Dielectric properties near the smectic-C^* –smectic-A phase transition of some ferroelectric liquid-crystalline systems with a very large spontaneous polarization

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The frequency and temperature dependence of the complex dielectric constant was measured near the smectic-C^*–smectic-A liquid-crystal phase (Sm-C^*–Sm-A) transition for two ferroelectric liquid crystals with a very large spontaneous polarization. The dielectric strengths as well as the corresponding relaxation frequencies of the dielectric modes were determined. Due to the large polarization we were able to resolve the contributions from the soft mode and the Goldstone mode in a comparatively large temperature interval in the Sm-C^* phase close to the transition to the Sm-A phase. In the Sm-A phase, the relaxation frequency and the inverse dielectric strength of the soft mode decrease linearly when approaching T_c. Comparing the experimental data with a recent theoretical calculation of the complex dielectric constant, we conclude that we have a fairly good understanding of the behavior of the complex dielectric constant in the whole Sm-C^*–Sm-A transition range.

I. INTRODUCTION

The ferroelectric smectic-C^* liquid-crystal (Sm-C^*) phase[1] provides a system which has gained an increasing amount of interest during the last several years and much effort has been devoted to characterizing the basic thermodynamic properties of the system.[2–6] In this context, the measurement[4] of the complex dielectric constant provides a powerful tool, because in the same experiment one can study the static (low-frequency dielectric constant) as well as the dynamic (frequency dependence of the dielectric constant) properties of the system. In order to describe the ferroelectric Sm-C^* phase one generally introduces two two-component order parameters.[5,6] These are the primary order parameter $\xi=(\xi_1,\xi_2)$ describing the director of the system, and the secondary order parameter, the in-plane polarization $\mathbf{P}=(P_x,P_y)$. Thus the dielectric response of the system consists (apart from the usual electronic contribution) of four modes.[7,8] Two of these are connected to fluctuations of the polarization order parameter and have[9] relaxation frequencies of the or-

der of 500 MHz. The other two, which are connected to the relaxation of director fluctuations[4,8] are of lower frequency and are commonly denoted the soft mode and the Goldstone mode. This division, as well as the general form of the total complex dielectric constant of the system, will be discussed in further detail in Sec. II.

In this paper we will study the dielectric properties of two different ferroelectric Sm-C^* liquid crystalline systems. One of these is a ternary mixture,[10] denoted by us as LC1, which has been synthesized by Mohr et al.[11]. The other is a one-component system[12] and has been provided by Merck. It has been denoted by us as LC2. In Sec. III we will present the experimental determination of the frequency and temperature dependence of the complex dielectric constant $\epsilon^*(\omega, T)$ of LC1 in a broad temperature interval around the Smectic-C^*–Smectic-A liquid crystal (Sm-C^*–Sm-A) phase transition temperature T_c. Since our experimental facilities do not allow us to extend the measurements to frequencies comparable to the relaxation frequencies of the polarization modes, the contribution from these together with the electronic con-

tribution will simply act as a background and will be considered as the high frequency part of the dielectric constant ϵ_∞. Due to the fact that LC1 has an extremely large polarization, we have been able to separate the contributions to the dielectric response from the soft mode and the Goldstone mode in a way which is normally not possible for systems with a smaller value of the spontaneous polarization. From the measurements we have determined the temperature dependence of the relaxation frequencies and of the dielectric strengths of the soft mode and the Goldstone mode. The dielectric properties of the Merck compound, LC2, with a larger spontaneous polarization than that of LC1, were studied only in the Sm-A phase.

Recently, we have presented[8] a theoretical calculation of the complex dielectric constant of the ferroelectric Sm-C* phase and of the corresponding Sm-A phase, which is based on a generalized[3,6] Landau expansion of the free-energy density of the system. In Sec. IV we will compare the predictions of this calculation with the outcome of the experiments. From this comparison we will draw the conclusion that the theoretical model describes the experimental behavior of the system in a qualitatively correct way. However, we will notice that there are still some open questions regarding the behavior of the system close to T_c.

