PHYSICAL REVIEW E **71**, 041704 (2005)

Dielectric spectroscopy of de Vries-type smectic-A^*–smectic-C^* transitions

Michael Krueger and Frank Giesselmann*
Institute for Physical Chemistry, University of Stuttgart, D-70550 Stuttgart, Germany

(Received 6 December 2004; revised manuscript received 18 January 2005; published 25 April 2005)

We report results of dielectric investigations on a number of ferroelectric liquid crystalline (FLC) compounds with different degrees of layer shrinkage in the smectic-A^*–smectic-C^* phase transitions. With a decreasing extent of layer shrinkage the investigated FLCs exhibit a significantly increasing soft-mode absorption, decreasing leading Landau coefficient α, and a considerably broader mean-field regime. We explain these tendencies by the fact that the low layer shrinkage materials come closer to the diffuse cone model of de Vries than to the common model of rigid rods which maintain their orientational order during tilting. In the case of the diffuse cone model the tilt-angle fluctuations are decoupled from variations of the smectic layer spacing, which explains the observed behavior.

DOI: 10.1103/PhysRevE.71.041704 PACS number(s): 61.30.−v, 64.70.Md, 77.22.Gm, 77.80.Bh

I. INTRODUCTION

Chiral liquid crystals possessing a smectic-C^*(Sm-C^*) phase are often called ferroelectric liquid crystals (FLCs) as surface stabilization in thin cells leads to the appearance of a macroscopic spontaneous polarization $\mathbf{P}_s$ in the Sm-C^* phase, which is switchable between two stable states $+\mathbf{P}_s$ and $-\mathbf{P}_s$ [1]. When lowering the temperature below the transition temperature T_C of the second-order smectic-A^*(Sm-A^*) to smectic-C^* transition, the director $\mathbf{n}$ continuously inclines with decreasing temperature against the smectic layer normal $\mathbf{z}$. The resulting nonzero angle Θ between $\mathbf{n}$ and $\mathbf{z}$ is a necessary requirement for the occurrence of a spontaneous polarization in chiral smectics [2].

In common ferroelectric liquid crystals the inclination of the optic axis Θ_{opt} (the optical tilt angle), which is generally a good measure of Θ [3], is connected to a significant shrinkage of the smectic layer thickness d. This is often explained by a molecular tilt of the same magnitude as the optical tilt, assuming the molecules behave as rigid rods. Using this approximation, the smectic layer spacing d_C in Sm-C^* decreases as

$$d_C = d_A \cos\Theta \approx d_A \cos\Theta_{\mathrm{opt}} \tag{1}$$

compared to the smectic layer spacing d_A in the Sm-A^* phase. The layer spacing in the Sm-C^* phase thus becomes temperature dependent through the temperature dependence of the director tilt angle. Figure 1 schematically illustrates the layer shrinkage due to the molecular tilt. However, measurements of d by means of small-angle x-ray scattering (SAXS) and measurements of Θ_{opt} revealed that Eq. (1) does not hold quantitatively for a broad variety of smectic liquid crystals, as different materials show a varying degree of shrinkage during the tilting transition [4].

When Diele *et al.* [5] found a virtually temperature independent layer spacing for a number of compounds in 1972 this stimulated academic interest only. But as it was recognized that the main obstacle in the application of FLCs in displays is the formation of so-called chevrons [6], which are induced by the competition between surface anchoring and layer shrinkage, the interest in non-layer-shrinkage materials increased significantly. Chevrons are folding instabilities of the smectic layer structure and lead to zigzag defects at the domain boundaries of different fold directions. These zigzag defects degrade the brightness and contrast of FLC displays, disadvantages that could be avoided by using non-layer-shrinkage materials.

A nowadays widely accepted explanation of the absence of layer shrinkage in some materials was first proposed by the crystallographer de Vries [7], who proposed (based on the experimental data of Diele *et al.*), that the molecules in Sm-A phases are already tilted, but in random directions. This is supported by the fact that the orientational order parameter S_2 in the Sm-A phase is well below unity, meaning that the orientational order is far from being perfect. However, this molecular tilt does not lead to a macroscopically observable tilt, as the molecules do not possess a long-range order of the *direction* of tilt. When reducing the temperature below the critical temperature T_C the molecular tilting directions become ordered and a macroscopic optical tilt angle $\Theta_{\mathrm{opt}} > 0$ appears in the Sm-C phase, without any reduction of the smectic layer spacing. A scheme of this de Vries-type Sm-A^*–Sm-C^* transition is shown in Fig. 2.

In the rigid-rod approximation for common smectic liquid crystals, director tilt-angle fluctuations are coupled to fluctuations of the smectic layer spacing, whereas in non-layer-shrinkage materials (which are nowadays often called de Vries materials) such fluctuations should have no influence

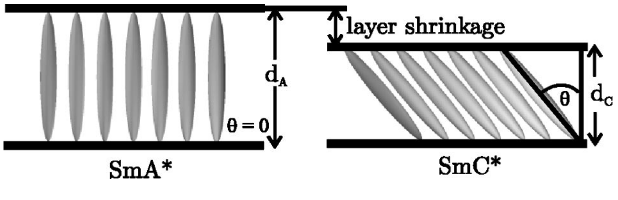

FIG. 1. Difference between the smectic layer spacing d_A in Sm-A^* (left) phases and d_C in Sm-C^* (right) phases according to the orientationally ordered rigid-rod approximation. When going from Sm-A^* to Sm-C^* the layer spacing is reduced by a factor of $\cos\Theta$.

