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THE THICKNESS MODE CONTRIBUTION TO THE PERMITTIVITY OF FERROELECTRIC LIQUID CRYSTALS

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Abstract Dielectric properties of a material prepared of valine in the ferroelectric SmC* phase are studied in the frequency range 100 Hz ÷ 1 MHz and for the sample thickness d between 6 and 100 μm for both helicoidal and twisted sample structure. In all studied samples a low frequency relaxation has been found with the relaxation frequency proportional to $1/d^2$ and with the contribution to permittivity proportional to d^2. We suggest this relaxation to be assigned to a 'thickness mode', which is a fluctuation of the molecular twist existing within the smectic layers in the direction of the sample plane normal. This twist deformation existing in both helicoidal and twisted samples is fixed by the anchoring on the sample surfaces. It is shown that the thickness mode is an important source of permittivity in the SmC* phase of the studied material.

INTRODUCTION

In ferroelectric liquid crystals (FLC) the static dielectric susceptibility χ, which describes the linear dielectric response $P = \varepsilon_0 \chi E$ is produced mainly by a low frequency mechanism with a typical relaxation frequency 0.1 ÷ 5 kHz. This mechanism is used to be ascribed to the Goldstone mode connected with the helicoidal structure in the ferroelectric SmC* phase, which is a fluctuation of director azimuthal angle with the wave vector $q = 4\pi / p$ (p is the helix pitch) directed along the smectic layer normal. The other contribution to χ is connected with the soft mode, which is a fluctuation of the tilt angle Θ of molecules from the smectic layer normal. The soft mode contribution is much smaller than the Goldstone mode one, its relaxation frequency is typically 10 ÷ 100 kHz. It is measurable near above the ferroelectric phase transition temperature T_C, below T_C it is overwhelmed by the low frequency mechanism.

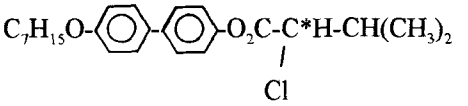
In sufficiently thin samples where the helicoidal structure is not present being unwound by the surface interaction[1] a low frequency dielectric contribution in the SmC* phase is also detected.[2] Its magnitude is comparable or higher than that in the helicoidal samples. We suggest this contribution is brought about by a 'thickness mode', which is a fluctuation of the molecular twist existing within the smectic layers in the direction of the sample plane normal. This twist deformation fixed by the polar planar anchoring on the sample surfaces is a change of azimuthal angle φ by π when going from one sample surface to the other.[3]

Preliminary considerations suggest that the contribution of the thickness mode might be thickness dependent. This idea is verified by the study of thickness dependence of dielectric properties of a material prepared of valine, which exhibits SmA $\rightarrow$ SmC* phase transition and forms non-helicoidal twisted structure in samples up to the thickness of 100 μm.

In the discussion of experimental results it is also shown that the thickness mode can explain the high values of permittivity in the ferroelectric SmC* phase which cannot originate in the Goldstone mode only.

EXPERIMENTAL RESULTS

The used liquid crystalline material



exhibits a phase sequence

SmG* 70.3 SmC* 73.1 SmA 81.1 Isotropic.

The samples confined between two electroded glass plates have got the 'bookshelf geometry'. The planar molecular anchoring has been achieved by rubbing of polymer layers on the glass plates. The alignment has been improved by application of the electric field 20 Hz, 4×10^3 kV/m in the SmA phase. The electrode area was 25 mm^2, the sample thicknesses $d = 6$, 12, 25, 50, and 100 μm were fixed by spacers.

The alignment and sample textures have been observed in the polarizing microscope.

Texture observations

When the samples have been slowly cooled to the SmC* phase without an application of electric field, no dechiralization lines appear below the phase transition. This state usually persists within the whole temperature range where the SmC* phase exists, except for the thick samples (d = 50 and 100 μm). With these samples the lines gradually spontaneously appear 1 or 2 K below T_C. On the other hand, a weak a.c. field applied anywhere in the SmC* phase induces an arising of dechiralization lines, which can persist even if the field is gradually diminished. In this way, it is possible on one sample to create a texture with and without lines.

