Dielectric study of the electroclinic effect in the smectic-A phase

Yu. P. Kalmykov
Institute of Radio Engineering & Electronics of the Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, Moscow Region 141120, Russia

J. K. Vij* and Huan Xu
Department of Microelectronics & Electrical Engineering, Trinity College, University of Dublin, Dublin 2, Ireland

A. Rappaport and M. D. Wand
Displaytech Inc., 220 Central Avenue, Suite C, Boulder, Colorado 80301
(Received 8 November 1993)

The dielectric properties of a smectic-A liquid crystal in the presence of a dc bias field are studied in the frequency range 100 Hz–1 MHz. It is shown that near the smectic-A–smectic-C^* phase transition the relaxation frequency and dielectric strength of the soft mode have nonlinear bias field dependencies resulting from an electroclinic coupling between the molecular tilt and the polarization. A simple mean field theory is proposed to explain the experimental results.

PACS number(s): 42.70.Df, 61.30.Cz, 61.30.Gd, 77.84.Nh

I. INTRODUCTION

Tilted ferroelectric liquid crystals (FLC's) in surface stabilized geometry offer high speed, high contrast and, bistable electro-optic switching characteristics [1,2]. Surface stabilized geometry allows the suppression of the intrinsic helix of FLC's and produces two stable states with opposite spontaneous polarization P_s, which can be switched from one state to another with a time constant of a few microseconds by applying a relatively small amount of external voltage. The spontaneous polarization exists only in chiral tilted smectic phases. However, in nontilted chiral smectic liquid crystals such as smectic-A ones, there exists a different and a faster switching mechanism, typically 100 times faster. This is due to the electroclinic effect [3,4]. This effect occurs when an electric field applied parallel to the smectic layers induces a molecular tilt relative to the layer normal [3]. The practical applications require an understanding of the electroclinic response to an applied electric field.

The origin of the electroclinic effect is explained as follows [3]. For the chiral smectic-A phase the long molecular axis or director $\mathbf{n}$ is parallel to the normal of the smectic layers. The molecules are free to rotate about their long axes. In the presence of a dc electric field $\mathbf{E}_0$ applied parallel to the smectic layers, this free rotation is biased due to the tendency of the transverse component of the permanent molecular dipole μ to orient along the field $\mathbf{E}_0$. For a nonchiral system, the plane containing $\mathbf{n}$ and $\boldsymbol{\mu}$ is a mirror plane. The chirality of the phase destroys all mirror symmetries. Therefore, the free energy for the molecular tilt is no longer symmetric about the $\mathbf{n}$-$\boldsymbol{\mu}$ plane and a molecular tilt is induced in the plane perpendicular to this plane. The linear connection between the polarization and the induced tilt represents the electroclinic response of the chiral smectic-A (Sm-A) phase [3].

The electroclinic effect in the Sm-A phase has been studied by both electro-optic (e.g., [3–6]) and dielectric spectroscopic [6] techniques. The electroclinic coefficient was found to be independent of the electric field [7], which implied a linear coupling between the induced tilt angle and the polarization. The relaxation frequency increases whereas the electroclinic coefficient decreases with an increase in temperature, except very close to the SM-A–nematic phase transition temperature [7,8]. Near the Sm-A–Sm-C^* transition temperature, a variety of strong bias field dependencies of the electro-optic response have been observed and an explanation of the experimental data [3,4] has been given in the context of the mean field theory. As for the dielectric study of the electroclinic effect only a few experimental data are available for the relaxation frequency of the soft mode [6,17] as a function of dc bias, and a simple analytical theory of the dielectric response in Sm-C^* and Sm-A phases is lacking in the literature. However, the theory of the dielectric response without dc bias has been carried out before by Carlsson *et al.* [9] and Costello, Kalmykov, and Vij [10], with dc bias in the Sm-C^* phase carried out by Žekš *et al.* [11]. Gouda *et al.* [17] have developed a theory for the problem under consideration, but it uses numerical evaluations of the dielectric quantities. A number of investigators have also determined the relaxation frequency [7,8] as a function of temperature in the Sm-A phase.