---

*Electronic address: f.giesselmann@ipc.uni-stuttgart.de

1539-3755/2005/71(4)/041704(8)/$23.00

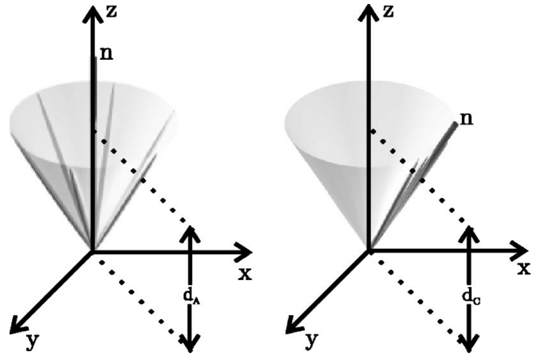

FIG. 2. de Vries model for explaining how the Sm-A^* layer spacing d_A (left) can be equal to the Sm-C^* spacing d_C (right). In the Sm-A^* phase the molecules are already inclined, but as the tilting direction is random, the director **n** is parallel to the smectic layer normal **z**, resulting in a vanishing macroscopic tilt angle $\Theta = 0$. When decreasing the temperature below the critical temperature of the Sm-A^*–Sm-C^* transition, the directional distribution is ordered, producing a director **n** that is no longer parallel to the smectic layer normal **z**, but inclined by a macroscopic tilt angle $\Theta > 0$. For simplicity, the cone is drawn with only one value of molecular tilt which is definitely not the case in reality. Indeed, the name of this model, the “diffuse cone model,” reflects the large fluctuations in molecular tilt.

on d. The main motivation of the work presented here was to investigate tilt-angle fluctuations of de Vries materials and to compare them with those of common FLCs. According to the fluctuation dissipation theorem [8,9] these fluctuations are detected by the corresponding relaxation observed in dielectric spectroscopy. To the best of the authors’ knowledge dielectric investigations of de Vries materials were never carried out in any systematic way before. As expected, major differences were observed which could be explained by the decoupling of tilt and layer spacing.

II. EXPERIMENT

The FLCs investigated were a semifluorinated phenylpyrimidine 8422[2F3] (in the following referred to as 3M FLC) with a virtually constant layer spacing [4], a homologous series of hexyl lactates (nHL) where the extent of layer shrinkage increased with the length of the alkyl chain, and a commercial mixture (Felix 017/100) exhibiting layer shrinkage. The de Vries material 3M FLC was provided by the 3M Company, St. Paul, MN, and has the structure and phase sequence shown in Fig. 3. The transition temperatures were determined by differential scanning calorimetry (DSC) and optical microscopy [4]. The homologous nHL series (Fig. 4) with $n=9,10,12$ for the number of carbon atoms in the alkoxy chain was synthesized by Kašpar *et al.* [10]. Electro-optical investigations and SAXS measurements for members of the nHL series were previously published by Giesselmann and co-workers [11,12]. The phase sequences for each homolog, which were determined by DSC, are shown in Table I.

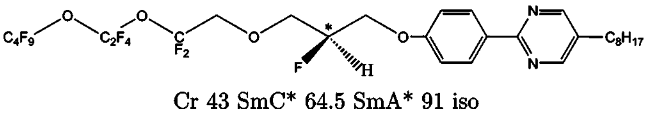

FIG. 3. Structure and phase sequence of the ferroelectric liquid crystal 3M FLC. The chiral center is indicated by a star.

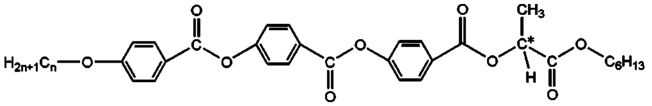

FIG. 4. Structure of the homologous series of ferroelectric liquid crystals nHL with $n=9,10,12$. The transition temperatures are listed in Table I.

As a regular FLC reference material we chose the FLC mixture Felix 017/100 (Clariant, Frankfurt, Germany) with a phase sequence of

$$\mathrm{Cr} \underset{-28\,^\circ\mathrm{C}}{\leftrightarrow} \text{Sm-}C^* \underset{73\,^\circ\mathrm{C}}{\leftrightarrow} \text{Sm-}A^* \underset{77\,^\circ\mathrm{C}}{\leftrightarrow} N^* \underset{85\,^\circ\mathrm{C}}{\leftrightarrow} \mathrm{Iso}.$$

SAXS measurements revealed a substantial layer shrinkage of about 4.9% throughout the A^* to C^* transition. A comparison of the relative layer shrinkages $d_{AC}-d_C/d_{AC}$ of all investigated compounds is found in Table II. The value d_C is the smectic layer spacing in the Sm-C^* phase 15 K below the transition temperature, d_{AC} the layer spacing at the Sm-A^*–Sm-C^* transition. As it is seen from Table II the degree of layer shrinkage in these materials increases according to the series

$$3\mathrm{M\ FLC} < 9\mathrm{HL} < 10\mathrm{HL} < \mathrm{Felix} < 12\mathrm{HL}.$$

For 3M FLC and Felix the temperature dependence of the smectic layer spacing is illustrated in Fig. 5.

Samples of all these materials were filled by means of capillary action into low-resistive polyimide-coated cells (for planar alignment) with indium tin oxide electrodes (MC2, Chalmers University of Technology, Gothenburg, Sweden) of 1.5 and 23.5 μm cell gap with an active electrode area of 4×4 mm^2.

