \tag{2}$$

where α is the usual coefficient contained in the temperature dependent term of the Landau free-energy density expansion, C is the temperature-independent coefficient of the piezoelectric bilinear coupling, and ε represents the dielectric permittivity at high temperature in the A^* phase. ε_0 is the vacuum electric permittivity. It can be seen that f_S and $\Delta\varepsilon_S$ are related to each other by the following relation

$$f_S \Delta\varepsilon_S = \left(\frac{\varepsilon^2 C^2}{2\pi\varepsilon_0}\right)\frac{1}{\gamma_\theta} \tag{3}$$

It is thus possible to trace the temperature dependence of γ_θ via the inverse of the temperature dependence of the product $f_S\Delta\varepsilon_S$. The absolute value of γ_θ can, however, be calculated if the coefficients ε and C are known. An alternative is to include the field dependence of the induced tilt angle which is significant for this compound. Using the same Landau expansion, the induced tilt angle θ_{ind} in the A^* phase can be written as

$$\theta_{\text{ind}} = \left(\frac{\varepsilon C}{\alpha (T - T_C)}\right) E \tag{4}$$

From equation (1), (2) and (4) the soft mode rotational viscosity is given by

$$\gamma_\theta = \frac{\varepsilon_0 \Delta\varepsilon_S}{2\pi f_S}\left(\frac{E}{\theta_{\text{ind}}}\right)^2 \tag{5}$$

Thus by knowing the soft mode dielectric strength $\Delta\varepsilon_S$, the relaxation frequency f_S, and the induced tilt angle θ_{ind}, the absolute value of the soft mode rotational viscosity can be determined.

It is worth pointing out here that, using this evaluation model, it is possible to determine the induced tilt angle by measuring the soft mode dielectric strength in the A^* phase at different bias electric field.

Goldstone Mode Elastic Constant and Rotational Viscosity in the *C** Phase

When the helical structure in the C^* phase is deformed and allowed to relax, it does with a single relaxation time τ to the unperturbed state driven by an elastic torque, and counteracted by a dissipative viscous torque, thus admitting the determination of the involved elastic constant and the rotational viscosity of the Goldstone mode.

By solving the viscoelastic equation of the C^* phase with the electric field E creating the external torque:[6,7]

$$K_\varphi \sin^2\theta \frac{\partial^2\varphi}{\partial z^2} - \gamma_\theta \sin^2\theta \frac{\partial\varphi}{\partial t} = PE \sin\theta \tag{6}$$

where K_φ contains contributions both from bend (K_3) and twist (K_2) elasticity present in the C^* phase, and is given by

$$K_\varphi = K_3\cos^2\theta + K_2\sin^2\theta$$

the following expressions of the Goldstone mode dielectric strength $\Delta\varepsilon_G$ and relaxation frequency f_G can be obtained

$$\Delta\varepsilon_G = \frac{P^2}{2\varepsilon_0 K_\varphi q^2 \theta^2} \tag{7}$$

$$\tau_G = \frac{\gamma_\varphi}{K_\varphi q^2} = \frac{1}{2\pi f_G} \tag{8}$$

where q is the wave vector of the helical pitch. From Equations (7) and (8), γ_φ and K_φ can be written as

$$\gamma_\varphi = \frac{1}{4\pi\varepsilon_0} \frac{P^2}{\theta^2(\Delta\varepsilon_G f_G)} \tag{9}$$

$$K_\varphi = \frac{1}{2\varepsilon_0 \Delta\varepsilon_G} \left(\frac{P}{q\theta}\right)^2 \tag{10}$$