The object of the present paper is to report the experimental and theoretical study of the low frequency dielectric relaxation of the smectic-A phase in the presence of a dc bias field. The relaxation process so studied is known as the soft mode.

*Author to whom correspondence should be addressed.

II. EXPERIMENTAL TECHNIQUES

A commercial ferroelectric liquid crystal mixture, manufactured by E. Merck, United Kingdom, SCE13, was studied. The sequence of the phase transition temperatures (in °C) is

$$\text{Sm-}C^* \underset{60.8^\circ\text{C}}{\leftrightarrow} \text{Sm-}A \underset{86.3^\circ\text{C}}{\leftrightarrow} N \underset{100.8^\circ\text{C}}{\leftrightarrow} I \; .$$

More details about the mixture can be found elsewhere [12].

The measurement cell consisted of indium-tin-oxide (ITO) coated glass plates with a separation of $d=20\ \mu$m. The surface resistivity of the ITO is 100 Ω per square. The dielectric measurements were carried out on a homogeneously aligned sample. This alignment was confirmed using a polarizing microscope fitted with a hot stage and a temperature controller (Instec, Boulder, CO). The dielectric measurements described here were carried out in the Sm-A phase, in the vicinity of the SM-A–Sm-C^* transition temperature. The dc bias and alternating electric fields were applied parallel to the smectic layers, thus allowing us to measure the transverse component of the complex dielectric permittivity $\varepsilon_\perp(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$. Permittivity of free space in cgs units is unity. Dielectric measurements in the frequency range 100 Hz–1 MHz were carried out using a Schlumberger 1255A frequency response analyzer and a Chelsea dielectric interface under a computer control. The accuracy of the dielectric measurements over the frequency range is better than $\pm 5\%$. dc bias voltages varied up to 40 V and an alternating voltage of 1 V rms were applied to the sample during the dielectric measurements.

The test cell was kept in a hot stage in which a desired sample temperature was maintained using the computer operated temperature controller. The temperature stability was better than $\pm 0.01\,^\circ$C. The dielectric measurements were carried out while the sample was cooled slowly from the Sm-A phase down to the Sm-A–Sm-C^* transition temperature.

Typical dielectric spectra $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ of the smectic-A liquid crystal under the influence of the bias field are shown in Figs. 1–3 for three temperatures of 61.3, 61.8, and 62.3 °C. We observe that the dielectric loss maximum $\varepsilon''(\omega)$ falls off while the relaxation frequency ω_m (which corresponds to the maximum dielectric loss) increases with an increase of the bias field strength.

