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Dielectric relaxation in a high-tilt-angle chiral-nematic–smectic-C^* ferroelectric liquid crystal

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The dielectric properties of a high-tilt-angle chiral-nematic–smectic-C^* phase ferroelectric liquid crystal are studied in the frequency range of 30 Hz to 1 MHz. Measurements of electric permittivity at different temperatures and biasing fields were taken in thin homogeneously aligned samples with the electric measuring field being parallel to the layer planes. In the smectic-C^* phase two relaxation mechanisms have been found, viz., the Goldstone mode originating due to the phase fluctuations of the director and 180° flip of the molecular relaxation connected with the reorientation of the liquid-crystal molecule around its short axis. Temperature and bias-field dependence of the dielectric permittivity and the critical relaxation frequency of the molecular mode in the smectic-C^* phase are studied and discussed.

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I. INTRODUCTION

Ferroelectric liquid crystals (FLC's) have been studied extensively in recent years due to both electro-optic effects, which make them appear promising for optical displays, and to their interesting basic properties [1]. The FLC materials showing a chiral-nematic (N^*) to smectic-C^* (Sm-C^*) phase transition have been scarcely studied so far because of the difficulty in obtaining well-aligned cells. Practically, however, these kinds of materials are very interesting, since their material constants, such as tilt angle, are as large as 45° and do not depend greatly on the temperature. Moreover, it is of great practical importance since the tilt angle of about 45° is better suited for preparing electro-optical switches [2] and guest-host displays.

Dielectric properties of FLC's showing the smectic-A (Sm-A) to Sm-C^* phase transition have been the subject of many experimental and theoretical investigations [3–6]. It is known that there are two important relaxation modes, namely, the Goldstone mode and the soft mode, which can be examined by dielectric relaxation spectroscopy. The Goldstone mode appears in the Sm-C^* phase because of the phase fluctuations in the azimuthal orientation of the director. The soft mode, which appears due to the fluctuations of the tilt angle, is seen practically in the vicinity of the Sm-A–Sm-C^* transition point.

The complex dielectric constant is given as

$$\epsilon^*(\omega,T)=\epsilon'(\omega,T)-i\epsilon''(\omega,T)\ , \tag{1}$$

where $\omega=2\pi\nu$ 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 frequency ν, contribute to $\epsilon^*(\omega,T)$. In order to best characterize the temperature dependence of the observed dielectric relaxation, the $\epsilon(\omega)$ data in the appropriate frequency range are given by the following single (Debye) relaxation time:

$$\epsilon(\omega,T)=\epsilon_\infty+\frac{\Delta\epsilon(T)}{(1+i\omega\tau_0)}\ , \tag{2}$$

where $\epsilon(\omega,T)$ is the frequency-dependent dielectric response, τ_0 is the characteristic mean relaxation time, and $\Delta\epsilon(T)$ is the dielectric strength of the mode, which is the difference between the low- and high-frequency contributions of the dielectric constant. This generalization of the Debye formulation describes a system with a distribution of relaxation times associated with a single process.

In FLC materials having a Sm-A–Sm-C^* phase transition, the ϵ component of the electric permittivity in the Sm-C^* phase exhibits, in addition to normal molecular relaxation, a spectacular relaxation, the so-called Goldstone mode [7]. This mode shows up in most cases in the low-frequency range, i.e., between a few hertz and about 10 kHz [3,5]. Additionally, in the vicinity of the Sm-C^*–Sm-A^* transition, a second relaxation region appears, the so-called soft mode [3,8]. The Goldstone-mode contribution to the electric permittivity ϵ is due to fluctuations in the phase (ϕ) of the order parameter, whereas the soft mode comes from the fluctuations of the magnitude of polarization P_0, i.e., from fluctuations of the tilt angle (θ_0). So, the frequency and temperature dependence of the ϵ component in the Sm-C^* phase can be written