Dielectric Anisotropy in the C* Phase

The dielectric anisotropy $\Delta\varepsilon$ is defined as the difference between the dielectric permittivity measured in a direction parallel $\varepsilon_\parallel$ and perpendicular $\varepsilon_\perp$ to the director; $\Delta\varepsilon = (\varepsilon_\parallel - \varepsilon_\perp)$. In the C^* phase, due to the tilt, the measured dielectric permittivity on a homeotropically aligned sample,[14] denoted $\varepsilon_{\parallel m}$, is a combination of $\varepsilon_\parallel$ and $\varepsilon_\perp$, and given by

$$\varepsilon_{\parallel m} = \varepsilon_\parallel \cos^2\theta + \varepsilon_\perp \sin^2\theta \tag{11}$$

In the case of planar orientation, due to the presence of the helix, the measured dielectric permittivity $\varepsilon_{\perp m}$ is given by

$$\varepsilon_{\perp m} = \frac{1}{2} [\varepsilon_\perp(1 + \cos^2\theta) + \varepsilon_\parallel \sin^2\theta)] \tag{12}$$

If the measurements are performed in the presence of a bias electric field to unwind the helix, the measured $\varepsilon_{\perp m}$ is equal to the correct perpendicular component $\varepsilon_{\perp}$. Let us denote the difference $(\varepsilon_{\parallel m} - \varepsilon_{\perp m})$ as $\Delta\varepsilon_m$, which can be written as

$$\Delta\varepsilon_m = (\varepsilon_{\parallel} - \varepsilon_{\perp}) - \frac{3}{2}(\varepsilon_{\parallel} - \varepsilon_{\perp})\sin^2\theta$$

Since $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, this equation can be written as

$$\Delta\varepsilon = \frac{\Delta\varepsilon_m}{1 - \frac{3}{2}\sin^2\theta} \tag{13}$$

The corresponding equation in case of a helix free sample is

$$\Delta\varepsilon = \frac{\Delta\varepsilon_m}{1 - \sin^2\theta} \tag{14}$$

If $\theta \approx 22°$ and $\Delta\varepsilon \approx 2$, the error due to the neglect of the correction due to the tilt in these measurements would be 27% in the presence of the helix, and it is equal 16% in case of helix free samples. In our case the investigated substance has a small tilt angle, and the measurements (in the case of planar orientation) in the C^* phase has been made in the presence of a bias electric field, so the correction is small.

IV. RESULTS AND DISCUSSION

The rotational viscosity of the soft mode γ_θ in the A^* phase and the Goldstone mode γ_φ in the C^* phase has been determined using Equations (4) and (9). The temperature dependence of γ_θ and γ_φ is shown in Figure 6. As can be seen from the figure γ_θ has been measured over a wide temperature range ≈ 15°C. At high temperature in the A^* phase, γ_θ is equal 1 Nsec m^{-2}. Upon cooling down toward the transition temperature T_C, γ_θ increases to 10Nsec m^{-2}. In the C^* phase γ_φ increases with decreasing temperature, and was found to vary between .01 Nsec m^{-2} (100 mPas) near the transition and 0.04 Nsec m^{-2} (400 mPas) at 13°C below T_C. These values of γ_φ are found to be in good agreement with reported results from BDH for other materials. The value of γ_φ has not been reported for this mixture (764E) probably because it has been synthesised as an electroclinic mixture where γ_θ in the A^* phase is rather of interest.

It is clear from Figure 6 that γ_θ in the A^* phase is larger than γ_φ in the C^* phase by almost two orders of magnitude. The only available result in literature with which we can compare the values of γ_θ is the measurements of the Moscow group,[15] where they have determined γ_θ in the C^* phase for an early ferroelectric liquid crystal substance. The values of γ_θ obtained from their measurements is about ≈10^4