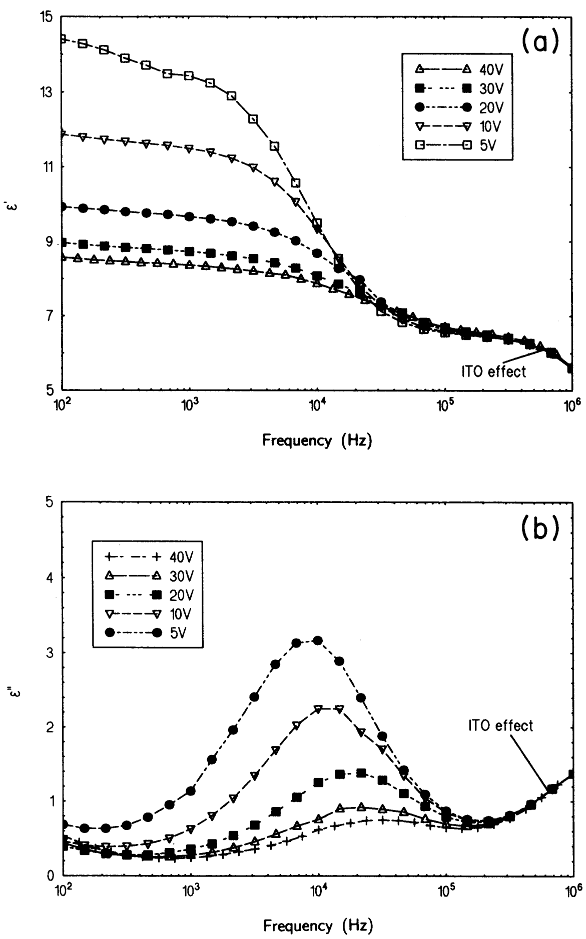

FIG. 1. Dielectric spectra of (a) the real $\varepsilon'(\omega)$ and (b) imaginary $\varepsilon''(\omega)$ parts of the complex permittivity of the smectic-A liquid crystal mixture under investigation at 61.3 °C for different values of the applied voltage.

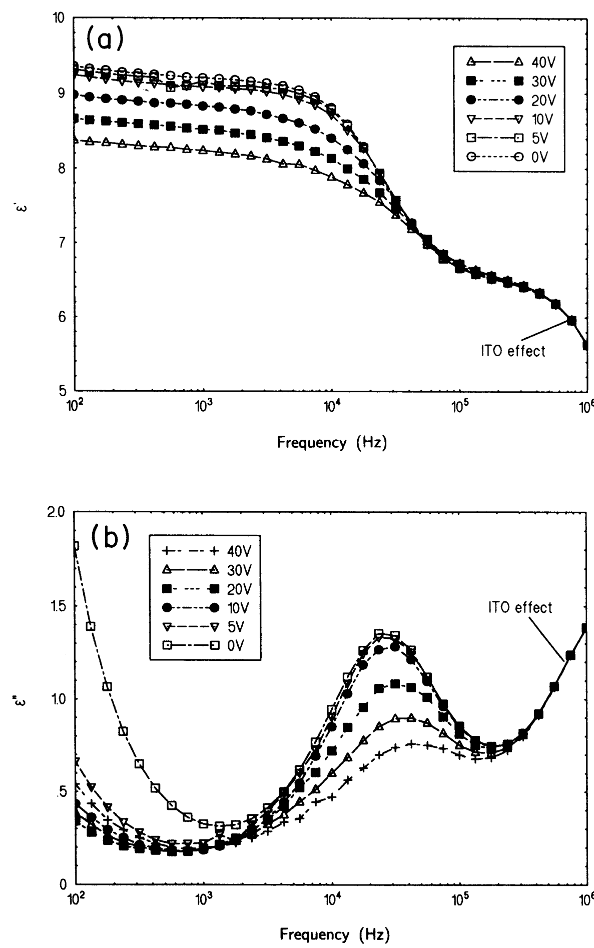

FIG. 2. Same as in Fig. 1 at 61.8 °C. (a) $\epsilon'(\omega)$ and (b) $\epsilon''(\omega)$.