The texture with the lines corresponds to the helicoidal sample structure with the helix pitch equal to the line distance.[3] It is about 5 μm. The structure of lines-free samples is non-helical, but twisted along the sample thickness due to the polar anchoring on the sample surfaces. Such a structure is typical of samples with d comparable to the pitch length,[2,3] but the our material under study exhibits it with all the samples under study. The disposition not to form the helicoidal structure seems to be common with all SmC* material with high spontaneous polarization P_S. The helix is inevitably accompanied with the dechiralization lines which are charged, the charge being proportional to P_S. The high charge of lines can cause the helicoidal structure with the lines becomes energetically disadvantageous.

Dielectric study

The permittivity measurements were performed at temperatures T_C −0.5 K and T_C −1.5 K stabilized to 0.05 K, using a Hewlett-Packard 4192A impedance analyzer in the frequency range 100 Hz ÷ 1 MHz. The frequency dependences of the real (ε') and imaginary (ε") parts of permittivity are shown in Figs. 1a,b for all studied samples without dechiralization lines. For the helicoidal samples (with the dechiralization lines) the character of dependences is the same. In Figs. 1a,b the results measured at T_C −0.5 K are shown. The same set of results has been obtained at the temperature T_C −1.5 K.

By fitting the Cole- Cole formula

$$\varepsilon^*(f) = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (jf/f_r)^{1-\alpha}}$$

on both measured $\varepsilon'(f)$ and $\varepsilon''(f)$, the contribution of the relaxation process $\Delta\varepsilon' = \varepsilon_0 - \varepsilon_\infty$ to the real part of permittivity and the relaxation frequencies f_r are determined. The results are summarized in Figs. 2a,b for both helicoidal and twisted samples. An pronounced thickness dependence is seen for both quantities. It can be seen that as for $\Delta\varepsilon'$ the results are nearly the same for both types of sample structure up to d = 25 μm.

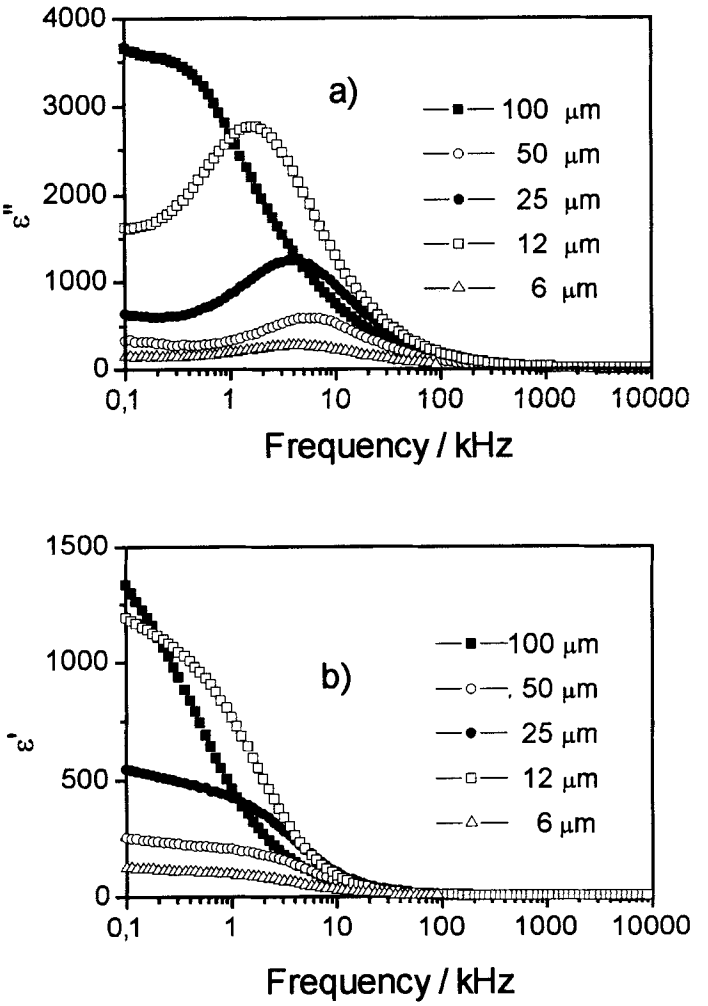


FIGURE 1 Frequency dependence of the imaginary (a) and the real (b) parts of permittivity at $T = T_C - 0.5$ K on twisted samples (without dechiralization lines) of different thicknesses.