II. COMPLEX DIELECTRIC CONSTANT

Let us introduce the complex dielectric constant $\epsilon^*(\omega,T)=\epsilon(\omega,T)-j\epsilon''(\omega,T)$, where $\omega=2\pi f$ is the angular frequency of the applied electric field and T is the temperature of the system. In general, several relaxation mechanisms, each of which is connected to a characteristic eigenfrequency f_i, are contributing to $\epsilon^*(\omega,T)$. In the case of ferroelectric liquid crystals in the Sm-C* phase, which are characterized by two two-component order parameters, we expect two relaxation modes connected to the reorientation of the director, two polarization modes, and (at least) one mode connected to the electronic properties of the medium. For each mode, at a given temperature, the contribution to the dielectric constant decreases with increasing frequency of the field, from the low-frequency value ($f \ll f_i$) to zero, which is the value adopted when the frequency of the applied electric field is so high ($f \gg f_i$) that the mode cannot follow the electric field. The difference between the low- and high-frequency contributions of the mode to the total dielectric constant is called the dielectric strength of the mode and will be denoted $\Delta\epsilon_i(T)$. This quantity is related to the average induced polarization $\langle P_i \rangle$ of the corresponding mode by the relation

$$\Delta\epsilon_i(T) = \lim_{E \to 0} \frac{\langle P_i \rangle}{E} , \qquad (1)$$

where E is the magnitude of an applied static electric field. We will only consider electric fields which are applied parallel to the smectic liquid-crystal layers.

The disturbance of the equilibrium order parameters when an electric field is applied to the system can be divided into two parts.[4,8] These are amplitude changes (magnitude of tilt and polarization) and phase changes

(direction of tilt and polarization). Hence the dielectric response of the system will consist of four parts (apart from the high frequency response $\Delta\epsilon_{el}$)— two which are connected to director reorientations and two connected to reorientation of the polarization. Linear combinations of the former two are what commonly are denoted the soft mode ($\Delta\epsilon_S$ is the dielectric strength and f_S the eigenfrequency) and the Goldstone mode ($\Delta\epsilon_G$ represents the dielectric strength and f_G the eigenfrequency). It can, however, be shown[8] that for practical purposes the soft mode can be identified as the response which is connected with the amplitude changes and the Goldstone mode as the response connected with the phase changes of the order parameter. The relaxation frequencies of these two modes are normally[4,13] of the order of $f_S \sim 1-10^4$ kHz and $f_G \sim 10-200$ Hz, respectively. The relaxation frequencies of the polarization modes have been reported by Benguigui[9] to be of the order of 500 MHz. This means that the study of these two modes will be beyond our experimental range.

With the assumption that the relaxation behavior of each mode is characterized by one single relaxation frequency (Debye relaxation), we can write the complex dielectric constant of the Sm-C* phase as

$$\epsilon^*(\omega,T) = \frac{\Delta\epsilon_G(T)}{1+j\omega t_G} + \frac{\Delta\epsilon_S(T)}{1+j\omega t_S} + \epsilon_\infty , \qquad (2)$$

where $t_i = 1/2\pi f_i$ is the relaxation time of the corresponding mode. This expression is valid for frequencies up to approximately 50 MHz, which is about one order of magnitude less than the reported values of the relaxation frequencies of the polarization modes. The constant ϵ_∞ in Eq. (2) represents the sum of the dielectric strengths of the two polarization modes and all other high-frequency mechanisms which might be present in the system.

In the Sm-A phase amplitude and phase fluctuations are degenerate. Thus the system exhibits one doubly degenerate soft mode and one doubly degenerate (high-frequency) polarization mode apart from the usual high-frequency electronic contribution to the dielectric relaxation. In this case we can write the complex dielectric constant as

$$\epsilon^*(\omega,T) = \frac{\Delta\epsilon_{SA}(T)}{1+j\omega t_A} + \epsilon_\infty . \qquad (3)$$

In Eq. (3) $\Delta\epsilon_{SA}$ represents the dielectric strength of the Sm-A soft mode while $t_A = 1/2\pi f_A$ is the corresponding relaxation time. The constant ϵ_∞ is the continuation into the Sm-A phase of the corresponding quantity of the Sm-C* phase.

