Influence of ions on the ''V-shaped'' electro-optic response of ferroelectric liquid crystals

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It has recently been shown that in surface-stabilized ferroelectric liquid crystal cells with high spontaneous polarization, the polarization charge self-interaction leads to a ''V-shaped'' optical response to an applied voltage. The presence of ionic free charges in the liquid crystal changes the internal electric field, and therefore also the spatial dependence of the polarization and optic axis orientation. We have numerically solved the nonlinear ion diffusion equation in the electric field due to external voltage, spontaneous polarization, and ions, and calculated the electro-optic response to a triangular applied voltage. When the period of the driving voltage is smaller than the zero-field diffusion time of the ions across the cell, and larger than the ion transit time in the applied field, an inverse hysteresis in the electro-optic response is obtained. At these time scales ions also cause characteristic changes in the shape of the electro-optic response.

I. INTRODUCTION

In some chiral smectic liquid crystals, for example some homologs of MHPOBC [1] and other high polarization smectics, a very interesting ''V-shaped'' high contrast electro-optic effect is found. Such cells are planar- aligned and surface stabilized (helix free), and exhibit electric-field-induced continuous reorientation of the optic axis, which is along the layer normal for zero applied voltage, $V = 0$. Recent experiments on V-shaped switching cells have demonstrated that the effect is a feature of the ferroelectric SmC^* phase [2], and that the rotation of the optic axis is due to the reorientation on the smectic C^* cone [2,3]. It was also shown that the effect is electrostatic in origin [4], a result of self-interaction of the spontaneous polarization **P**, which becomes important in materials having sufficiently high polarization.

The mechanism can be understood in the following way. Consider a slab of SmC^* material in a planar bookshelf structure with a thickness L, as depicted in Fig. 1. The cell is formed by two conducting electrodes separated from the liquid crystal by insulating alignment layers of thickness a and dielectric constant ε_1. Let $V = 0$ initially. The anchoring at the surface is planar, so that the minimum surface energy is obtained for **P** perpendicular to the surface. The energies for **P** pointing into or out of the surface are usually not the same, and the surface anchoring energy can be decomposed into a nonpolar part invariant with respect to polarization reversal, and a polar part which depends on the sign of **P**. The nonpolar part gives rise to the well known bistability. The perpendicular (x) component of **P** creates a surface polarization charge which must be compensated for by free charges on the electrodes. Since these are separated from the liquid crystal by the alignment layer, an electric field is created in the alignment layer. When the electrostatic energy of this field is greater than the nonpolar part of the surface anchoring energy, it is energetically favorable for the surface anchoring to break so that the polarization is parallel to the cell plates. This situation is of course monostable. The importance of the

field in the alignment layer was already recognized in Ref. [5]. The polar part of the anchoring causes **P** to be splayed in both monostable and bistable states, and so through polarization charges in the splayed region it always gives a positive contribution to the electrostatic energy. A more detailed analysis, to be published separately, shows that polar anchoring favors the monostable state. As the electrostatic energy of the alignment layer is proportional to P^2, while the nonpolar contribution to the anchoring energy is independent of P, a monostable state is obtained for high P materials.

When an external voltage is applied to the monostable cell, **P** turns by an angle ϕ from the horizontal (y) axis, so that the total field in the liquid crystal remains zero. The voltage across the cell is entirely due to a field which must appear in the alignment layer due to the polarization charge density $P \sin \phi$ at the boundary between the liquid crystal and the alignment layer. This leads to a very simple relation between V and ϕ [4]:
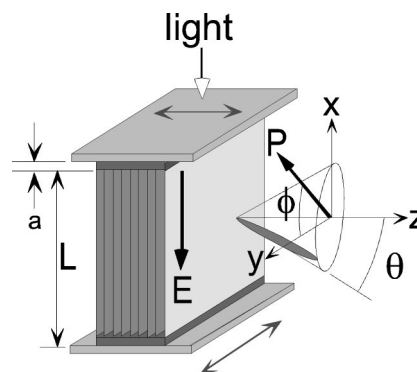