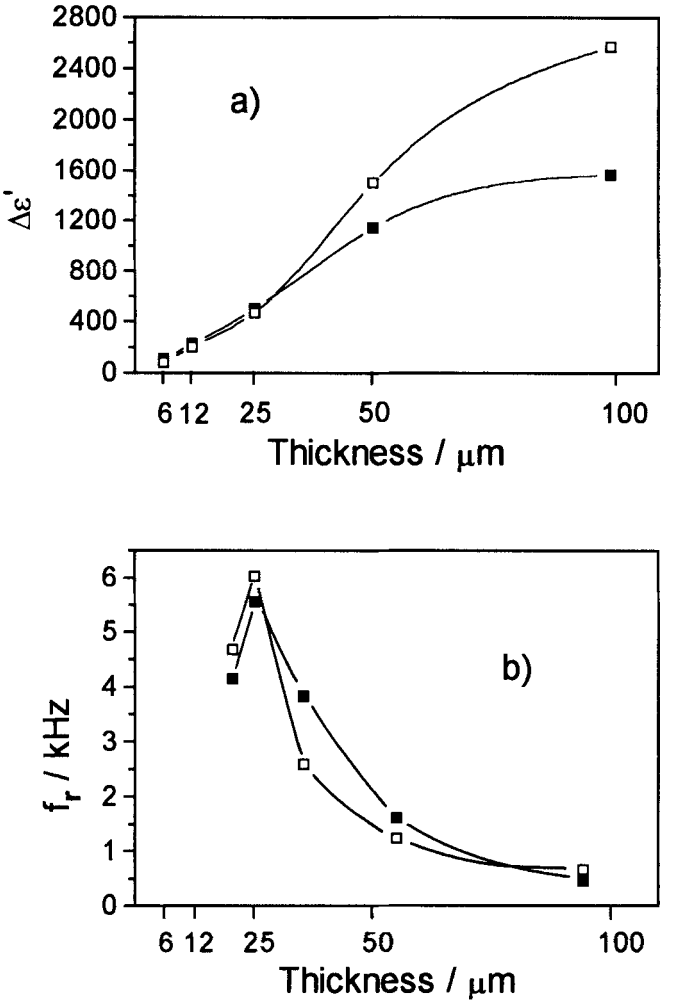


FIGURE 2 Contribution to permittivity of a low frequency relaxation (a) and its relaxation frequency (b) as a function of the sample thickness. The data for twisted ■ and helicoidal ▫ samples are shown.

Only for higher d the helicoidal samples exhibit higher $\Delta\varepsilon'$ than the twisted ones. As for relaxation frequencies (see Fig. 2b), no significant difference is observed between helicoidal and twisted samples. The relaxation frequency is decreasing with increasing d, except for the sample with $d = 6$ μm, which is out of the monotoneous curve.

The temperature dependence of ε' has been measured for all studied samples at the frequency 200 Hz during slow continuous cooling. A detailed study in the paraelectric SmA phase of this material has been performed in Ref. 4. It has been shown the soft mode contribution obeys the Curie - Weiss law. In this paper we have taken aim to study the behaviour in the SmC* phase only.

During the measurement the sample texture has been checked in polarizing microscope. As the samples are treated only with very low measuring field (20 V/cm), the helicoidal structure manifested by the existence of dechiralization lines does not come into appearance. Only with the samples 50 and 100 μm thick, the lines can appear spontaneously.

On cooling to the SmC* phase, ε' reaches very high value at T_C depending on d and then remains mostly constant across the whole SmC* phase. In some cases it slightly gradually decreases (see e.g. Fig.3) or increases. An increase is used to be observed in samples 100 μm thick and is connected with an appearance of dechiralization lines.