$$\epsilon^*(\omega,T)=\Delta\epsilon_{\text{el}}(T)+\frac{\Delta\epsilon_M(T)}{1+i\omega\tau_M}+\frac{\Delta\epsilon_G(T)}{1+i\omega\tau_G}+\frac{\Delta\epsilon_S(T)}{1+i\omega\tau_S}\ , \tag{3}$$

where $\Delta\epsilon_{\text{el}}$ is the high-frequency limit of electric permittivity and $\Delta\epsilon_M$, $\Delta\epsilon_G$, and $\Delta\epsilon_S$ are the dielectric increments due to the molecular relaxation, the Goldstone mode, and the soft mode, respectively; τ_M, τ_G, and τ_S are the respective relaxation times.

In this article, we report the dielectric-relaxation studies of a ferroelectric liquid crystal with a phase sequence of N^*–Sm-C^* in a thin cell (10 μm) of FLC in the frequency range 30 Hz to 1 MHz, and at different temperatures and biasing voltages. The dielectric measurements performed in this work have shown that there is a dominant Goldstone mode, whereas for higher biasing voltages the Goldstone mode disappears and a 180°-flip molecular relaxation around the short axis is seen in the Sm-C^* phase.

II. EXPERIMENT

Dielectric measurements were carried out in a shielded parallel-plate condensor described by Haase, Pranoto, and Bormuth [9]. The highly conducting indium tin oxide (ITO) glass plates were used for electrodes. The distance between the plates was kept around 10 μm and this distance can be considered as thin compared with the helical-pitch value (15 μm) of the material. The cells were first calibrated using air and toluene as standard references. The material was introduced in the cell by means of the capillary action at elevated temperatures to ensure that the filling took place in its isotropic (iso) phase. The ferroelectric liquid-crystal material (CS-2004, Chisso Corporation, Japan) used in this study has the following phase sequence:

$$\text{cryst} \underset{-9\,^\circ\text{C}}{\leftrightarrow} \text{Sm-}C^* \underset{62\,^\circ\text{C}}{\leftrightarrow} N^* \underset{71\,^\circ\text{C}}{\leftrightarrow} \text{iso} .$$

Uniform alignment of the FLC sample is obtained with one surface buffed, which has been pretreated with adhesion promoter and nylon. A well-defined monodomain sample is obtained [10,11] by applying an ac field of 50-Hz frequency and 20 V_{pp} peak to peak. The effect of the electric field on a randomly aligned sample is to unwind the suppressed helix and to force the molecules in a layer to lie parallel to the buffing direction. When the sample is cooled to the Sm-C^* phase there is a possibility that the molecules at the buffed surface are aligned and the bulk is unaligned, resulting in the formation of focal-conic domains. When a field is applied, the randomly aligned focal-conic domains reorient to conform to the oriented surface structure. This structure is energetically more favorable and develops gradually as the sample is switched back and fourth on applying the ac field. The molecule thus aligns along the buffing direction and the smectic layers' normal is tilted by 44° (tilt angle of the material) with respect to FLC molecules. It is seen that the entire sample is well aligned and no defects are present when viewed under a polarizing microscope (Olympus BH2).

The dielectric measurements were done using a HP 4192 impedance analyzer in the frequency range 30 Hz to 1 MHz. To study the low-frequency molecular relaxation in the Sm-C^* phase, a dc electric field ($\pm$) 0 to 30 V/10 μm generated by the analyzer was used at different temperatures.

III. RESULTS AND DISCUSSION

In this article the dielectric-relaxation processes are discussed in the high-tilt-angle (44°) FLC material having a chiral-nematic to smectic-C^* phase transition. In thin and homogeneously aligned samples the smectic layers' normal is assumed to be parallel to the plane of the electrodes and an electric field is applied parallel to the smectic layers. The tilt of the molecules is parallel to the plane of the plates. For this cell thickness (10 μm), the pitch of the helix (15 μm) is suppressed due to surface forces and can therefore be thought of as having a very large value.