FIG. 1. Bookshelf geometry of a tilted chiral smectic. The liquid crystal is between glass plates with transparent ITO electrodes coated with nonconducting alignment layers. The smectic layers are normal to the plates. Shown are the tilt cone of the molecules with an angle θ relative to the layer normal **z**, the spontaneous polarization **P**, and the azimuthal orientation ϕ of **P**. V-shaped switching is observed with normally incident light between crossed polarizers.

$$V = 2\frac{aP \sin \phi}{\varepsilon_1 \varepsilon_0}. \qquad (1)$$

When $V > V_c = 2aP/\varepsilon_1\varepsilon_0$, the polarization is aligned perpendicular to the cell plates and can no longer compensate for the external field so the total field inside the liquid crystal is no longer zero. The direction of the optic axis is directly related to ϕ, and with the cell between crossed polarizers with one axis along the layer normal the characteristic V-shaped optical transmission versus applied voltage is obtained.

In V-shaped switching, the dominant interaction is electrostatic. In particular, during the switching process, when **P** is not perpendicular to the cell, the field inside the liquid crystal must be zero. In reality, there will always be some ionic impurities present in the liquid crystal, so it is of interest and also potentially important for applications to see how ionic charges influence the switching process and the optical transmission curves. In this paper we present the results of calculations of ion transport and its effect on V-shaped switching.

Two main features can be expected. Let us suppose that the cell is driven by a symmetric triangular voltage. The field inside the liquid crystal layer at high V will cause an inhomogeneous distribution of ions that partly screens the applied field. During switching, the ion sheets drift and diffuse from one side of the cell to the other, creating an additional inhomogeneous electric field. As the total field is still zero, the field due to **P** is also inhomogeneous. This means that the optic axis position is no longer the same throughout the cell and the optical response becomes nonsymmetric around the extinction point. Also, as the ionic contribution to the field opposes the external field, the polarization field crosses zero before $V = 0$, so that going (for example) from the negative voltage peak optical extinction also occurs for some small negative value of V; that is, we obtain an inverse hysteresis, which is also observed experimentally in some cases [6,7]. The authors of Ref. [7] also presented some model calculations, assuming, however, that the liquid crystal is in the antiferroelectric phase.

II. MODEL

The geometry of the problem is shown in Fig. 1. We wish to compute the distribution of ions and the polarization and optic axis direction as a function of V. The direction of $\mathbf{P}(x)$ is specified by the angle ϕ of **P** with respect to the y axis. We first write the equation for the balance of torques,

$$\gamma \frac{\partial \phi}{\partial t} = K \frac{\partial^2 \phi}{\partial x^2} + PE \cos \phi, \qquad (2)$$

where γ is an effective rotational viscosity, K is the splay elastic constant for the c director, and E is the total field due to external voltage, polarization, and ion distribution. In our case all the quantities depend only on x, and E has only an x component, so that it can be expressed in the form

$$E = \frac{\sigma}{\varepsilon\varepsilon_0} + \frac{e}{\varepsilon\varepsilon_0}\int_0^x [\rho_+(x) - \rho_-(x)]dx' - \frac{1}{\varepsilon\varepsilon_0}P \sin \phi, \qquad (3)$$

where σ is the charge density on the electrodes, ε is the dielectric constant of the liquid crystal, e is the elementary charge, and ρ_+ and ρ_- are the concentrations of the positive and negative ions. In expressing E we have neglected the dependence of ε on ϕ (i.e., the dielectric anisotropy of the liquid crystal), which would make the expression considerably more complicated. As the basic equation [Eq. 1] governing the V-shaped switching does not depend on ε, and we are looking for the effect of ions when their concentration is not too large, we expect that the anisotropy of ε and its spatial variation will only have a small effect on the results.