III. EXPERIMENTAL RESULTS

The frequency and temperature dependence of the complex dielectric constant was measured for LC1 in a temperature interval ~ 15 K around the Sm-C*–Sm-A phase transition temperature T_c, which in our case was determined to be 41.2 °C. The frequency range covered by the experiments was between 20 Hz and 100 kHz.
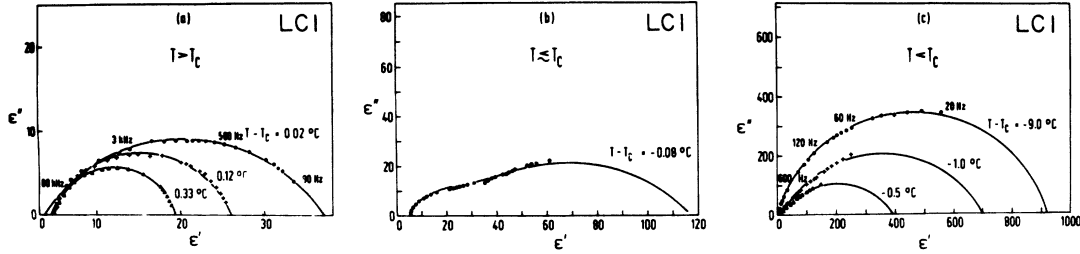
FIG. 1. (a) Cole-Cole diagrams of LC1 in the Sm-A phase, (b) in the Sm-C* phase close to T_c and (c) in the Sm-C* phase away from T_c. Close to T_c, in the Sm-C* phase, two relaxations are present which is indicated by the observed superposition of two semicircles in (b).

The experimental details and the analysis of the data for this type of experiment has been discussed by us elsewhere.[4] By constructing Cole-Cole diagrams,[14] i.e., by plotting the imaginary part of the complex dielectric constant as function of the real part parametrized by the frequency of the applied electric field, we expect to get a semicircle if only one relaxation mechanism is present. If two or more relaxation mechanisms are interacting we instead expect a distorted semicircle. In Fig. 1 we show a sequence of Cole-Cole diagrams for some different temperatures. In the Sm-A phase we observe a single relaxation behavior which is due to the soft mode. We notice that the dielectric strength decreases rapidly as the temperature increases. However, due to the large polarization of LC1 we can cover an unusually large temperature range in the Sm-A phase by the experiments. In the Sm-C* phase, far from T_c, we also observe a single relaxation behavior, which is due to the Goldstone mode. Only close to T_c, in the Sm-C* phase, do we observe strongly distorted semicircles. This is due to the presence of both the soft-mode and the Goldstone-mode relaxations. Normally the soft mode is very hard to resolve from the Goldstone mode because the dielectric strength of the soft mode is rapidly decreasing as $T_c - T$ is increased. Thus the dielectric response from the soft mode rapidly drowns in the Goldstone-mode response. Due to the very

large polarization of LC1 we have, however, been able to resolve the soft mode from the Goldstone mode at three different temperatures, a separation which is normally not possible to do for compounds with a lower polarization.

Figures 2(a) and 2(b) show the dielectric strengths of the Goldstone mode and the soft mode, respectively. We notice the different scales being used in the two figures, emphasizing that in the Sm-C* phase almost all contributions to the static dielectric constant come from the Goldstone mode. The Goldstone-mode dielectric strength exhibits a broad maximum a few degrees below T_c. The pitch of LC1 was not measurable. In Fig. 3 we have therefore plotted the wave vector of the pitch of p-(n-decyloxybenzylidene)-p-amino-(2-methyl-butyl) cinnamate (DOBAMBC) (Ref. 6) in order to display the general performance of the pitch in the Sm-C* phase. We will demonstrate in Sec. IV how the maximum of the Goldstone mode dielectric strength and the maximum of the pitch are connected.