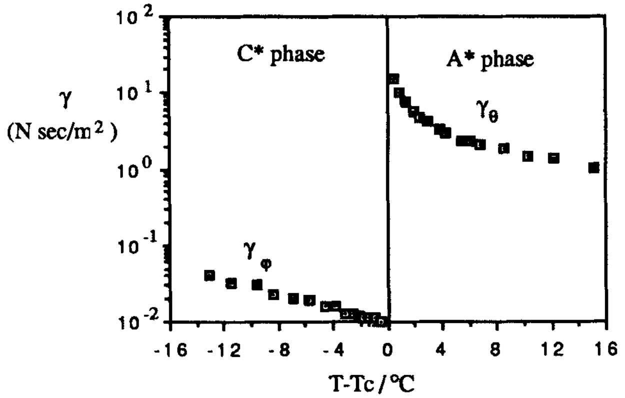

FIGURE 6 Temperature dependence of the soft mode and the Goldstone mode rotational viscosities in the A^* and C^* phases respectively.

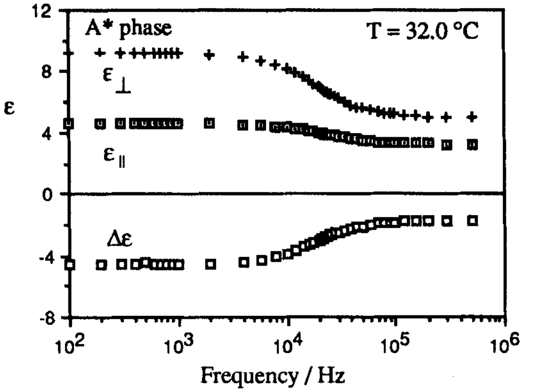

FIGURE 7a Frequency dependence of the parallel $\varepsilon_\parallel$ and perpendicular $\varepsilon_\perp$ components of the dielectric permittivity, and the dielectric anisotropy in the A^* phase.

mPas, a value which is in agreement with our results. It is worth mentioning here that such results of γ_θ in the A^* phase is published for the first time in the present paper.

Using Equation (10), it is possible to estimate the value of K_φ. However, the helical pitch values of the studied compound are not available, therefore we are not able to determine the value of K_φ.

Figure 7 shows the frequency dependence of the parallel component $\varepsilon_\parallel$, the perpendicular component $\varepsilon_\perp$, and the dielectric anisotropy Δε in the A^* and the C^* phases in the frequency regime 10^2–10^6 Hz. The A^* phase shows a relaxation with relaxation frequency equal 22 kHz, connected with single molecular rotation around the short axis. The perpendicular component exhibits a relaxation which is associated with the soft mode and the relaxation frequency is equal to 19 kHz. The dielectric anisotropy Δε varies between -4.5 at 10^2 Hz and -1.5 at and above 10^5 Hz. In the C^* phase, the corresponding frequency dependence is shown in Figure 7b. The parallel component $\varepsilon_\parallel$ has a relaxation frequency at 7 kHz, and $\varepsilon_\perp$

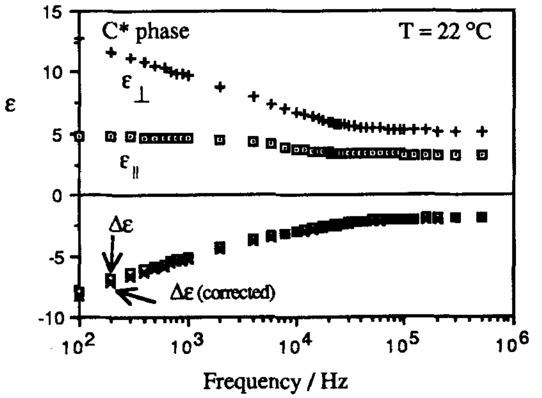

FIGURE 7b Frequency dependence of the parallel $\varepsilon_\parallel$, perpendicular $\varepsilon_\perp$ components of the dielectric permittivity, and the dielectric anisotropy measured and corrected in the C^* phase.

has a relaxation frequency at 2 kHz. The measurements in the planar orientation have been made in this case under a bias electric field. The tilt angle in the C^* phase is only about 10° therefore the correction is small. The corrected values have been obtained using Equation (14) which is relevant in our case.

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