As it is the voltage between the electrodes that is specified in an experiment, not σ, we also have the condition

$$\int_0^L E dx + \frac{2\sigma a}{\varepsilon_1\varepsilon_0} = -V, \qquad (4)$$

which fixes σ. The second term is due to the insulating alignment layers.

We still need the equation of motion for the ions. As we have seen that the total field in the liquid crystal can be zero due to the screening by the polarization charges, we must include both the drift and diffusion terms,

$$\frac{\partial \rho_\pm}{\partial t} = \pm \mu_\pm e \frac{\partial}{\partial x}(E\rho_\pm) + D_\pm \frac{\partial^2 \rho_\pm}{\partial x^2}, \qquad (5)$$

where $\mu_\pm$ is the mobility of the positive or negative ions and $D_\pm$ the corresponding diffusion constant, which is related by $D_\pm = \mu_\pm k_B T$.

Before embarking on solving Eqs. (2–5), it is worthwhile to examine the relevant time scales. There are two related to the reorientation of **P**: the elastic reorientation time, $\tau_K = \gamma L^2/K$, and the reorientation in the electric field due to **P** itself, $\tau_P = \varepsilon\varepsilon_0\gamma/P^2$. Taking $\gamma = 1$ P, $K = 10^{-11}$ J/m, $\varepsilon = 10$, $L = 2$ μm, and $P = 300$ nC/cm^2, we obtain $\tau_K = 4 \times 10^{-2}$ s and $\tau_P = 10^{-4}$ s. The important times for the ion motion are the ion transit time τ_T in the field $P/\varepsilon\varepsilon_0$ and the diffusion time τ_D for the ions to cross the cell. Taking $e\mu = 10^{-11}$ m^2/V s [8,9] for the ion mobility, we obtain $\tau_T = 0.1$ s and $\tau_D = 15$ s. Thus the motion of ions is much slower than the reorientation of **P**, and when the applied voltage changes over time scales which are long compared to τ_P and τ_K, **P** adiabatically follows the motion of the ions. This means that we can set the viscous torque, that is the left side of Eq. (2), to zero.

If we also assume that P is large enough to break the surface anchoring, as discussed in Sec. I, we can also neglect the elastic term in Eq. (2). Then we are left with a very simple condition that the electric torque must be zero,

$$PE \cos \phi = 0, \qquad (6)$$

requiring that either $E = 0$ or $\phi = \pm \pi/2$. In other words, if **P** is not perpendicular to the cell plane, it completely screens

the field inside the liquid crystal. Conditions (6) and (4), and Eq. (3), also immediately lead to Eq. (1).

In this approximation we only need the boundary conditions for ρ. We assume that the number of ions in the cell is constant, so the ionic currents at both boundaries must be zero:

$$\pm\mu_{\pm}eE\rho_{\pm}-D_{\pm}\frac{\partial\rho_{\pm}}{\partial x}\Bigg|_{x=0,L}=0. \tag{7}$$

The whole problem is now reduced to solving the ion diffusion equation (5) with boundary conditions (7), and subject to conditions (4) and (6). We carried out numerical integration of Eq. (5) on a lattice of up to 200 points using the semi-implicit Crank-Nicholson scheme. At each step $E(x)$ was recalculated using Eqs. (3) and (4), and condition (6). The optical transmission was calculated using the Jones formalism. The cell was assumed to consist of uniaxial slices between lattice points, with optic axis direction determined by the local value of ϕ.