In Fig. 4 the relaxation frequencies of the soft mode and of the Goldstone mode, which can be determined from the corresponding Cole-Cole diagrams, have been plotted. We notice again the different scales being used for the two quantities. The Goldstone-mode frequency, which is of the order of 20 Hz, is varying slowly with
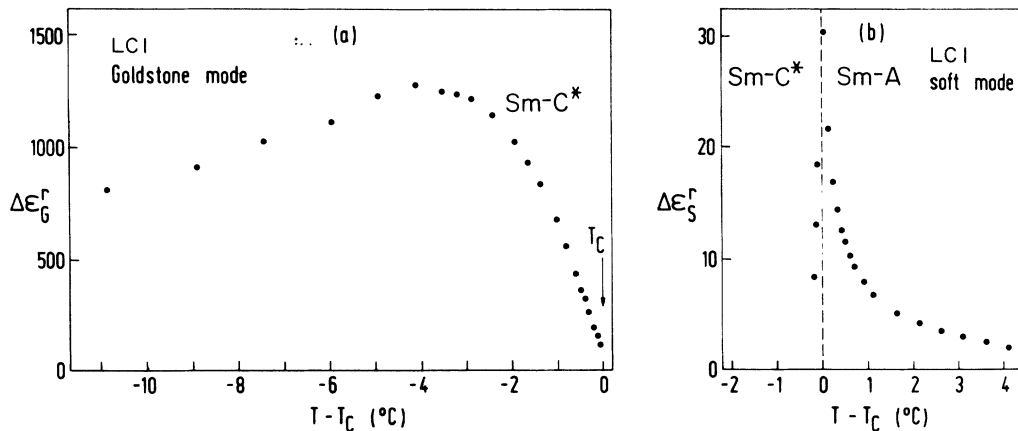

FIG. 2. Experimentally determined dielectric strengths of the (a) Goldstone mode and (b) the soft mode. We have preferred to plot the relative dielectric strengths $\Delta\epsilon_G^r = \Delta\epsilon_G/\epsilon_0$ and $\Delta\epsilon_S^r = \Delta\epsilon_S/\epsilon_0$, where ϵ_0 is the permittivity of free space.
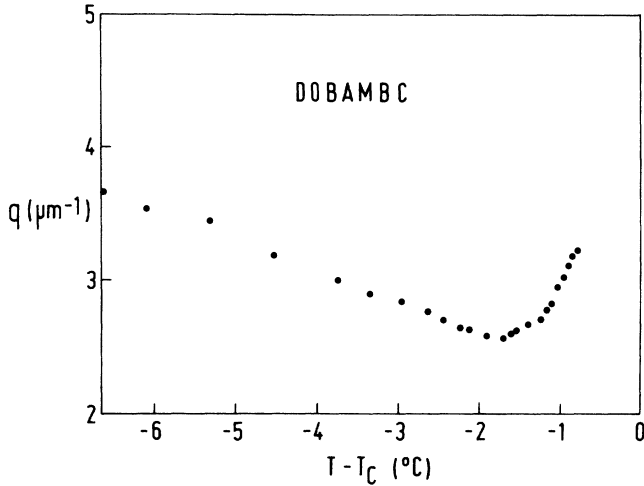
C. FILIPIČ *et al.*

FIG. 3. Experimentally determined wave vector of the pitch of DOBAMBC. The data have been taken from Ref. 6

FIG. 5. Experimentally determined frequency and temperature dependence of the relative dielectric constant $\epsilon^r = \epsilon/\epsilon_0$, where ϵ_0 is the permittivity of free space.

temperature while the soft mode frequency, being in the kHz region, is very rapidly increasing with $|T_c - T|$.

In Fig. 5 we show the temperature dependence of the total dielectric constant for some frequencies in the range 20 Hz–1 kHz. In the Sm-C* phase almost all of the low-frequency response comes from the Goldstone mode, which has a relaxation frequency which is of the order of 20 Hz. Thus the dielectric constant of the Sm-C* phase is rapidly decreasing when the frequency is increased beyond this value and at 1 kHz only the response of the soft mode and ϵ_∞ is left. As can be seen from Fig. 2(b), the soft-mode dielectric strength decreases very rapidly as $|T_c - T|$ is increased, which means that except close to T_c the 1-kHz curve just represents a measure of ϵ_∞. As we discussed in Sec. II, in our model ϵ_∞ represents the sum of the dielectric strengths of the polarization modes and other high-frequency relaxations.

