

## Electric-Field-Induced Chirality Flipping in Smectic Liquid Crystals: The Role of Anisotropic Viscosity

M. Nakata,<sup>1</sup> R.-F. Shao,<sup>1</sup> J. E. MacLennan,<sup>1</sup> W. Weissflog,<sup>2</sup> and N. A. Clark<sup>1</sup>

<sup>1</sup>*Department of Physics and Liquid Crystal Materials Research Center, University of Colorado, Boulder, Colorado 80309, USA*

<sup>2</sup>*Institut für Physikalische Chemie, Martin-Luther-Universität, Halle-Wittenberg, Germany*

(Received 19 September 2005; published 16 February 2006)

We demonstrate the homogeneous and permanent reversal of the chirality of a condensed phase by an applied electric field. Tilted chiral smectic layers exhibit a coupled polarization density and molecular orientation fields which reorient about the layer normal as couple of fixed handedness in response to small applied electric fields. Experiments on some bent-core smectics show that above a threshold field the induced rotation can occur instead about the molecular long axis and that, as a result, the handedness of the phase can be flipped. The effect is quantitatively described by a nonequilibrium dissipative model of chiral smectic dynamics with anisotropic rotational viscosities.

DOI: 10.1103/PhysRevLett.96.067802

PACS numbers: 61.30.-v

The chirality of materials originates in arrangements of atoms that lack reflection symmetry. For any such chiral organization there exists another, obtained by mirror reflection, which, apart from the weak interaction, has the same energy. Thus in order to make a material of fixed handedness these mirror reflection states must be separated by some sort of energy barrier. This barrier can be intramolecular, i.e., covalent in nature as in organic molecules synthesized to be chiral, or can be collective, as in spontaneously chiral crystals [1] or liquid crystals [2,3], which can form from otherwise achiral molecules. In this Letter we show how it is possible to use an applied electric field to flip the collective handedness of a spontaneously chiral material, homogeneously pushing a fluid chiral smectic of achiral bent-core molecules over an energy barrier separating mirror reflection states [the positive (+) chirality versus negative (−) chirality in Figs. 1(a) and 1(b)].

Tilted chiral fluid smectic phases are characterized by translational organization into planar fluid layers, coherent tilt of the mean molecular long axis, given by the director  $\mathbf{n}$ , through an angle  $\theta$  away from the layer normal,  $\mathbf{z}$ , and in-layer polar ordering, generating a macroscopic polarization density  $\mathbf{P} = P_0 \mathbf{n} \times \mathbf{z}$ , parallel to the layer plane. The resulting layer structure is monoclinic, of  $C_2$  symmetry, with one of the principal optic axes along  $\mathbf{P}$ , the  $C_2$  axis, and the other two in the  $\mathbf{n}$ ,  $\mathbf{z}$  (tilt) plane. In the calamitic chiral Sm-C\* phase, the polarization  $\mathbf{P}$  appears [4] with the sign of  $P_0$  determined by covalent molecular chirality, which breaks the reflection symmetry about the tilt plane. In the bent-core  $B_2$  (Sm-CP) phases, the polarization arises because of a spontaneous broken symmetry [3], with energetically degenerate domains of both signs of  $\mathbf{P}$  appearing. In either case the equilibrium local molecular orientation [tilt =  $\theta$  and  $\beta = 0$ , Fig. 1(d)] is enforced by collective torques  $\tau_c$  (gradients of a generalized potential energy surface) stabilizing a free energy minimum. This minimum is degenerate in energy with respect to uniform reorientation of the tilt plane, its azimuth  $\varphi$  acting as a

Goldstone variable. The portion of the energy surface relevant to chirality reversal,  $U_b(\beta)$ , a path corresponding to reorientation about the molecular long axis, exhibits in the Sm-CP phase degenerate minima at the two mirror reflection states ( $\beta = 0$ ,  $\beta = \pi$ ) separated by a barrier of height  $U_{\max}$  at  $\beta = \pi/2$  and  $3\pi/2$  [see Fig. 1(e)]. In the Sm-C phase the  $0-\pi$  degeneracy is lifted by the molecular chirality but a barrier can still exist.