A Hewlett-Packard impedance analyzer HP4192A was used to measure the dielectric dispersion (ε') and absorption (ε'') in the frequency range from 5 Hz to 13 MHz. The temperature of the sample was regulated by a Novotherm temperature controller (Novocontrol, Hundsangen, Germany) with a resolution of 0.1 °C.

TABLE I. Phase sequence of the homologous series nHL observed by differential scanning calorimetry. Transition temperatures in °C.

	Cr–Sm-C^*	Sm-C^*–Sm-A^*	Sm A^*–iso
9HL	40	64	138
10HL	50	85	133
12HL	50	102	126

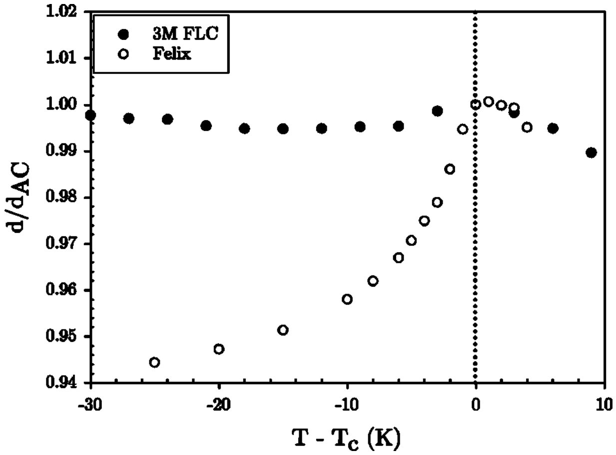

FIG. 5. Temperature dependence of the reduced smectic layer spacing d/d_{AC} of 3M FLC (filled symbols) and Felix (empty symbols) obtained by small-angle x-ray scattering (SAXS) where d_{AC} is the smectic layer spacing at the Sm-A^*–Sm-C^* transition. 3M FLC exhibits a virtually constant layer thickness throughout the transition. For Felix the layer spacing decreases significantly with temperature. SAXS data for 3M FLC reproduced from [4].

III. RESULTS AND DISCUSSION

A. Soft-mode absorption

The dielectric absorption spectra $\varepsilon''(f,T)$ of 3M FLC, 9HL, and Felix obtained in thin cells (1.5 μm) and in the absence of any dc-bias voltage are depicted in Fig. 6. Comparing these spectra, one can easily see a significant difference in the absolute values of the dielectric absorption at the transition temperature. The collective mode appearing around the Sm-A^*–Sm-C^* transition temperature is the so-called soft mode and corresponds to fluctuations of the tilt angle (electroclinic effect). We will restrict ourselves to considerations of the soft mode, as we are mainly interested in fluctuations of the tilt angle. The Goldstone mode, the second collective mode, which is active in the Sm-C^* phase only, is influenced by effects like surface anchoring which can hardly be quantified. The soft-mode absorption for the de Vries materials reaches values of approximately $\varepsilon''=35.6$ (3M FLC) and 17.9 (9HL) and is even larger than the Goldstone-mode absorption. Despite the fact that in these small cells the Goldstone mode is suppressed by surface effects, this is still a very rarely observed feature. In clear contrast, the soft mode of the mixture Felix is not visible as it is covered by the Goldstone mode. Hence ε'' due to the soft-mode absorption in Felix has to be smaller than 3. For 10HL and 12HL the Goldstone mode was also dominating, so that the soft-mode absorption could not be distinguished from the Goldstone mode.

Since the suppression of the Goldstone-mode absorption by an additionally applied dc-bias field is far more effective than the suppression of the soft-mode absorption [13], one can easily make the soft mode visible by applying such a field. The next series of measurements presented in Fig. 7 are the dielectric absorption spectra for 3M FLC, 9HL, and Felix under an applied dc bias of 3.5 V (over 1.5 μm). The dielectric susceptibilities χ_s of the soft modes corresponding to approximately twice the maximum absorption ε'' are listed in Table III. The fitting procedure to obtain χ_s is explained in Sec. III B. Selected examples of measurements at $T=T_C$ are depicted in Fig. 8.

TABLE II. Summary of the relative layer shrinkage $(d_C - d_{AC})/d_{AC}$ of the ferroelectric liquid crystals investigated. The value d_C is the layer spacing 15 K below the A^*-C^* transition temperature, d_{AC} the layer spacing at the transition temperature.

	3M FLC	9HL	10HL	Felix	12HL
$\frac{(d_{AC}-d_C)}{d_{AC}}$	0.5%	1.8%	3.4%	4.9%	6.4%

In order to reduce surface effects, measurements were repeated in 23.5 μm thick cells. For a dc bias of 10 V we obtain the fitted soft-mode dielectric susceptibilities χ_s listed in the bottom of Table III. These measurements yield the same series of decreasing dielectric soft-mode absorption like those for the thin cells:

$$\text{3M FLC} \gg \text{9HL} > \text{12HL} > \text{10HL} > \text{Felix}.$$

Except for the position of 12HL (which has a higher soft-mode absorption than expected, a fact that can be explained in part by its large spontaneous polarization) this is the same series as for the increasing extent of Sm-C^* layer shrinkage. The typical de Vries materials thus exhibit the largest soft-mode absorptions. The exceptionally strong soft-mode fluctuations of de Vries materials correspond to the recent investigations of Huang *et al.* [14], who found pronounced critical fluctuations at the A^*-C^* transition of 3M FLC in calorimetric experiments.