In the Sm-A phase we also performed a detailed study of the compound LC2. This compound has an even

larger polarization than that of LC1. In Fig. 6 we have plotted the inverse of the dielectric strength and the corresponding relaxation frequency versus temperature for these two compounds. We notice that both $1/\Delta\epsilon_{SA}$ and f_A are linearly temperature dependent, as we will discuss in Sec. IV.

IV. COMPARISON WITH THEORY AND DISCUSSION

In view of Eqs. (2) and (3) we see that all information needed in order to establish the frequency dependence of the complex dielectric constant of the system is the dielectric strength of the dielectric modes and the corresponding relaxation frequencies. The experimental values of these quantities of LC1 are given by Figs. 2, 4, and 6(a). In a recent paper[8] we have presented a theoretical model of the complex dielectric constant of the ferroelectric Sm-C* phase which is based on a generalized[6] Landau model. In this section we will review some of the general features of this model and compare these results with the experimental data.

In the Sm-A phase the theoretical model predicts[8] that the inverse dielectric strength and the relaxation frequency of the soft mode decrease linearly with temperature when approaching T_c,

$$\Delta\epsilon_{SA} = \frac{\epsilon^2 C^2}{\alpha(T - T_c) + (K_3 - \epsilon\mu^2)q_0^2} , \qquad (4a)$$

$$f_A = \frac{\Gamma}{2\pi}[\alpha(T - T_c) + (K_3 - \epsilon\mu^2)q_0^2] . \qquad (4b)$$

In these equations α is the usual coefficient contained in the temperature-dependent term of the Landau expansion of the free-energy density. The constant K_3 is the twist elastic constant while μ and C are the coefficients of the flexoelectric and piezoelectric bilinear coupling. The constant ϵ represents the dielectric strength of the polarization mode in the Sm-A phase while q_0 is the wave vector of the pitch at T_c. We have also introduced one kinetic coefficient Γ, which generally can be viewed upon[15]
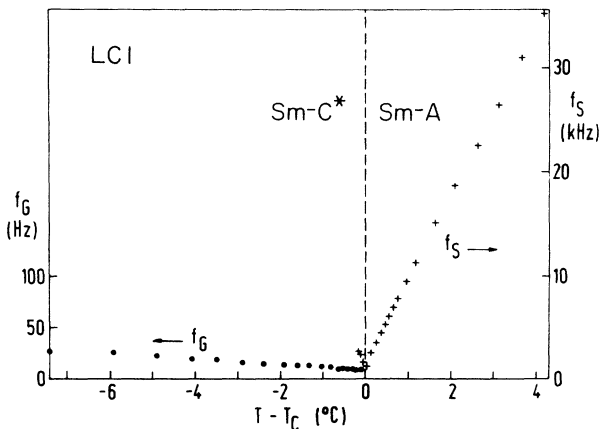
FIG. 4. Experimentally determined relaxation frequencies of the soft mode and of the Goldstone mode. Note the different scales which are being used for the two modes.
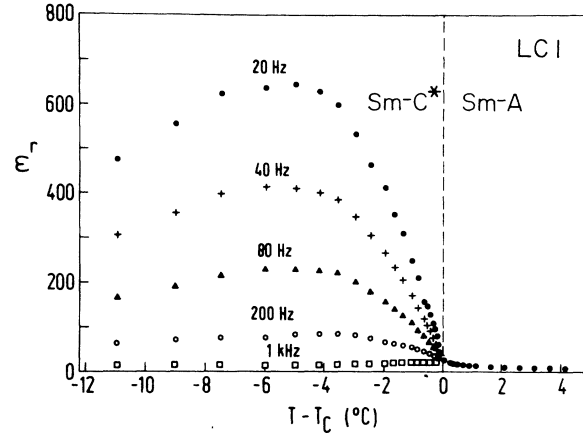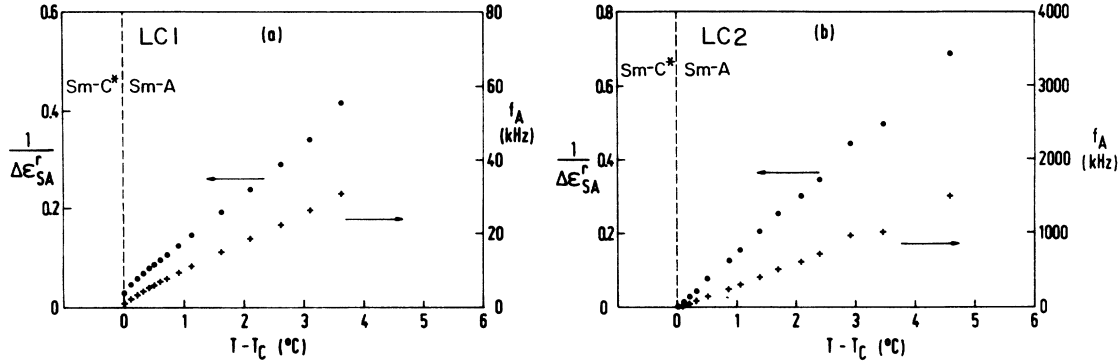
FIG. 6. Relaxation frequency f_A and inverse of relative dielectric strength $1/\Delta\epsilon_{SA}^r = 1/(\Delta\epsilon_{SA}/\epsilon_0)$ vs temperature obtained in the Sm-A phase for (a) LC1 and (b) LC2. ϵ_0 is the permittivity of free space.