A. Goldstone mode in the Sm-C^* phase

The complex electric permittivity was measured in the frequency range 30 Hz to 100 KHz. The Goldstone-mode contribution to the real part of the complex electric permittivity (ϵ') is dominant in the frequency range between a few Hz to a few kHz. The temperature dependences of ϵ' obtained at different frequencies for the N^*, Sm-C^*, and iso phases are shown in Fig. 1(a). As is seen, there is practically no dispersion effect in the N^* and isotropic phases in the frequency range studied and a static dielectric constant ϵ_0 has been observed. In the vicinity of the transition temperature (T_c) N^*–Sm-C^* phase, a dispersion effect begins to appear, and then just below the transition temperature there is a tremendous dispersion effect connected with the Goldstone mode. However, for high frequency (above 10 kHz) the contribution of the Goldstone mode to the electric permittivity is negligible. The frequency dependences of the real part of the complex electric permittivity (ϵ') are shown in Fig. 1(b). As is seen, the electric permittivities measured at low frequencies are very high and are temperature dependent in the Sm-C^* phase. The critical frequencies of the Goldstone mode have been computed from the position of maxima on the tanδ (loss factor) versus $\log_{10}\nu$ plot [Fig. 1(c)], since the dielectric spectrum could not be presented in this case in the form of Cole-Cole plots or regular dispersion and absorption curves. As is seen in the figure, the relaxation frequency of the Goldstone mode is nonlinear (non-Arrhenius type) over the large measured temperature range. This may be due to the fact that the tilt angle (44°) of the material is constant, since the sample is thin, the helix of the material is unwound, and independent of temperature [12]. It is worth mentioning here that the relaxation frequency of the Goldstone mode in Sm-C^* phase of the FLC's is either weakly temperature dependent [5] or nonlinear with temperature [6].

In the present investigations the FLC material does not show the Sm-A phase (transition is from the N^* to the Sm-C^* phase), and hence above the Sm-C^* phase, there would not be any contribution arising from the soft mode or the Goldstone mode to the permittivity. The dielectric permittivity in the N^* phase is due to the molecular relaxation and high-frequency limit of electric permittivity. In the N^* phase the complex dielectric constant can be written as

$$\epsilon^*(\omega,T)=\Delta\epsilon_{\mathrm{el}}(T)+\frac{\Delta\epsilon_M(T)}{1+i\omega\tau_M} . \tag{4}$$

In the Sm-C^* phase most of the dielectric response comes from the Goldstone mode (Fig. 1), which has a relaxation frequency around 1 kHz. The dielectric permittivity of the Sm-C^* phase rapidly decreases when the frequency is increased beyond the value of 10 kHz [Fig. 1(b)] and only the response due to molecular contribution remains. As shown theoretically [13] and verified experimentally [14], the soft-mode intensity in the Sm-C^* phase is rapidly absorbed in the Goldstone mode as the temperature of the system is lowered from T_c. One way to observe the soft mode over a broad temperature interval in the Sm-C^* phase is to apply a static electric bias field parallel to the smectic layers. If the bias field is strong enough, the helix of the system is unwound and thus the Goldstone mode is suppressed.

In the present investigation we have not found the soft-mode contribution to the dielectric permittivity near the transition temperature. It is interesting to note here that a dielectric relaxation was observed when a strong bias field was applied to unwind the suppressed helix in the Sm-C^* phase, which will be discussed in detail in the following section. This dielectric relaxation in Sm-C^* phase is due to the molecular relaxation around the short axis and not due to the soft-mode contribution. This is due to the fact that the relaxation frequency of this mode increases linearly with temperature on approaching T_c, whereas in the case of the soft mode, the relaxation frequency decreases linearly with temperature on approaching T_c.