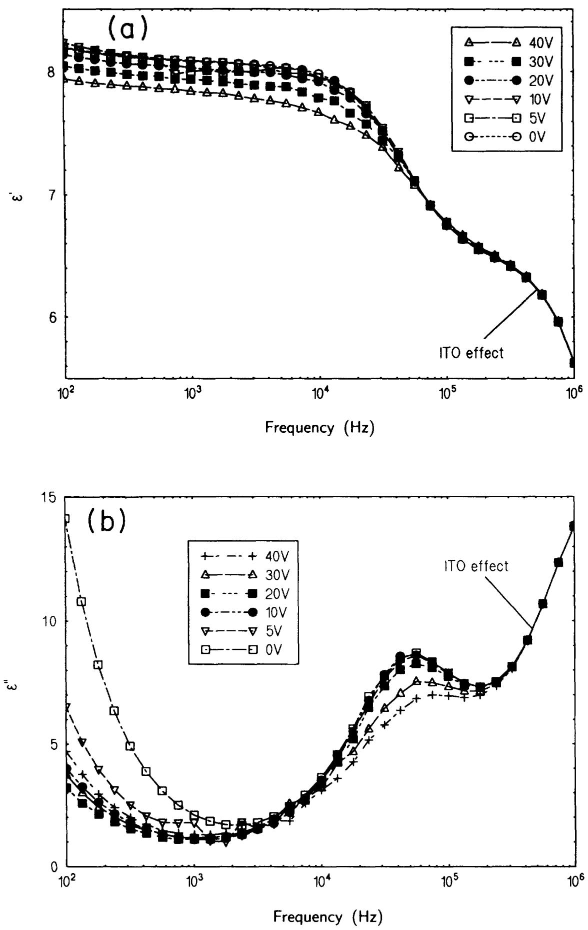

FIG. 3. Same as in Fig. 1 at 62.3 °C. (a) $\epsilon'(\omega)$ and (b) $\epsilon''(\omega)$.

III. THEORY AND DATA EVALUATION

In order to describe the main features of the dielectric behavior of the smectic-A phase and to explain the experimental results, we shall develop the mean field theory [3,4] with a particular application to the problem of dielectric relaxation.

In the presence of a constant electric field $\mathbf{E}_0$ applied parallel to the smectic layers and in the absence of the shear stress, the free energy density g of a chiral smectic-A liquid crystal up to θ^4 induced tilt angle term can be written as [3,4]

$$g = g_0 + \tfrac{1}{2}A'\theta^2 + \tfrac{1}{4}B\theta^4 + \tfrac{1}{2}\chi^{-1}P^2 - c\theta P - PE_0 - \frac{1}{8\pi}\varepsilon_0 E^2 + \cdots , \quad (1)$$

where g_0 represents contributions to the free energy from the undisturbed smectic-A phase, P is the component of the average molecular polarization parallel to $\mathbf{E}_0$, ε_0 is the dielectric constant without contributions from the permanent dipoles, χ is a generalized susceptibility, and c is the electroclinic coupling constant. The constant A' goes to zero at the "unrenormalized" transition temperature T_0, i.e., $A' \propto (T - T_0)$, and B is a temperature independent constant. Here the tilt angle θ is assumed to be relatively small.

On minimizing the free energy g from Eq. (1) with respect to P and θ, i.e., setting $\partial g/\partial\theta$ and $\partial g/\partial P$ separately equal to 0, one can derive the equations governing the induced equilibrium polarization P_0 and tilt θ_0 of the system, namely,

$$A\theta_0 + B\theta_0^3 - c\chi E_0 = 0 , \quad (2)$$

$$P_0 - \chi c\theta_0 - \chi E_0 = 0 , \quad (3)$$

where

$$A = A' - \chi c^2 . \quad (4)$$

The new constant A goes toward zero at a temperature T'. This means $A = a(T - T')$, where a is a constant, and indicates a renormalization of the transition temperature from T_0 for the nonchiral transition. The renormalization is primarily due to the coupling between P and θ [3]. The solution of the cubic equation (2) gives three roots for θ_0 out of which only one has a physical meaning. This is given by [4,5]

$$\theta_0 = \{Q + [Q^2 + R^3]^{1/2}\}^{1/3} + \{Q - [Q^2 + R^3]^{1/2}\}^{1/3} , \quad (5)$$

where Q and R are the dimensionless parameters defined as

$$Q = c\chi E_0/2B, \quad R = A/3B .$$

On substituting Eq. (5) into Eq. (3) we obtain an equation for the equilibrium polarization P_0, namely

$$P_0 = \chi E_0 + \chi c(\{Q + [Q^2 + R^3]^{1/2}\}^{1/3} + \{Q - [Q^2 + R^3]^{1/2}\}^{1/3}) . \quad (6)$$