III. RESULTS

The important parameters of the problem are P, the number of ions, and μ. The ion diffusion constant is related to the mobility thorough the Einstein relation. A convenient unit of time is the ion diffusion time across the cell: $\tau_D = L^2/\mu k_B T \simeq 15$ s. A natural unit for the electric field is $E_0 = k_B T/eL \simeq 0.013$ V/μm. The corresponding unit for polarization is $P_0 = E_0/\varepsilon\varepsilon_0 \simeq 0.13$ nC/cm^2, assuming $\varepsilon = 10$. Also taking the unit of length to be L, Eq. (5) becomes dimensionless with no parameters, so the only remaining relevant quantities are P and the number of ions per unit area N_0. For computational convenience we take $P = 200P_0 \simeq 26$ nC/cm^2. In typical surface stabilized cells this value is probably too low to give monostable V-shaped switching, but we can assume that either the alignment layer is sufficiently thick or the anchoring energy sufficiently small that the cell is in the monostable regime. We take N_0 to be such that the internal field due to ions is comparable to the polarization field. This means that $N_0 = P/e$, or that the equilibrium concentration of ions is about $10^{16}/$cm^3. When the ion concentration is substantially smaller, their effect on the switching characteristics of the cell becomes negligible. For simplicity we also assume the mobilities for positive and negative ions to be equal, $\mu_+ = \mu_-$, so that the dynamics only need to be computed for one species of ions. For the alignment layers we take $2\varepsilon_1 a = 0.1L$.

With this choice of parameters we first consider the ion distribution as a function of time for a triangular applied voltage with a period $t = 0.2\tau_D$ and an amplitude $V_0 = 100k_B T/e$, that is about two times the voltage necessary for complete switching. One cycle is shown in Fig. 2. As expected, starting with $V(t=0) = V_0$ we obtain a narrow screening layer of ions at the cell boundary, with a peak ion concentration about 60 times the average. At zero external voltage the ion concentration is still quite inhomogeneous— the ions are still bunched up near $x/L = 1$—so that there is an appreciable field due to ions. The polarity of this ionic field
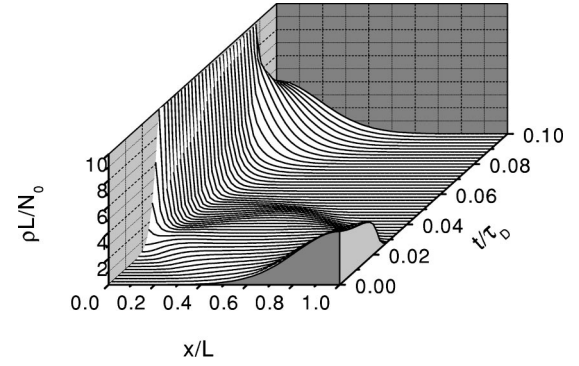

FIG. 2. Positive ion distribution ρ, relative to the equilibrium ion concentration N_0/L, as a function of time for triangular applied voltage with period $0.2\tau_D$ and amplitude $100k_B T/e$. One half-period is shown. Negative ions are symmetrically distributed. When the voltage is zero, i.e., at $t=0$ and 0.1, the ions are not evenly distributed and give a negative inhomogeneous contribution to the total field which is canceled by the polarization field. The peak concentration at the cell surfaces is about 60 times the equilibrium concentration. τ_D is the ion diffusion time $L^2/\mu k_B T$.

is of course opposite to the externally applied field at the preceding peak voltage. This reverse ionic field causes an inverse hysteresis of the optical response.

The direction ϕ of the spontaneous polarization at several points in the voltage sweep is shown in Fig. 3. As explained above, whenever $\phi \neq \pm\pi/2$, the total internal field must be zero, that is, the polarization field must cancel the ionic and external fields. As the ionic field is inhomogeneous, ϕ must also vary across the cell. Also note that at the moment when $V=0$, the average value of ϕ has already reoriented past the zero position due to the reverse ionic field.

Figure 4 shows the total internal field E during one period of the driving voltage. At all points where **P** is reorienting
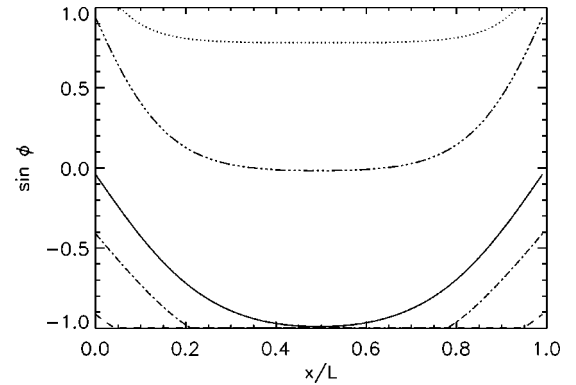