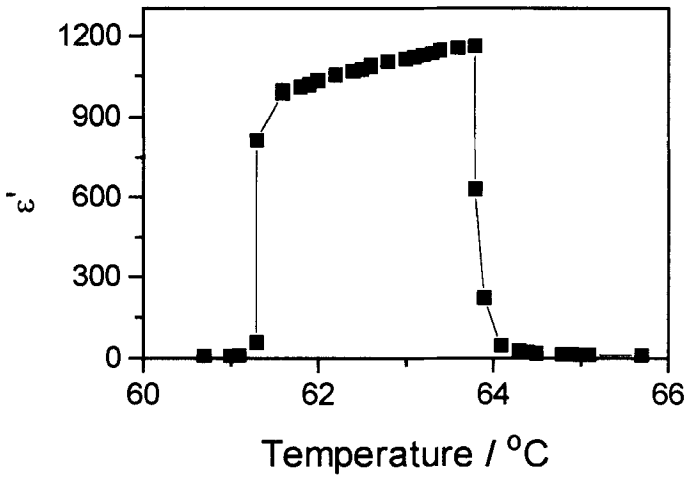


FIGURE 3 Temperature dependence of the real part of permittivity for the twisted sample, $d = 50$ μm.

DISCUSSION AND CONCLUSIONS

Properties of the thickness mode

In helix-free samples the existence of a low frequency dielectric relaxation mechanism, different from the Goldstone mode, is confirmed. This mode (here defined as a 'thickness

mode') is not a bulk property of FLC's. It is a fluctuation of the non-uniformly deformed structure which is fixed by the planar surface anchoring. The equilibrium state of this structure is represented by a deformation within the smectic layer. In this deformation the director azimuthal angle φ is regulary changed by π along the sample plane normal.

The theoretical description of this structure based on the free energy, as well as its dynamic properties, will be published in detail elsewhere.[5] The results show that the twisted structure exhibits a Goldstone-like mode, with the wave vector $q_t = 2\pi/d$, which is perpendicular to the Goldstone mode wave vector q_G, and with the contribution to dielectric susceptibility

$$\chi_t = \frac{2\varepsilon_0 \chi_h C d^2}{\pi K}, \tag{1}$$

where ε_0 is the permittivity of vacuum, χ_h is the dielectric susceptibility from hard polarization modes, K is an elastic constant, and C is an interaction constant between P and Θ.

In Fig. 2a one can see that with samples 6, 12, and 25 μm thick, $\Delta\varepsilon'$ is practicaly the same for helicoidal and helix-free samples and thickness dependent. One can infer that in these samples $\Delta\varepsilon'$ is determined by the thickness mode, because the twist responsible for the thickness mode is present even in helicoidal samples.[3] In the helicoidal samples, both the Goldstone mode and thickness mode, contribute to $\Delta\varepsilon'$, but only one relaxation is detected, which is dependent on d. The $f_r(d)$ dependence as it is shown in Fig.2b roughly obeys the relation $f_r(d) \propto 1/d^2$ which follows from the dynamics of the twisted structure.[5] The irregular values for $d = 6$ μm remain unexplained.

The thickness dependence of permittivity (Eq.1) is not exactly fulfilled in the experiment mainly for thick samples (see d = 100 μm in Fig. 2a). The reason is in different measuring conditions of samples with different d. It is true, we have used the same measuring field for all samples, but paradoxially it does not ensure equal conditions. From the theory[5] it follows that the electric field inducing an equivalent deformation of the twisted structure depends on the sample thickness as $E \propto 1/d^2$.

It means that the field used for 100 μm thick sample should be 270 times weaker than that for 6 μm one to obtain the same deformation. From this point of view it is probable that the measurement of thick samples has been performed in a non-linear regime, which could result in still lower permittivity values when increasing the sample thickness. On the other hand, the requisite lowering of measuring field for thick samples becomes non-realistic, because of the sensitivity of the measuring technique fails at low voltages.

Temperature dependence of dielectric susceptibility

Theoretical descriptions of bulk properties.