This correlation can be explained by considering that the major part of the restoring force to the tilt-angle fluctuations (soft-mode fluctuations) generally should be the elastic energy associated with tilt-induced changes of the smectic layer spacing. The smaller the smectic layer shrinkage in these materials, the smaller the elastic energy needed to change the director tilt and, consequently, the smaller the restoring force to the tilt-angle fluctuations. In other words, the weaker the coupling between tilt and layer spacing, the stronger the soft-mode absorption.

B. Curie-Weiss regime

In order to come to a more quantified description of the soft-mode behavior we analyzed the experimental data by means of the Cole-Cole [15] equation

$$\varepsilon^*(\omega) = \sigma(\omega) + \varepsilon_\infty + \sum_{k=1}^{n} \frac{\chi_k}{1 + (i\omega\tau_k)^{\alpha_k}} \tag{2}$$

where $\varepsilon^*(\omega)=\varepsilon' + i\varepsilon''$ is the complex dielectric permittivity, and n denotes the number of modes that contribute to the spectrum in the investigated frequency range. Each mode k is

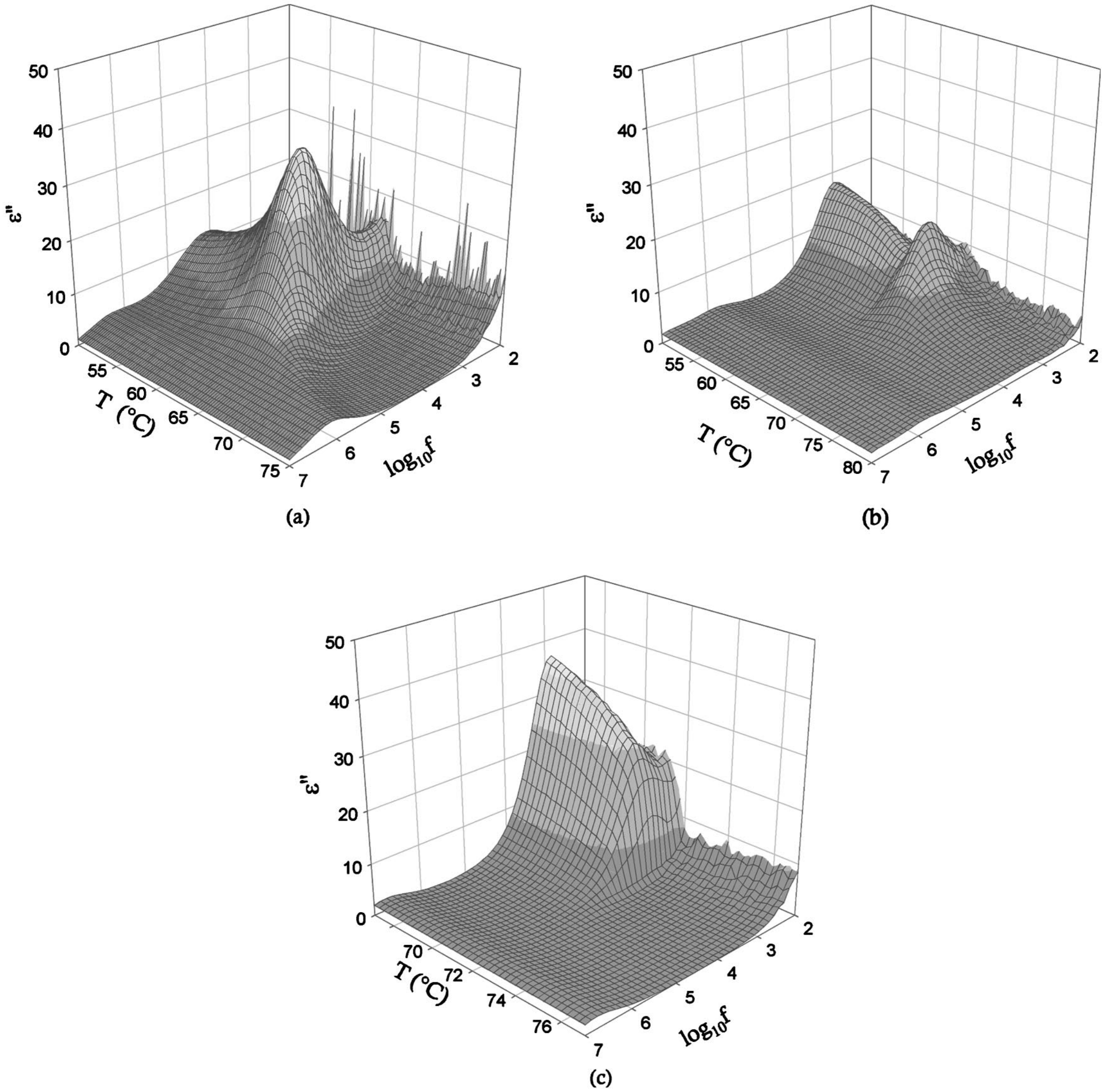

FIG. 6. Dielectric absorption (ε'') spectra under a dc-bias field of 0 V over a sample thickness of 1.5 μm in dependence on temperature T and frequency f. For 3M FLC (a) the soft-mode absorption at the Sm-A^*–Sm-C^* transition temperature with a magnitude of $\sim$35 is larger than the Goldstone-mode absorption in the Sm-C^* phase even without an applied dc-bias field. For 9HL (b) the soft mode with a magnitude of $\sim$18 is as large as the Goldstone mode. For the common ferroelectric liquid crystals Felix (c) the soft-mode absorption is too small to be observed compared to the Goldstone-mode absorption.