FIG. 3. Polarization angle vs position at several voltages for a triangular applied voltage with a period $0.2\tau_D$ and an amplitude $100k_B T/e$, going from a positive to a negative peak. $\cdots$: $V = 20k_B T/e$; $-\cdots-$: $V = 10k_B T/e$; $—$:$V=0$; $-\cdot-\cdot$: $V = -10k_B T/e$; $- - -$: $V = -20k_B T/e$. For $V=0$ the polarization angle is already negative; the field due to ions causes inverse hysteresis. The spatial dependence of the polarization angle also implies an inhomogeneity of the optic axis orientation and an asymmetric optic response around the extinction point. τ_D is the ion diffusion time $L^2/\mu k_B T$.
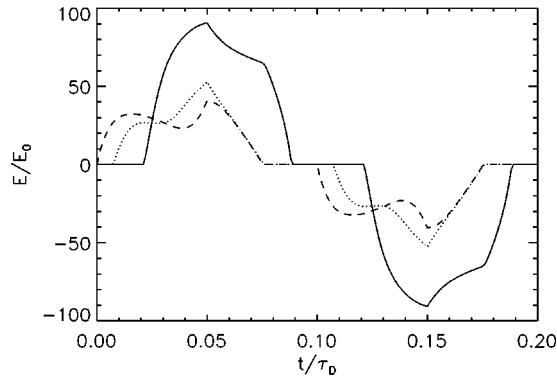
FIG. 4. Total internal field, in units of $E_0 = k_B T/eL$, vs time at several positions in the cell for triangular applied voltage with a period $0.2\tau_D$ and an amplitude $100k_BT/e$. The field is zero whenever the polarization is not perpendicular to the cell plane. Solid line: $x=0$; dots: $x=0.25L$; dashes: $x=0.5L$. τ_D is the ion diffusion time $L^2/\mu k_B T$.

between the extreme positions $\phi = \pm \pi/2$, we have $E=0$, and in that part of the voltage sweep the ions are freely diffusing instead of being driven by the external and ionic fields. It is in fact difficult to imagine any other physical situation in which an inhomogeneous distribution of charged particles could decay by field-free diffusion.

In Fig. 5 we show the optical transmission of the cell between crossed polarizers as a function of increasing V for three different cell thicknesses corresponding to $\lambda/2$, $3\lambda/4$, and λ wave plates (i.e., $\Delta nL = \lambda/2$, $3\lambda/4$, and λ) when $\phi = \pm \pi/2$ (i.e., when they are fully switched). The smectic cone angle is taken to be $\theta = 28°$. Looking first at the $\lambda/2$ cell, the thickness typically used in display applications, we see that the zero transmission point is shifted ahead of $V =0$, i.e., there is inverse hysteresis effect. The V shape is also asymmetrically distorted, which is due to the curved
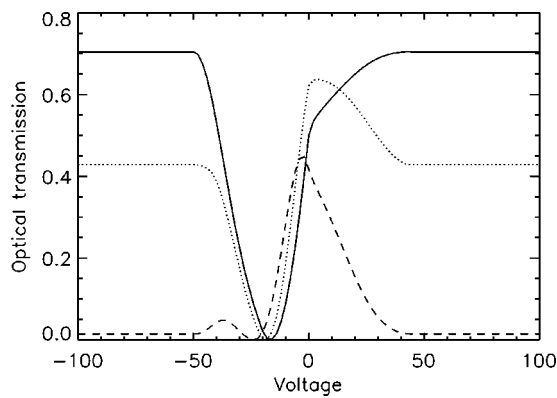