We now consider the dynamic equations for the tilt angle θ and polarization P. The dynamics of θ and P in the presence of a small ac electric field $\mathbf{E}(t) = \mathbf{E}\exp(i\omega t)$ $[|E(P_0 - P)| \ll kT]$ applied parallel to the field $\mathbf{E}_0$ obey the phenomenological Landau-Khalatnikov equations [9]

$$\gamma_S \frac{\partial\theta}{\partial t} = -\frac{\partial g}{\partial\theta} = -(A'\theta + B\theta^3 - cP) , \quad (7)$$

$$\gamma_P \frac{\partial P}{\partial t} = -\frac{\partial g}{\partial P} = -[P/\chi - c\theta - E_0 - E(t)] , \quad (8)$$

where γ_S and γ_P are the rotational viscosities associated with the rotation of the director and the molecules around their long axes, respectively. In order to derive Eqs. (7) and (8) we have assumed that the free energy g in the presence of the ac field $\mathbf{E}(t)$ is given by Eq. (1) with the additional term $-\mathbf{P}\cdot\mathbf{E}(t)$.

From Eqs. (7) and (8) one can see that, just as in the absence of the bias field, the dynamic dielectric response consists of two modes, the high frequency polarization mode and the soft mode. The soft mode corresponds to the in-phase fluctuations of θ and P and is responsible for the appearance of the ferroelectric order at the phase transition temperature.

Introducing a time dependence of the order parameters as

$$\theta(t) \cong \theta_0 + \Delta\theta\exp(i\omega t), \quad P(t) \cong P_0 + \Delta P\exp(i\omega t) , \quad (9)$$

where θ_0 and P_0 are given by Eqs. (5) and (6), respectively, and it is assumed that $\Delta\theta \ll \theta_0$, $\Delta P \ll P_0$, we can obtain from Eqs. (7)–(9) the set of linearized equations:

$$i\gamma_S\omega\Delta\theta = -(A' + 3B\theta_0^2)\Delta\theta + c\Delta P \ , \tag{10}$$

$$i\gamma_P\omega\Delta P = -\Delta P/\chi + c\Delta\theta + E \ . \tag{11}$$

On solving the set of linear equations (10) and (11) we can obtain the complex dielectric permittivity $\varepsilon_\perp(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, defined as

$$\varepsilon_\perp(\omega) = \varepsilon_0 + 4\pi\Delta P/E \ ,$$

which is given by

$$\varepsilon_\perp(\omega) = \varepsilon_0 + \frac{4\pi\chi(1+i\omega\tau_S)}{(1+i\omega\tau_P)(1+i\omega\tau_S) - D} \ , \tag{12}$$

where

$$\tau_P = \chi\gamma_P \ , \tag{13}$$

$$\tau_S = \gamma_S/(A + \chi c^2 + 3B\theta_0^2) \ , \tag{14}$$

$$D = \chi c^2/(A + \chi c^2 + 3B\theta_0^2) \ , \tag{15}$$

and θ_0 is given by Eq. (5). It can be shown that in the absence of the dc bias field (i.e., when $\theta_0 = 0$) Eqs. (12)–(15) reduce to the well-known equations for the dielectric parameters of the smectic-A phase (see, for example, [9,10]).

In the present investigations we have confined ourselves to the study of the low frequency relaxation (soft mode) only. For this case Eq. (12) can be simplified as follows. For a FLC $\gamma_P \ll \gamma_S$ and hence $\tau_P \ll \tau_S$ [9,10]; therefore at frequencies $\omega \ll \tau_P^{-1}$ we can neglect the contribution of the high frequency polarization mode and we can obtain from Eq. (12)

$$\varepsilon_\perp(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + i\omega/\omega_m} \ , \tag{16}$$

where the relaxation frequency ω_m, dielectric strength $\Delta\varepsilon$, and high frequency permittivity ε_∞ are given by