We consider in detail the dynamics of  $\varphi(t)$  and  $\beta(t)$ , which respond to an applied in-plane electric field  $\mathbf{E}$  to minimize the electrostatic energy  $U_E = -\mathbf{P} \cdot \mathbf{E}$ . In the limit of small  $E$ , the azimuthal reorientation of  $\mathbf{n}$  is slow and  $\theta$  is nearly constant. The polarization  $\mathbf{P}$  maintains its orientation tangent to the tilt cone [ $\beta = 0$ , Fig. 1(d)], and thus the chirality of the phase is maintained. The reorientation rates about the molecular long and short axes,  $\dot{\psi}_l$  and  $\dot{\psi}_s$  [see Fig. 1(c)2], respectively, are constrained by  $\dot{\psi}_l/\dot{\psi}_s \equiv \tan\theta$ . Such low-field-induced reorientations are thus typically visualized as motion of the  $\mathbf{n}$ - $\mathbf{P}$  couple,  $\mathbf{n}$  moving around the tilt cone of constant  $\theta$  with  $\mathbf{P}$  always normal to the tilt plane. This field-induced motion is typically limited by viscosity, with the molecular reorientation reaching its “terminal” angular velocity after an unobservably short inertial response [5]. In the limit of large  $E$ , the field-induced torques overwhelm the collective torques  $\tau_c$ . The dynamic behavior is then determined solely by the balance of electric and viscous torques, and the dynamics become particularly simple: the molecules reorient primarily about their long axes, i.e., in  $\psi_l$ , the coordinate of minimum viscous drag. In the case of the Sm-CP phase the resulting response to high field reversal is the reorientation of molecules in  $\beta$ , giving a reversal of  $\mathbf{P}$  through the tilt plane barrier ( $\beta = \pi/2$ ) and, remarkably, a homogeneous and permanent reversal of the chirality of the phase. We demonstrate such chirality flipping experimentally in the bent-core LC **H91** and develop a nonequilibrium dynamic model that successfully describes the effect, showing the key role of viscous anisotropy

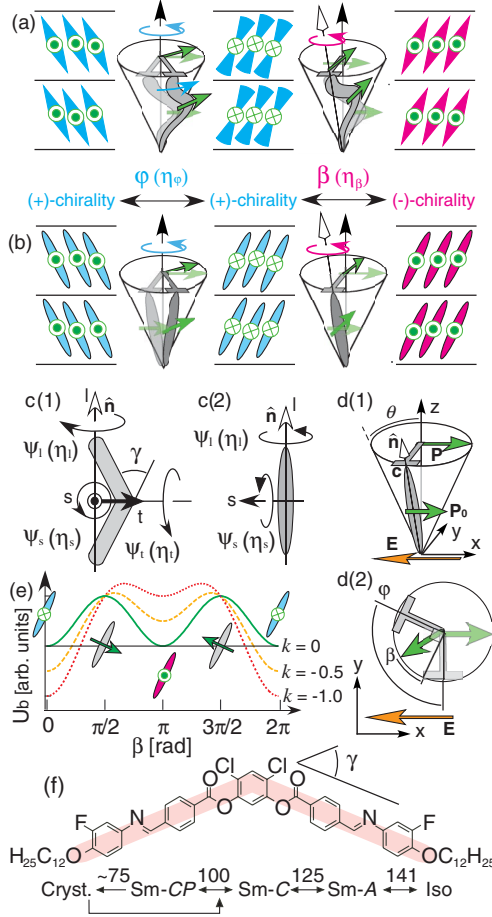


FIG. 1 (color online). Two modes of response to field reversal in fluid tilted smectic phases of (a) achiral bent-core molecules and (b) chiral rodlike molecules. From the center state to the left state, molecules rotate around the tilt cone ( $\varphi$  rotation, viscosity  $\eta_\varphi$ ) as the polarization reverses, maintaining the handedness of the layer. On the other hand, from the center state to the right state, each molecule rotates around its long axis  $\mathbf{n}$  ( $\beta$  rotation, viscosity  $\eta_\beta$ ) and the handedness of the layer reverses [between (+) layer and (-) layer] as the polarization reverses. In a bent-shaped molecular coordinates (c1), three independent rotation modes are defined. In simplified generalized rod-shape molecular coordinates (c), two rotation modes  $\varphi$  and  $\beta$  resolve into two independent rotations, respectively, about the molecular short axis  $\psi_s$  (viscosity  $\eta_s$ ) and about the molecular long axis  $\psi_l$  (viscosity  $\eta_l$ ). (d) shows the molecule in the layer coordinate frame of the tilted smectic. (e) Free energy  $U_b$  vs the  $\beta$ -rotation angle for achiral molecules (solid line) and chiral molecules (dotted lines). The bent-core system exhibits equivalent energy minima for states of opposite handedness, separated by an energy barrier in between. These states are not equivalent for covalently chiral molecules. (f) **H91**, the achiral bent-core molecule used in the experiment, with phase transition temperatures in  $^{\circ}\text{C}$  [4].