FIG. 5. Optical transmission for cells of different thickness between crossed polarizers with one polarizer directed along the layer normal as a function of applied triangular voltage, in units of k_BT/e, with a period $0.2\tau_D$ going from the negative peak to the positive peak. Solid line: $L\Delta n = \lambda/2$; dots: $L\Delta n = 3\lambda/4$; dashed line: $L\Delta n = \lambda$. Note that extinction occurs $10k_BT/e$ before $V=0$ (inverse hysteresis). The V is also asymmetric, with a pronounced peak on the trailing part for the $3/4\lambda$ and full wave cells. τ_D is the ion diffusion time $L^2/\mu k_B T$.
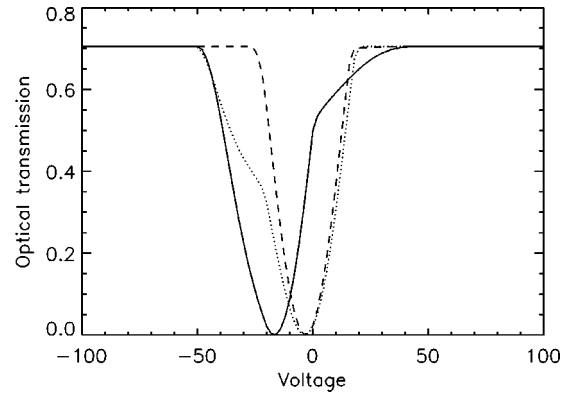

FIG. 6. Optical transmission for three periods t_0 of the triangular applied voltage, in units of k_BT/e, starting from the negative peak. Dotted line: $t_0 = 2\tau_D$; solid line: $t_0 = 0.2\tau_D$; dashed line: $t_0 = 0.01\tau_D$. For low and high frequencies the inverse hysteresis disappears, while it is largest for $t_0 = 0.2\tau_D$. The asymmetric shape of the low-frequency V is caused by the relaxation of the ion distribution when the internal field becomes zero. For high frequencies the viscous drag, neglected in our calculation, gives a normal hysteresis, causing the extinction point to shift to positive voltage. τ_D is the ion diffusion time $L^2/\mu k_B T$.

distribution of $\phi(x)$, presented in Fig. 2. This asymmetry is even more obvious for $3\lambda/4$ and λ cells, where we obtain asymmetric peaks of transmission at the beginning and end of the V. These peaks are due to the fact that for ϕ close to $\pm \pi/2$, the projection of the optic axis on the plane of the cell is near its extremes, but as the optic axis is tilted out of the cell plane, the effective optical anisotropy is smaller than the maximum value at $\phi = \pm \pi/2$ and the optical cell thickness is reduced toward that of a $\lambda/2$ plate which gives the highest transmission. While without the ions the two peaks are symmetric, the smaller peak at the beginning of the V even disappears for smaller cone angles.

In Fig. 6 we present the dependence of the optical transmission on the period of the applied voltage. For $t_0 = \tau_D$ the
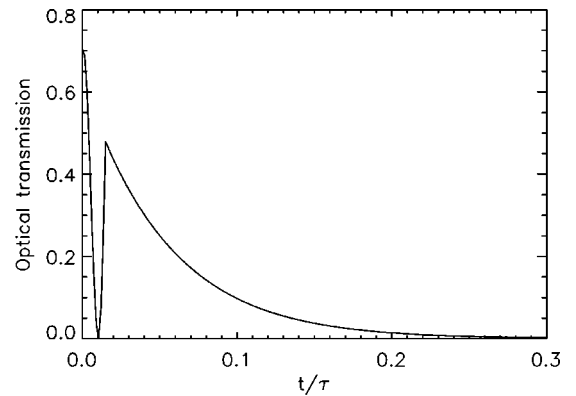

FIG. 7. Optical transmission vs time as the voltage is suddenly switched off from a value above V_c. The ionic part of the field initially drives the polarization to the reverse direction. The ion distribution then decays to equilibrium by field-free diffusion. The amplitude of the response is proportional to the ion concentration, and the decay time is $\tau = (L/\pi)^2/D$.