$$\omega_m = (A + 3B\theta_0^2)/\gamma_S = \omega_m^0(\{\sqrt{Z^2+1} + Z\}^{2/3} + \{\sqrt{Z^2+1} - Z\}^{2/3} - 1) \ , \tag{17}$$

$$\Delta\varepsilon = 4\pi c^2\chi^2/(A + 3B\theta_0^2) = \frac{\Delta\varepsilon^0}{\{\sqrt{Z^2+1} + Z\}^{2/3} + \{\sqrt{Z^2+1} - Z\}^{2/3} - 1} \ , \tag{18}$$

$$\varepsilon_\infty = \varepsilon_0 + 4\pi\chi \ . \tag{19}$$

Here

$$\omega_m^0 = A/\gamma_s \quad \Delta\varepsilon^0 = 4\pi(\chi c)^2/A$$

are the relaxation frequency and dielectric strength in the absence of the dc field, respectively. The dimensionless parameter Z appearing in Eqs. (17) and (18) is given by

$$Z = C\frac{V}{(T - T')^{3/2}} \ , \tag{20}$$

where the temperature and field independent coefficient C is defined as

$$C = \frac{3c\chi(3B)^{1/2}}{2a^{3/2}d} \ , \tag{21}$$

and we have used $E_0 = V/d$, d being the thickness of the cell. The coefficient C from Eq. (21) is actually the only adjustable parameter of the theory.

It follows from Eq. (20) that two factors are responsible for the nonlinear dielectric behavior: the electroclinic coupling and the nonlinear field dependence of the induced tilt. These are due to the $c\theta P$ and $B\theta^4$ terms in Eq. (1), respectively.

In the low dc field limit $E_0 \to 0$ ($Z^2 \ll 1$) we have from Eqs. (17) and (18)

$$\omega_m - \omega_m^0 \cong \gamma_S(A/c\chi)^2 C_1 E_0^2 \ , \tag{22}$$

$$\Delta\varepsilon - \Delta\varepsilon^0 \cong -4\pi C_1 E_0^2 \ , \tag{23}$$

while in the opposite limit ($Z^2 \gg 1$) we obtain the asymptotic formulas

$$\omega_m \cong C_2 E_0^{2/3} \ , \tag{24}$$

$$\Delta\varepsilon \cong C_3 E_0^{-2/3} \ , \tag{25}$$

where the constants C_1, C_2, and C_3 are given by

$$C_1 = 3B(c\chi/A)^4 \ , \quad C_2 = 3\omega_m^0 B^{1/3}(c\chi)^{2/3}/A \ , \quad C_3 = 4\pi(c\chi)^{4/3}/3B^{1/3} \ . \tag{26}$$

Thus by increasing the dc bias field $\mathbf{E}_0$, the relaxation frequency ω_m of the soft mode increases as described by Eqs. (22) and (24). For the same condition the dielectric strength $\Delta\varepsilon$ decreases from $\Delta\varepsilon^0$ to zero in accordance with the laws given by Eqs. (23) and (25).

From the data shown in Figs. 1–3 we can determine the field dependencies of the relaxation frequency ω_m and the dielectric strength $\Delta\varepsilon$ of the soft mode. Figures 1–3 show that in addition to the soft mode relaxation band there are excessive dielectric losses both at the low and high frequency ranges. The low frequency contribution is due to dc conductivity, which follows the law

$$\varepsilon_\perp(\omega) = 4\pi\sigma_0/\omega \ , \tag{27}$$

where σ_0 is the dc conductivity. The edge of the high frequency loss, which occurs above 100 kHz, is caused by the resistance of the ITO coating layer on the glass of the test cell. This effect on dielectric measurements has also been reported elsewhere [13]. The contributions of the dc conductivity and ITO effect have been subtracted from the observed dielectric loss spectra in order to separate the soft mode band from these spectra. Then the dielectric data were fitted using a standard computer program which allows fitting the experimental dielectric data to the Havriliak-Negami equation [14],