characterized by its (static) dielectric susceptibility χ_k,[1] distribution parameter α_k, and relaxation time $\tau_k = 1/(2\pi f_k)$, with f_k being the maximum-absorption frequency of the mode. The angular frequency of the applied field is $\omega = 2\pi f$, ε_∞ is the high-frequency permittivity, and $\sigma(\omega)$ is a term related to the dc conductivity of the sample. The introduction of an asymmetric distribution parameter (as in the Havriliak-Negami equation [16]) was not necessary to fit the equation to the experimental data. Based on about 3500 single fits we obtained the soft-mode susceptibility χ_s, absorption frequency f_s, and distribution parameter α_s for any given material, dc-bias field, and each temperature measured.

As a basic result of mean-field theory the susceptibility χ of order-parameter fluctuations around a second-order transition point T_C (like the soft-mode susceptibility χ_s in our case) diverges according to

$$\chi = \frac{1}{m(T - T_C)}, \tag{3}$$

where m is a constant. The plot of the reciprocal dielectric susceptibility $1/\chi_s$ as a function of the difference between temperature and transition temperature $T - T_C$ is the so-called Curie-Weiss plot, the transition temperature being the Curie point. Examples of the Curie-Weiss plots for 3M FLC, 9HL, and Felix are shown in Fig. 9.

---

[1] Although the notation "dielectric increment $\Delta\varepsilon_k$" of the modes is often used in the literature, we prefer to use the "mode susceptibility χ_k" in order to prevent mix-ups with the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$.