inverse hysteresis disappears, but some asymmetry of the V remains. At $V = -V_c$ the ions are still unevenly distributed, but they have time to diffuse to the equilibrium during the switching process, so they do not affect the end part of the V. For the chosen ion number, the maximum inverse hysteresis is obtained at $t_0 \simeq 0.2\tau_D$. For $t_0 \lesssim 0.04\tau_D$ the ions can no longer follow the field and are more or less evenly distributed, so the V becomes symmetric and free of hysteresis as if the ions were absent. We must note, however, that at higher frequencies the viscous dynamics of the liquid crystal, which is neglected in the present calculation, becomes important and causes normal hysteresis in the optical response. Note too that the trailing parts of the V are the same for both low $(t_0 = \tau_D)$ and high $(t_0 \simeq 0.04\tau_D)$ frequencies, as in both extremes the dynamics is unaffected by the ions.

The response of the cell when the applied voltage is suddenly switched from some value above V_c to 0 is shown in Fig. 7. The response first crosses zero due to the reverse ionic field. Then the ionic distribution decays to equilibrium by field-free diffusion, and the polarization follows. This overshoot of the optical response, followed by slow (on the order of 10 s) exponential decay to zero, is perhaps the easiest way to detect the presence of ions experimentally in a given cell. It also provides a way to measure the ion diffusion constant. In reality, the decay will be somewhat faster than τ_D due to the elasticity of the liquid crystal. The spatial dependence of ϕ causes an elastic restoring torque which must be countered by some small electric field which also acts on the ions and drives them toward equilibrium. This effect can be properly analyzed only by simultaneously solving both the polarization and ion equations (2) and (5).

To conclude, we have presented an analysis of the effect of ions on the V-shaped switching of monostable bookshelf ferroelectric liquid crystal cells. The ions mainly influence the cell when the period of the external driving voltage is a few times smaller than the ion diffusion time across the cell. They cause an inverse hysteresis and lead to an asymmetry in the optical response.

[1] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, and A. Fukuda, J. Mater. Chem. **6**, 671 (1996); S.S. Seomun, B. Park, A.D.L. Chadani, D.S. Hermann, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, J. Appl. Phys. **37**, L691 (1998); A. Fukuda, Y. Takanishi, K. Ishikawa, and H. Takezoe, J. Mater. Chem. **4**, 997 (1994).

[2] N.A. Clark, J.E. Maclennan, R. Shao, D. Coleman, S. Bardon, T. Bellini, D.R. Link, G. Natale, M.A. Glaser, D.M. Walba, M.D. Wand, X.H. Chen, P. Rudquist, J.P.F. Lagerwall, M. Buivydas, F. Gouda, and S.T. Lagerwall, J. Mater. Chem. **9**, 1257 (1999); P. Rudquist, R.F. Shao, D. Coleman, S. Bardon, D.R. Link, T. Bellini, J.E. Maclennan, X.H. Chen, D.M. Walba, J.P.F. Lagerwall, M. Buivydas, F. Gouda, S.T. Lagerwall, and N.A. Clark (unpublished).

[3] B. Park, S. Seomun, M. Nakata, M. Takahashi, Y. Takanishi, and H. Takezoe, Jpn. J. Appl. Phys., Part 1 **38**, 1474 (1999).

[4] N.A. Clark, D. Coleman, and J.E. Maclennan, Liq. Cryst. **27**, 985 (2000).

[5] K.H. Yang, T.C. Chieu, and S. Osofsky, Appl. Phys. Lett. **55**, 125 (1989).

[6] A.D.L. Chandani, Y. Cui, S.S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Liq. Cryst. **26**, 167 (1999).

[7] Yu.P. Panarin, V. Panov, O. Kalinovskaya, and J.K. Vij, Ferroelectrics **246**, 941 (2000).

[8] T.C. Chieu and K.H. Yang, Jpn. J. Appl. Phys., Part 1 **28**, 2240 (1989).

[9] H. Naito, M. Okuda, and A. Sugimura, Phys. Rev. A **44**, R3434 (1991).