From the simplest free energy[6] for the SmA → SmC* phase transition taking into account bilinear interaction only between the tilt angle and the polarization, $CP\Theta$, the contributions to susceptibility from the soft, χ_s, and the Goldstone, χ_G, modes can be determined[7]

$$\chi_s = \frac{\varepsilon_0 \chi_h^2 C^2}{\alpha(T - T_C) + \tilde{K} q_0^2} \qquad \text{for} T > T_C \tag{1a}$$

$$\chi_s = \frac{\varepsilon_0 \chi_h^2 C^2}{4\alpha(T_C - T) + 2\tilde{K} q_0^2} \qquad \text{for } T < T_C \tag{1b}$$

$$\chi_G = \frac{\varepsilon_0 \chi_h^2 C^2}{2\tilde{K} q_0^2} \qquad \text{for } T < T_C \tag{2a}$$

$$\varepsilon_0 \chi_G \equiv 0 \qquad \text{for } T > T_C \tag{2b}$$

Where α is the soft mode susceptibility, $\tilde{K}$ is a renormalized elastic constant describing the helicoidal modulation of the SmC* structure, q_0 is the equilibrium modulation wave vector. The expression (2a) can be rewritten as

$$\chi_G = \frac{1}{2\varepsilon_0 \tilde{K} q_0^2} \left(\frac{P_S}{\Theta_S} \right)^2, \tag{3}$$

if the origin of P_S is in the linear interaction only, i.e. $P_S^{lin} = \varepsilon_0 \chi_h \Theta_S$, where Θ_S is the spontaneous tilt angle.

The theoretical dependence $\chi(T) = \chi_s + \chi_G$ exhibits a maximum at T_C, which is twice the Goldstone mode contribution. The experimental data obtained so far with any FLC material as well as the results seen in Fig.2 differ significantly from this theoretical dependence, mainly as to the non-existence of the peak in T_C. It implies the measured susceptibility in SmC* phase is much higher than that predicted by the theory.

To explain this discrepancy (and also the disagreement between the dependences $q_0(T)$, $P_S(T)$, $\Theta_S(T)$ found experimentaly and those calculated fom the simplest free energy), a higher order term $\Omega P^2 \Theta^2$ has been considered in the free energy.[8] The

extended free energy gives satisfactory results for $q_0(T)$, $P_S(T)$, $\Theta_S(T)$. As for dielectric properties it gives the same expression for χ_s in the SmA phase and nearly the same in the SmC* phase as the simplest free energy. For χ_G, an approximate expression have been derived, which is formally the same as Eq.3, but with P_S originating from both the bilinear and biquadratic interactions[9]

$$\chi_G^{tot} = \frac{1}{2\varepsilon_0 \tilde{K} q_0^2}\left(\frac{P_S^{lin} + \Delta P_S}{\Theta_S}\right)^2. \qquad (4)$$

This expression might explain the usually found χ(T) dependences only in the case, if ΔP_S constitutes the main part of the total P_S value.

The comparison with experimental results

By measuring both dielectric susceptibility and electroclinic coefficient in the SmA phase, the linear coupling constant $\varepsilon_0 \chi_h C$ between P and Θ has been determined.[4] Knowing Θ_S, $P_S^{lin} = \varepsilon_0 \chi_h C \Theta_S$ has been calculated at the temperature $T_C - 2$ K as 127.1 nC/cm^2. At the same temperature the measured total P_S = 136.5 nC/cm^2.[10]

Taking into account Eq.(4) one can estimate that in this material the high order interation can enhance χ_G by 14% only. This increase cannot explain the high value of ε' found in the SmC* phase, overwhelming the soft mode peak at T_C, which is twice as high as χ_G originating in linear interaction. This comparison shows that in the SmC* phase another contribution to ε has to be taken into account. The results presented in this paper enable us to suggest the thickness mode is an important source of permittivity in the SmC* phase.

This conclusion directs our attention to a serious predicament. The measured values of permittivity in SmC* phase as well as its relaxation frequencies might not represent characteristic dielectric bulk properties of the studied material, but could originate in the 'thickness mode' and thus reflect the real structure in finite samples. The thickness dependence of found permittivity values is a significant property which shows the relevant share of the thickness mode.

ACKNOWLEDGEMENT

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