$$\varepsilon_\perp(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (i\omega/\omega_m)^\alpha]^\beta} \ , \tag{28}$$

where α and β are the parameters that characterize the

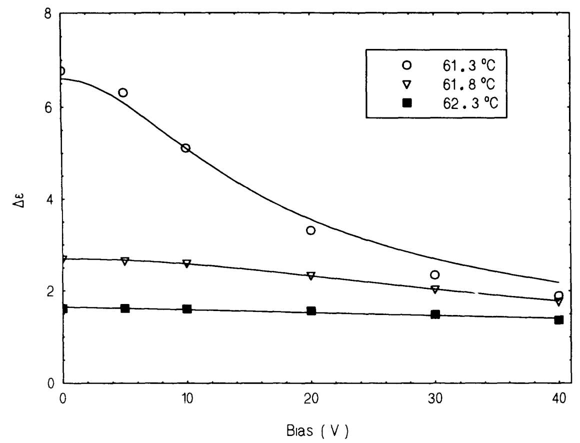

FIG. 4. Comparison of the experimental and theoretical (solid lines) dielectric strength $\Delta\varepsilon$ vs voltage V applied across the cell.

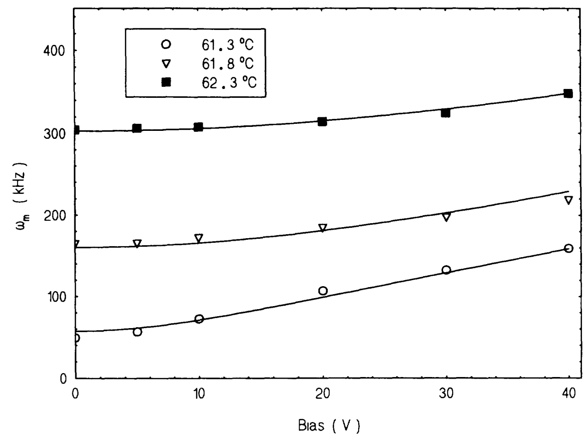

FIG. 5. Comparison of the experimental and theoretical (solid lines) relaxation frequency ω_m vs applied voltage V.

distribution of the relaxation frequencies ω_m. For the case under consideration the best fit gives these parameters to be $\alpha \cong 0.96 \pm 0.02$ and $\beta \cong 1$. Errors in fitting were less than 1%. On taking into account experimental uncertainty ($\sim 5\%$) the values of α and β obtained are in accordance with our approximation of the single relaxation frequency, which corresponds to $\alpha = 1$ and $\beta = 1$. So the evaluated relaxation frequency ω_m is approximately equal to the experimental frequency of the soft mode band maximum, while the dielectric strength $\Delta\varepsilon \cong 2\varepsilon''(\omega_m)$. [The Debye equation (16) predicts that the maximum of dielectric loss $\varepsilon''(\omega)$ at the frequency ω_m with $\varepsilon''(\omega_m) = \Delta\varepsilon/2$.]

In Figs. 4 and 5 we compare the experimental and theoretical dielectric strength $\Delta\varepsilon$ and relaxation frequency ω_m as functions of voltage V applied across the cell. The voltage dependence of ω_m is described by algebraic equation (17), exhibiting a crossover from the squared law $\sim V^2$ at small V to the asymptotic behavior $\sim V^{2/3}$ in the limit of high bias field [see Eqs. (22) and (24)]. A reciprocal behavior of the dielectric strength $\Delta\varepsilon$ on V is given by Eq. (18). Such a behavior is in accordance with the experimental data shown in Figs. 4 and 5. In agreement with Eq. (20), the nonlinear behavior is much more pronounced close to the phase transition temperature. This result is in qualitative agreement with the electro-optic observations of a characteristic relaxation time τ of the electro-optic response [4]. The nonlinear behavior of τ is similar to that of ω_m^{-1}.