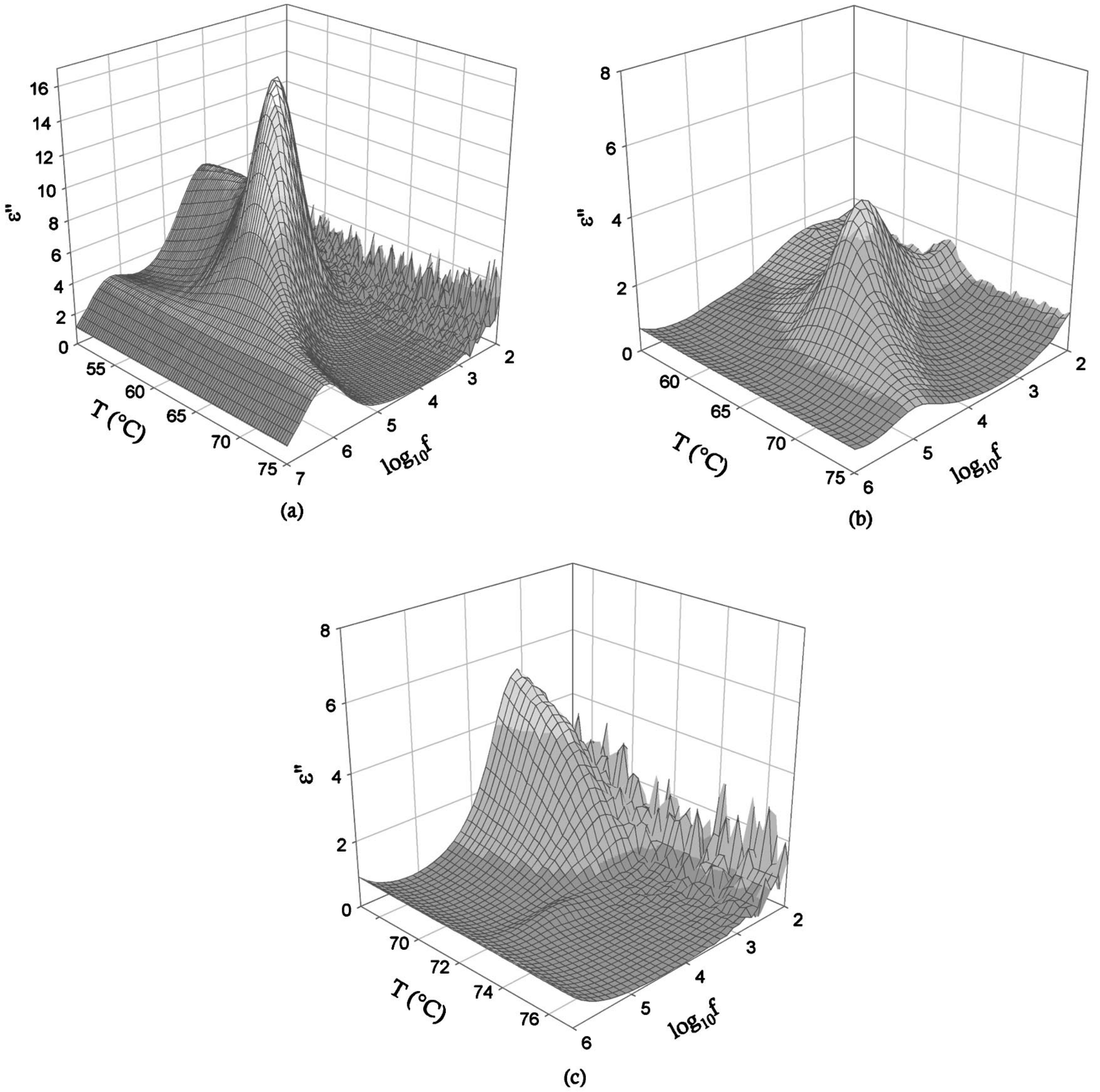

FIG. 7. Dielectric absorption (ε'') spectra under a dc-bias field of 3.5 V over a sample thickness of 1.5 μm in dependence on temperature T and frequency f. For 3M FLC (a) the soft-mode absorption has still a magnitude of ~14, and for 9HL (b) still ~9. Due due the stronger suppression of the Goldstone mode, the soft-mode absorption becomes visible for Felix (c) under the applied dc-bias field and has a magnitude of ~0.6. Please note the different scaling of the plot for 3M FLC.

The ratios of the slopes m_{C^*}/m_{A^*} in these plots (as well as in those for all other dc-bias fields for which the Cole-Cole equation was fitted to the dielectric data in the same way) are in good accordance with the theoretical value [13] of -2 over a certain temperature range. This temperature range corresponds to the mean-field regime (the Curie-Weiss law is valid in this regime only) characterized by

TABLE III. Summary of the dielectric susceptibilities of the soft modes χ_s of the ferroelectric liquid crystals investigated in 1.5 μm cells with an applied dc bias of 3.5 V and in 23.5 μm cells with an applied dc bias of 10 V at the respective A^*-C^* transition temperatures.

	3M FLC	9HL	10HL	Felix	12HL
χ_s, d=1.5 μm	28.80	9.08	4.85	1.20	5.20
χ_s, d=23.5 μm	64.93	24.01	8.18	0.30	17.05

$$T_C - T_0 \approx \frac{3b^2}{4\alpha c} \tag{4}$$

where T_0 is the crossover temperature from mean-field to tricritical behavior and α, b, and c are the coefficients from a Landau expansion of the free energy density g,

$$g = g_0 + \frac{1}{2}\alpha(T - T_C)\Theta^2 + \frac{1}{4}b\Theta^4 + \frac{1}{6}c\Theta^6 + \cdots , \tag{5}$$

with the tilt angle Θ and a nonsingular term g_0 in the free energy corresponding to Sm-A^*.

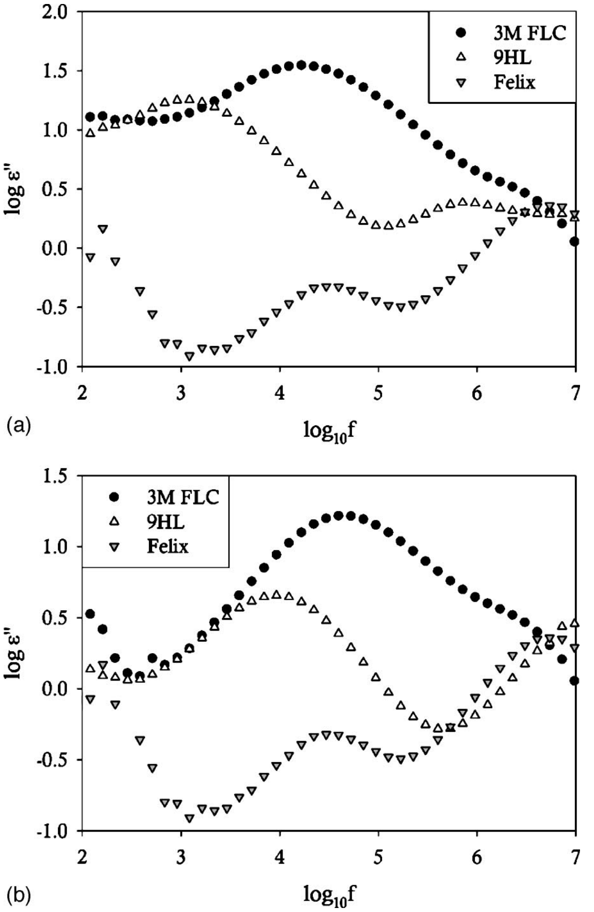

FIG. 8. Dielectric absorption $\varepsilon''(f)$ at the A^*-C^* transition temperature T_C of 3M FLC, 9HL, and Felix at 0 (a) and 3.5 (b) V bias. Note that the soft-mode absorption of Felix at $\log_{10} f \approx 4.5$ is about 2 orders of magnitude weaker than in the de Vries compounds 3M FLC and 9HL.

As one can see from Fig. 9 the Curie-Weiss regime is far broader for 3M FLC (~22 K) than for 9HL (~10 K), which in turn has a much broader range than Felix (~4.5 K). This again leads to the same series as that of decreasing extent of layer shrinkage for these materials.

It should also be noted that the absolute values of the slopes are significantly larger for Felix than for the de Vries compounds. The reason for this is simply that Felix exhibits a drastically weaker soft-mode absorption, as described in Sec. III A. Therefore $1/\chi_s$ as well as the temperature variations in $1/\chi_s$ become large, which is reflected by a high value of m_{A^*} in Eq. (3).

TABLE IV. Slopes $m_{P\Theta}$ from the plot of polarization vs tilt angle, values of the slopes m_{A^*} from the Curie-Weiss plots, and resulting coefficients α for 3M FLC, 9HL, and Felix. In the case of 3M FLC and 9HL m_{A^*} is basically independent of the electric bias field applied, whereas for Felix m_{A^*} varies between 4.6 K^{-1} (at 3.3 MV m^{-1} bias) and 3.2 K^{-1} (at 4.7 MV m^{-1} bias).