as an inverse rotational viscosity, $\Gamma = 1/\gamma_1$. Equations (4) imply that $1/\Delta\epsilon_{SA}$ as well as f_A are linear functions of temperature. That this is indeed the case can be seen from Fig. 6. Furthermore, the slopes of $1/\Delta\epsilon_{SA}$ and f_A are not independent. It can be seen from Eqs. (4) that $\Delta\epsilon_{SA}$ and f_A are expected to be connected in such a way that their product is temperature independent,

$$f_A \Delta\epsilon_{SA} = \frac{\Gamma}{2\pi}\epsilon^2 C^2 . \tag{5}$$

This is a general result and is not a consequence of our specific Landau model. Any Landau model, however complicated, would give the result that this product is constant in the Sm-A phase if the dynamics is assumed to be described by a single kinetic coefficient Γ. In Fig. 7 we show this product obtained from the experimental values of Fig. 6 for both LC1 and LC2. We notice that in most of the temperature interval this product is constant, however, it show a pronounced drop close to T_c. Thus the expressions of Eqs. (4) describe the experimental situation fairly well. Only very close to T_c does the theory predict too large a value of f_A or $\Delta\epsilon_{SA}$ or both. This type of discrepancy between theory and experiment is also well known from the study of other ferroelectric systems.[16]

The soft mode in the Sm-C* phase the experimental data, consisting only of three points, is too scarce to per-

mit any quantitative comparison with the theory. However, we point out that the theoretical model predicts an approximate linear dependence of the relaxation frequency with temperature, with a slope which is twice as large than that of the soft mode in the Sm-A phase. The theoretical model also predicts a rapid decrease of the soft-mode dielectric strength when $T_c - T$ is increased. These general considerations are qualitatively in agreement with the experimental data.

For the Goldstone mode it is possible to derive[4,8] expressions where the dielectric strength and the relaxation frequency are expressed in terms of the spontaneous polarization P_0, the tilt θ_0, and the wave vector of the pitch q,

$$\Delta\epsilon_G = \frac{1}{2K_3}\left[\frac{P_0}{q\theta_0}\right]^2 , \tag{6a}$$