The above fitting of the experimental data allows us to extract information about the phenomenological coefficients appearing in Eq. (1). The adjustable coefficient C from Eq. (21) is found from the analysis to be 0.028. This value has reasonable order of magnitude as can be evaluated from the available literature data for the $c\chi$, B, and a coefficients [4,15,16].

IV. CONCLUSIONS

We show the nonlinear field dependencies of the dielectric permittivity as a function of the dc bias field of a smectic-A liquid crystal in the vicinity of the Sm-A–Sm-C^* phase transition. This is mainly due to nonlinear behavior resulting from the large electroclinic coupling between the induced molecular tilt and the polarization. In order to describe the dielectric properties of the smectic-A phase in the presence of a dc bias field and to explain the experimental results, we develop the mean field theory. This theory allows us to evaluate the temperature and field dependencies of the complex dielectric permittivity and to compare the dielectric and the electro-optic responses of the FLC's. The mean field theory proposed may be considered as a simplification of that by Gouda *et al.* [17]. The theory [17] is based on a more general expansion of the free energy density that does not allow one to obtain analytic solutions for the relaxation frequency ω_m and dielectric strength $\Delta\varepsilon$ and, moreover, introduces several adjustable parameters—difficult to evaluate both experimentally and theoretically.

ACKNOWLEDGMENTS

The authors (Y.P.K., J.K.V., and H.X.) acknowledge the European Commission for Grant No. SC*0291 awarded under the Science Laboratory Twinning Programme. One of the authors (J.K.V.) thanks the Department of Foreign Affairs for the support to work in the University of Colorado, Boulder, CO, and Professor N. A. Clark for hospitality and useful discussions. We also thank Dr. F. Gouda for bringing his work [17] to our attention.

[1] N. A. Clark and S. T. Lagerwall, Ferroelectrics **59**, 25 (1984).
[2] M. A. Handschy and N. A. Clark, Ferroelectrics **59**, 69 (1984).
[3] S. Garoff and R. B. Meyer, Phys. Rev. A **19**, 338 (1979).
[4] S. Lee and J. S. Patel, Appl. Phys. Lett. **55**, 122 (1989).
[5] G. Andersson, I. Dahl, P. Keller, W. Kuczynski, S. T. Lagerwall, K. Sharp, and B. Stebler, Appl. Phys. Lett. **51**, 640 (1987).
[6] J. Pavel and M. Glogarova, Ferroelectrics **121**, 45 (1991).
[7] C. H. Bahr and G. Heppke, Liq. Cryst. **2**, 825 (1987).
[8] Z. Li, R. B. Akins, G. A. DiLisi, C. Rosenblatt, and R. G. Petschek, Phys. Rev. A **43**, 852 (1991).
[9] T. Carlsson, B. Žekš, C. Filipič, and A. Levstik, Phys. Rev. A **42**, 877 (1990).
[10] P. G. Costello, Yu. P. Kalmykov, and J. K. Vij, Phys. Rev. A **46**, 4852 (1992).
[11] B. Žekš, T. Carlsson, I. Musevič, and B. Kutnjak-Urbanc, Liq. Cryst. **15**, 103 (1993).
[12] *Liquid Crystals, Catalog of the British Drug House* (now E. Merck, United Kingdom), June 1989.
[13] F. Gouda, K. Skarp, and S. T. Lagerwall, Ferroelectrics **113**, 165 (1991).
[14] S. Havriliak and S. Negami, J. Polym. Sci. **C14**, 99 (1966).
[15] T. Carlsson, B. Žekš, C. Filipič, A. Levstik, and R. Blinc, Mol. Cryst. Liq. Cryst. **163**, 11 (1988).
[16] C. C. Huang and S. Dumrongrattana, Phys. Rev. A **34**, 5020 (1986).
[17] F. Gouda, G. Andersson, S. T. Lagerwall, K. Skarp, B. Stebler, T. Carlsson, B. Žekš, C. Filipič, and A. Levstik, Liq. Cryst. **6**, 219 (1989).