B. Effect of static field on the Goldstone mode

Dielectric permittivity has been measured in the Sm-C^* phase by applying different bias fields at different temperatures. Figure 2(a) shows dielectric permittivity

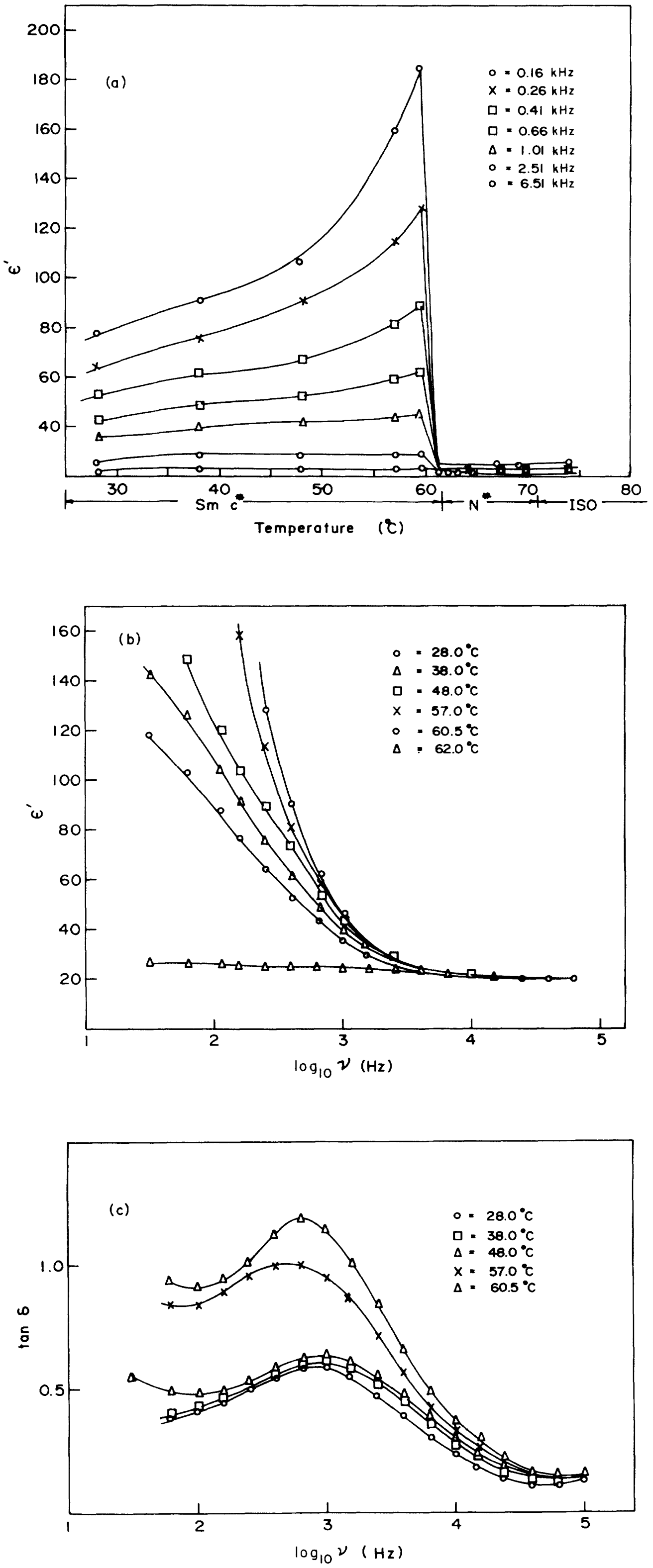

FIG. 1. (a) Temperature dependences of the dielectric permittivity (ϵ') measured at different frequencies. (b) Dispersion curves (ϵ') due to the Goldstone mode as a function of frequency at different temperatures. (c) Frequency dependences of tanδ (loss factor) ($\tan\delta = \epsilon''/\epsilon'$) measured at different temperatures in the Sm-C^* phase.