$$f_G = \frac{\Gamma K_3}{2\pi}q^2 , \tag{6b}$$

where in Eq. (6b) we have replaced the factor $K_3 - \epsilon\mu^2$ which appears in the original expression with K_3, an approximation which can be expected to be "almost exact". The physics behind these expressions is easy to under-
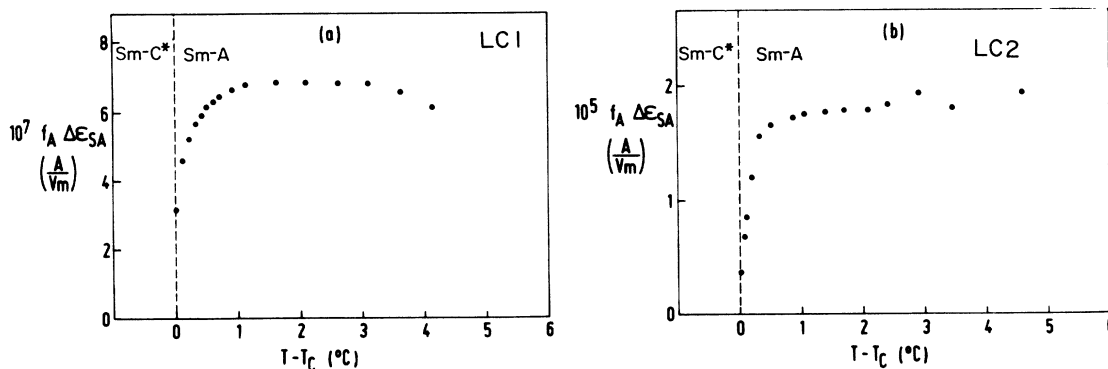

FIG. 7. Experimentally determined product $f_A\Delta\epsilon_{SA}$ in the Sm-A phase for (a) LC1 and (b) LC2.

stand. The coupling of the spontaneous polarization to the external field increases with P_0. This suggests $\Delta\epsilon_G \sim P_0^2$ as the response cannot depend on the sign of P_0. Furthermore, the elastic energy associated with the pitch is given by $g_K = K_3 q^2 \theta_0^2/2$. This suggests $\Delta\epsilon_G \sim 1/K_3 q^2 \theta_0^2$. Therefore we expect the Goldstone-mode dielectric strength to obey $\Delta\epsilon_G \sim P_0^2/K_3 q^2 \theta_0^2$, which is simply the result of Eq. (6a). The restoring torque of the Goldstone mode is determined by the twist elasticity of the system. Applying a uniform electric field will create a distortion of wave vector q and thus the restoring torque should be proportional to $K_3 q^2$ since it cannot depend on the sign of q. This torque is counteracted by a rotational torque which is proportional to the rotational viscosity $\gamma_1 = 1/\Gamma$. We thus expect $f_G \sim K_3 \Gamma q^2$, in accordance with Eq. (6b). In order to compare the theoretical expressions of Eqs. (6) with the experimental data, we first have to determine P_0, θ_0, and q. Unfortunately, the pitch was not measurable for LC1. We know that the aim when mixing the compounds which build up this system was to increase the pitch. Thus we can expect the pitch to be large and slowly varying. In Fig. 4 we see that the Goldstone-mode frequency is slowly increasing as $T_c - T$ is increased. If the temperature dependence which is generally observed for the wave vector of the pitch in Sm-C* liquid crystal (c.f. Fig 3) has been maintained when mixing this system, we can understand this slow increase in light of Eq. (6b). The theoretically expected temperature dependence of the Goldstone-mode dielectric strength is given by Eq. (6a). The ratio P_0/θ_0 is normally a monotonically increasing function of $T_c - T$, adopting one value at T_c and another saturated value[2] away from T_c. A similar temperature dependence of P_0/θ_0 can be obtained also for LC1 by using the experimental data[11] for P_0 and θ_0. Having this in mind and assuming a slowly varying pitch when $T_c - T$ is increased, we see that the measured Goldstone-mode dielectric strength present in fig. 2(a) (the small contribution $\Delta\epsilon_S$ which also is presented in this figure is completely negligible except very close to T_c) agrees qualitatively with what is expected from Eq. (6a).