Liquid crystal	$m_{P\Theta}$ (nC cm^{-2})	m_{A^*} (K^{-1})	α (kN m^{-2} K^{-1})
3M FLC	185	0.024	9.4
9HL	201	0.039	18
Felix	100	3.2–4.6	430

Assuming that the coefficients b and c should be in the same order of magnitude for all substances, a smaller value of the leading Landau coefficient α for the materials with smaller layer shrinkage should according to Eq. (4) lead to the observed broadening of the Curie-Weiss regime in these materials. This coefficient represents a measure of the ease of changing the tilt angle by small external perturbations. Physically speaking, our explanation of the larger dielectric soft-mode absorption in the low-layer-shrinkage materials in Sec. III A should indeed lead to a smaller coefficient α, as a small restoring force to the tilt-angle fluctuations means that changes in these fluctuations can easily be achieved by external perturbations.

C. The Landau coefficient α

Blinc and Zěkš [17] calculated the dielectric susceptibility of the soft mode in Sm-A^* phases $\chi_s^{A^*}$ to

$$\chi_s^{A^*} = \frac{\varepsilon_0 C^2 \chi_\infty^2}{\alpha(T - T_C)} \tag{6}$$

where ε_0 is the dielectric permittivity of vacuum, $\chi_\infty = (\varepsilon_\infty - 1)$, and C the coupling constant between tilt angle and polarization according to the equation (valid for small tilt)

$$P = \chi_\infty \varepsilon_0 C \Theta + \chi_\infty \varepsilon_0 E. \tag{7}$$

From Eq. (6) the slope of the Curie-Weiss plot in the Sm-A^* phase is obtained as

$$m_{A^*} = \frac{\alpha}{\varepsilon_0 C^2 \chi_\infty^2}. \tag{8}$$

On the other hand, one can easily see from Eq. (7) that plotting the polarization P as a function of the tilt angle Θ leads to a slope $m_{P\Theta}$ of

$$m_{P\Theta} = \chi_\infty \varepsilon_0 C. \tag{9}$$

By inserting $C^2\chi_\infty^2$ from Eq. (9) into Eq. (8) one obtains the following expression for the coefficient α:

$$\alpha = \frac{m_{A^*} m_{P\Theta}^2}{\varepsilon_0}. \tag{10}$$

The slopes m_{A^*} were directly taken from the Curie-Weiss plots and represent averages over all investigated dc-bias fields. The polarization and tilt-angle data were provided by 3M [18] for 3M FLC and our group for 9HL [12] and Felix [19]. The resulting values for α are shown in Table IV. The data for 10HL and 12HL were not analyzed, as these compounds have completely different spontaneous polarizations $\mathbf{P}_s$ and bilinear coupling coefficients C. Therefore, they are difficult to compare to the other substances.

As expected, 3M FLC possesses the smallest coefficient α, followed by 9HL. Felix contrasts with an α value that is between 1 and 2 orders of magnitude larger. It has to be