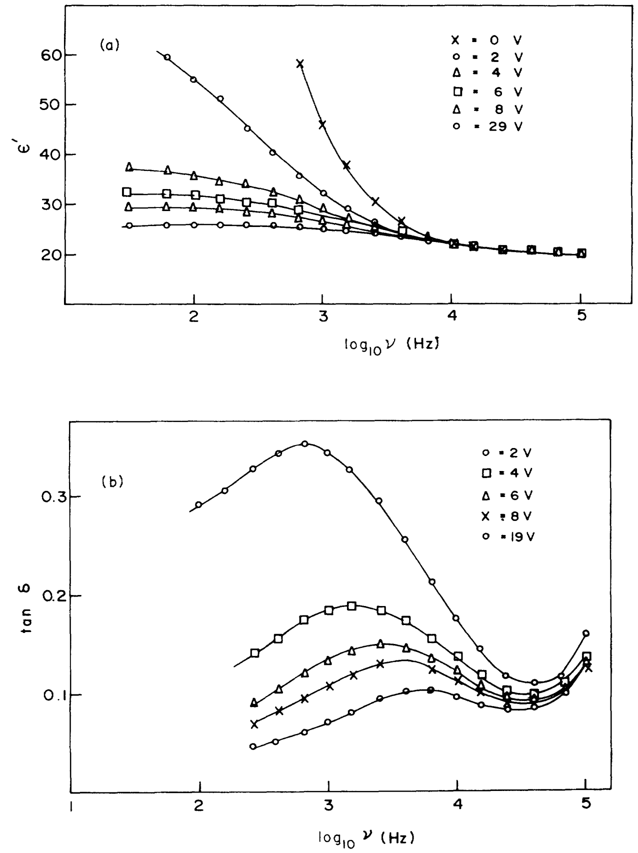

FIG. 2. (a) Dielectric permittivity (ϵ') vs $\log_{10}\nu$ (Hz) at different biasing voltages. (b) tanδ vs $\log_{10}\nu$ (Hz) at different biasing voltages at room temperature (28 °C) in the Sm-C^* phase.

dependence on the applied frequency at different biasing voltages. It is seen that at zero bias field the contribution to the dielectric permittivity comes from the Goldstone mode. As the bias field increases (to greater than 0.8 V/μm), the suppressed helix gets unwound and the Goldstone mode is suppressed, which results in a static dielectric constant above the bias voltage of 8 V [Fig. 2(a)]. This means that at 8 V the suppressed helix gets completely unwound. The relaxation processes at different biasing voltages in the Sm-C^* phase have been seen by plotting tanδ versus $\log_{10}\nu$, as shown in Fig. 2(b). Clearly, the relaxation frequency shifts towards the higher side as the bias voltage is increased.

The origin of the low-frequency contribution to the dielectric constant in the Sm-C^* phase is due to the deformation of the structure by an external field because the thin (10-μm) sample is unwound by boundary conditions, but the twist along the sample thickness remains. This deformation consists in the change of the surface layer thickness of the partially unwound structure along the suppressed helical axis (the so-called Goldstone mode) and in the deformation of the twist along the sample thickness. If a biasing field is applied on this sample, all these deformations that are connected with a polarization change are suppressed proportionally to the field so that the dielectric constant decreases with increasing bias field [Fig. 2(a)]. For the structure that is completely unwound, this contribution should disappear and the value of ϵ' will not depend on the field. However, in the present case even at higher voltage ($\pm$30V) the value ϵ' does show some dispersion (for lower frequencies) due to the contribution coming from the 180° molecular flip at high fields, which will be discussed in the following section. The low-frequency contributions to ϵ' due to the deformation structure still play a decisive role. The contribution exhibits a relaxation behavior with relaxation frequency, which is seen in Fig. 2(b). When a biasing field is applied a shift of the relaxation frequency to higher values appears. Similar types of observations were also presented by Paval, Glogarova, and Bawa [15] in thin samples of FLC material.