From Eqs. (6) we can derive the following relation:

$$\Delta\epsilon_G f_G = \frac{\Gamma}{4\pi}\left[\frac{P_0}{\theta_0}\right]^2 . \tag{7}$$

Thus the product of the dielectric strength and the relaxation frequency of the Goldstone mode should be expected to be proportional to $(P_0/\theta_0)^2$. In Fig. 8 we have plotted the experimentally determined temperature dependence of this product. We see that, starting at T_c, this quantity increases with decreasing temperature as expected. However, it does not saturate as P_0/θ_0 but starts to decrease with decreasing $T_c - T$ at lower temperatures. One reason for this could be that $\Gamma = 1/\gamma_1$ generally is a temperature-dependent quantity. Being a viscosity, γ_1 should be expected to decrease with increasing temperatures. This could be one reason for the decrease of the $\Delta\epsilon_G f_G$ curve with $T_c - T$ at lower temperatures.

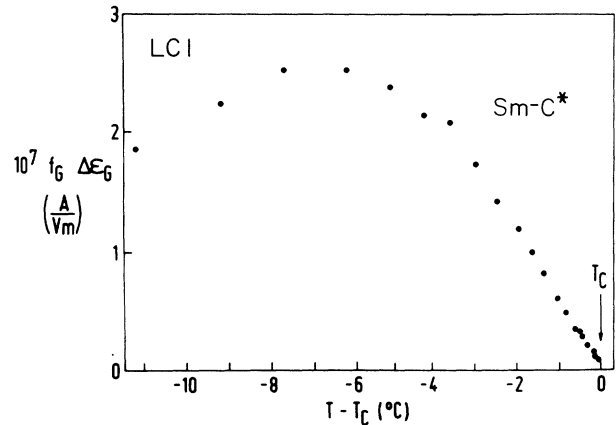If we take P_0/θ_0 values from the literature[11] and our

FIG. 8. Experimentally determined product $f_G \Delta\epsilon_G$ for LC1.

values for $\Delta\epsilon_G f_G$ we obtain from Eq. (7) an estimation for the rotational viscosity coefficient $\gamma_1 = 1/\Gamma$ of the order 0.5 Ns/m^2, which is of the same order of magnitude as γ_1 obtained from optical rise-time measurements.[17] (The reader should please note that our definition of γ_1 differs[15] by a factor $\sin^2\theta_0$ from the one which is commonly used by some other authors.) Detailed analysis of the data is not possible because the measurements of P_0 and θ_0 in Ref. 11 were performed on a different sample with a different transition temperature. Further on the reported values of θ_0 correspond to the tilt at a given value of external electric field and not to the spontaneous tilt.

Finally, we would like to discuss the behavior of the relaxation frequencies at T_c. From a general point of view, amplitude and phase fluctuations would be expected to be degenerate at T_c. Thus we expect the relaxation frequencies f_G, f_S, and f_A to be degenerate at the phase transition. This is also predicted by our theoretical model, from which if we replace $K_3 - \epsilon\mu^2$ with K_3 also in Eq. (4b) we obtain

$$f_G(T_c) = f_S(T_c) = f_A(T_c) = \frac{\Gamma K_3}{2\pi}q_0^2 . \tag{8}$$

It is hard to see from the experimental values of Fig. 4 if this relation is fulfilled or not. Due to the large slope of the curves of the soft mode relaxation frequencies, a very accurate determination of T_c is needed in order to establish a correct value of $f_A(T_c)$. Belonging to the same mode, $f_S(T_c) = f_A(T_c)$ and we can determine this value as the intersection of the corresponding two lines. However, the data of $f_S(T)$ are scarce for $T < T_c$ and suffer from a relatively large experimental inaccuracy since it is obtained as the background of the large Goldstone-mode response. It is clear from Fig. 7 that our theoretical model fails to describe the behavior of the system close T_c. On the other hand any theoretical model which is built with the underlying assumption that amplitude and phase fluctuations are degenerate at T_c will also lead to the result that the relaxation frequencies are degenerate at this temperature. We thus would like to leave this question open and conclude that more careful measurements close to T_c have to be performed in order to establish the final solution to this problem

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