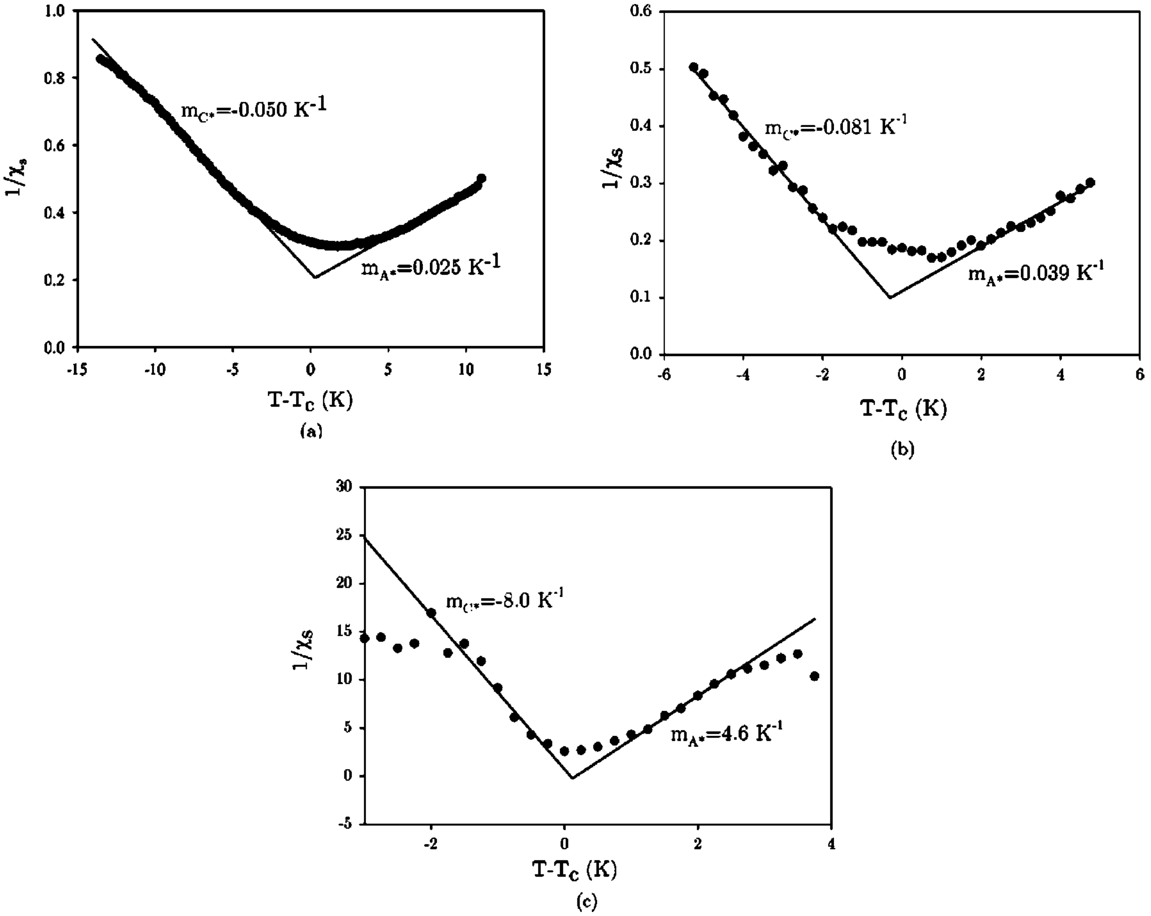

FIG. 9. Curie-Weiss plots of the reciprocal dielectric soft-mode susceptibility $1/\chi_s$ vs difference between temperature and transition temperature $T-T_C$. For 3M FLC (a) the temperature range in which the Curie-Weiss law is valid (mean-field regime) is far broader (~22 K) than for 9HL (b) (~10 K) and Felix (c) (~4.5 K). All ratios of the slope in the Sm-C^* phase to the slope in the Sm-A^* phase m_{C*}/m_{A*} (a) −2.0, (b) −2.1, and (c) −1.7 are in good accordance with the theoretical value of −2. The weak soft-mode response in the case of Felix leads to considerable deviations from the Curie-Weiss behavior as well as increased scattering in comparison to the data obtained for the de Vries compounds.

stressed that the method used to evaluate α is an estimation, not an exact calculation, due to the uncertainties in the calculation of the slope from the polarization and tilt-angle data. However, these estimates lend strong support to the idea of a weaker coupling between changes of the tilt angle and changes of the smectic layer spacing in de Vries materials as the cause for the observed differences compared to regular ferroelectric liquid crystals.

IV. CONCLUSION

We have shown for the investigated FLCs that with a decreasing extent of layer shrinkage the dielectric soft-mode absorption significantly increases, the leading Landau coefficient α decreases and, therefore, the mean-field regime in which the Curie-Weiss law applies becomes considerably broader. This was explained by the fact, that for materials with a lower extent of layer shrinkage the tilt-angle fluctuations are decoupled from variations of the smectic layer spacing.

These results, especially the fact that all the differences are gradual tendencies correlated with the degree of layer shrinkage, indicate that the two existing models to explain the behavior of the smectic layer spacing at the phase transition are idealized borderline cases and that the behavior of ferroelectric liquid crystals which is observed in reality can be explained to a greater or lesser extent by a combination of both models.

ACKNOWLEDGEMENTS

The authors thank Dr. Jan Lagerwall for stimulating discussions and comments on the manuscript. M.K. gratefully acknowledges financial support by the International Max Planck Research School for Advanced Materials (IMPRS-AM).

[1] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).
[2] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris), Lett. **36**, L69 (1975).
[3] F. Giesselmann, A. Langhoff, and P. Zugenmaier, Liq. Cryst. **23**, 927 (1997).
[4] J. P. F. Lagerwall, F. Giesselmann, and M. Radcliffe, Phys. Rev. E **66**, 031703 (2002).
[5] S. Diele, P. Brand, and H. Sackmann, Mol. Cryst. Liq. Cryst. **16**, 105 (1972).
[6] S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals* (Wiley-VCH, Weinheim, 1999).
[7] A. de Vries, Mol. Cryst. Liq. Cryst. Lett. **41**, 27 (1977); A. de Vries, A. Ekachai, and N. Spielberg, *ibid.* **49**, 143 (1979).
[8] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).
[9] F. Kremer and A. Schönhals, *Broadband Dielectric Spectroscopy* (Springer-Verlag, Berlin, 2003).
[10] M. Kašpar, V. Hamplová, S. Pakhomov, A. Bubnov, F. Guittard, H. Sverenyak, I. Stibor, P. Vanek, and M. Glogarová, Liq. Cryst. **24**, 599 (1998).
[11] F. Giesselmann, P. Zugenmaier, I. Dierking, S. T. Lagerwall, B. Stebler, M. Kašpar, V. Hamplová, and M. Glogarová, Phys. Rev. E **60**, 598 (1999).
[12] S. Bezner, M. Krueger, and F. Giesselmann (unpublished).
[13] F. Gouda, K. Skarp, and S. T. Lagerwall, Ferroelectrics **113**, 165 (1991).
[14] C. C. Huang, S. T. Wang, X. F. Han, A. Cady, R. Pindak, W. Caliebe, K. Ema, K. Takekoshi, and H. Yao, Phys. Rev. E **69**, 041702 (2004).
[15] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[16] S. Havriliak and S. Negami, J. Polym. Sci., Part C: Polym. Symp. **14**, 99 (1966).
[17] R. Blinc and B. Zĕkš, Phys. Rev. A **18**, 740 (1978).
[18] M. Radcliffe (private communication).
[19] S. Bezner (private communication).