C. 180°-flip molecular relaxation

The dielectric permittivity due to 180°-flip molecular relaxation around the short axis in the Sm-C^* phase has been computed by applying high bias voltage (8 V). This field is sufficient to unwind the helix, making the Goldstone mode disappear [Fig. 2(a)] and the dielectric permittivity (ϵ') become almost static. The 180°-flip molecular relaxation measurements could not be computed by means of the Cole-Cole plot since the ϵ' versus ϵ'' is not a semicircle [Fig. 3(a)]. This is due to the fact that the cell has been buffed on one side (to align the liquid crystal) and not on the other. The molecular long axis coincides with the rubbing direction and does not respond to the low applied field as compared with the unrubbed surface, which results in a different relaxation of the molecules (switching) at two surfaces. Such an asymmetric optical and electrical switching behavior has also been observed in these materials [2,11].

The dielectric permittivity due to the molecular relaxation around the short axis has been computed by absorption curves, and from the peak of the curve one can find out the relaxation frequency of the mode. Figure 3(b) shows the imaginary part (ϵ'') of the dielectric permittivity versus frequency at different temperatures in the Sm-C^* phase when the applied bias voltage is around 8 V (i.e., the helix is unwound). As is seen in the figure, the relaxation frequency shifts toward the higher-frequency side as the temperature increases. The behavior of the critical relaxation frequency with the temperature of the molecular relaxation around the short axis has been shown in Fig. 4. As is seen in Fig. 3 the orientation of molecules around its short axis (i.e., 180° jumps around the short axis) shows up in the planar structure where the layers are perpendicular and the molecules are parallel to the plates. One should add that the planar alignment was excellent and optically controlled. The low-frequency relaxation (180° flip) is substantiated for this component of the dielectric permittivity tensor in the Sm-C^* phase. Such an effect was reported earlier [16,17], but the experi-

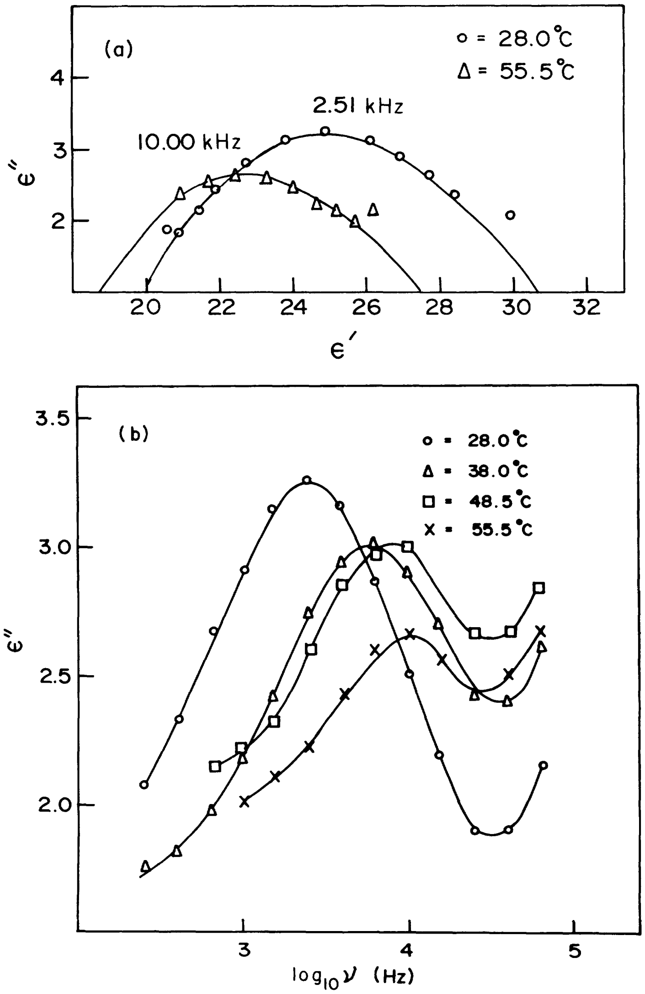

FIG. 3. (a) Cole-Cole representation of the molecular relaxation at two temperatures for a static field of +8 V/10 μm. (b) Absorption curves (ϵ'' vs $\log_{10}\nu$) obtained for 180°-flip molecular relaxation at 8 V for different temperatures in the Sm-C^* phase.

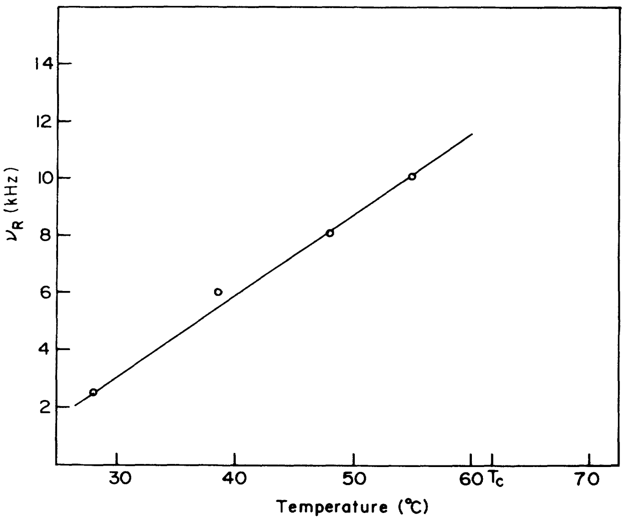

FIG. 4. Relaxation frequency vs temperature obtained for molecular relaxation around the short axis in the Sm-C^* phase at +8 V biasing voltage.

mental evidence was not as good. In our study the 180°-flip molecular relaxation around the short axis is seen very clearly and it obeys the temperature dependence of relaxation frequency behavior (Fig. 4) in the Sm-C^* phase that has been predicted theoretically and observed experimentally in most of the liquid-crystal materials. It is worth mentioning here that the reorientation of molecules around the long axis also gives the contribution to the electric permittivity, but its dispersion takes place at a much higher frequency (100-MHz range) [17]. Therefore, the molecular relaxation observed in this study is due to the 180° jumps around the short axis.

From the molecular-dynamics standpoint the Sm-A, Sm-A^*, Sm-C, and Sm-C^* structures resemble two-dimensional liquids. Within a layer of one of these phases molecules can easily perform lateral diffusion. They can also easily reorient around their long axis, which has been verified by the dielectric relaxation method [18]. However, it has been established that in the Sm-C and Sm-C^* phases the reorientation around the long molecular axis is biased [19] and is a nonuniform one. It means that there is always one preferred direction for the short molecular axis. In the present case, the molecules close to the rubbed surface are strongly anchored and the polar surface interaction is low because of the random nature of the layered structure on the unbuffed surface [10]. Therefore, they have a strong correlation between them. It is well known that the molecules in the Sm-C^* phase rotate freely around the normal to the smectic layers with constant tilt angle θ in the thick cell. However, if the thickness of the cell is thin and the tilt angle θ is quite large (44°) then the free rotation of the director on the cone is also restricted, only two positions (azimuthal angles $+\theta_0$ and $-\theta_0$) should be allowed, and the electric field can switch from one orientation to the other, as suggested by Clark and Lagerwall [20]. This means the correlations between the layers would be stronger in a buffed and thin cell with high-tilt-angle materials, which results in a molecular relaxation (180° flip) around the short axis.

It would be interesting to study the 180°-flip molecular relaxation in this material in a thick cell, without buffing the surface, where the conditions at both the surfaces of the FLC cell are identical.

IV. CONCLUSION

(i) It has been found that the Goldstone mode makes a large contribution to the dielectric permittivity in the Sm-C^* phase. It is a collective process showing a non-Arrhenius-type (nonlinear) behavior of the critical frequencies.

(ii) The contribution to the electric permittivity due to the Goldstone mode decreases with the bias field. When the suppressed helix is completely unwound in the dc electric field, the contribution to ϵ' falls off. The relaxation frequency of the mode increases with increasing dc field.

(ii) The 180°-flip molecular relaxation around the short axis has been observed in the Sm-C^* phase. Its relaxation frequency has been found to be temperature dependent.

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