$\eta_\beta/\eta_\varphi$ , the ratio of effective viscosities for  $\beta$  and  $\varphi$  rotations, discussed below.

Shown in Fig. 1(f) is the molecular structure and phase behavior of **H91**, the bent-core material studied [6,7]. The Sm-CP phase is monotropic, but stable on cooling. **H91**

exhibits a Sm-A phase and hence alignment was quite uniform in test cells consisting of two glass plates with transparent conductive layers (ITO) and rubbed polyimide surfaces. Neither the Sm-A or Sm-C phase responds to applied electric field, indicating that these phases are non-polar, even though LC **H91** is a bent-core LC. This suggests that in its Sm-CP phase  $U_b$  may be relatively weak, making **H91** a good candidate for chirality flipping. Since  $\theta$  is practically the same in the Sm-C and Sm-CP phases, it can be taken to be unchanged under field application and fixed in the modeling, which deals only with field-induced changes in  $\varphi$  and  $\beta$ .

In the Sm-CP phase of **H91**, the ground state structure is chiral Sm- $C_A P_A$  which has molecules anticlinic and anti-polar in neighboring layers. With application of a field, the antiferroelectric Sm- $C_A P_A$  switches to the chiral ferroelectric Sm- $C_S P_F$  (synclinal and ferroelectric in neighboring layers) for  $E_{th} > \sim 10 \text{ V}/\mu\text{m}$ , and in the case of a triangular wave this Sm- $C_A P_A$  – Sm- $C_S P_F$  transition always occurs without change of the phase chirality. However, as shown in Fig. 2, in a square wave field, chirality reversal was observed above a second threshold,  $E_c$ , given in the dynamic phase diagram of Fig. 3. The chiral coupling of optic axis orientation to polarization, characteristic of tilted chiral smectics, makes this polarization/chirality reversal unambiguous. As shown in Fig. 2, near the threshold some areas of the cell exhibit chirality flipping, while others retain their chirality. Above the threshold for chirality reversal, no optical texture change is observed but the spontaneous polarization does reverse as evidenced by a polarization reversal current peak. Similar observations were reported in the Sm-CP phase of bent-core mesogens structurally similar to **H91** [8–10], in the two-dimensional modulated columnar phase ( $B_{\text{tilt}}$  phase) [11], and in the Sm-CPG bilayer phase [12].

We have formulated a model of the field-induced response of  $\varphi(t)$  and  $\beta(t)$ , exploring the conditions for chirality reversal under the assumption that the reorientation is spatially uniform, which will be the case in the high field limit. Molecular reorientation dynamics are governed by a biaxial tensorial viscosity  $\boldsymbol{\eta}$ , which is modeled by the viscous drag on a rod, bent at the middle through an angle  $\gamma$ , reorienting about its center of mass in a viscous fluid. Such a calculation shows that  $\boldsymbol{\eta}$  is diagonal with elements  $\eta_l$ ,  $\eta_s$ ,  $\eta_t$  in the  $(l, s, t)$  frame [Fig. 1(c)1], and for the shape of **H91** ( $\gamma \sim 60^\circ$ ),  $\eta_t \sim 1.3\eta_s$  and  $\eta_s \sim 2.5\eta_l$ , so that  $\boldsymbol{\eta}$  is close to being uniaxial. Consequently, in order to reduce the model to its essential elements, we take  $\boldsymbol{\eta}$  to be uniaxial, so that all rotations of the long molecular axes have the same rotational viscosity, with diagonal  $(l, s, t)$  elements given by  $\eta_l$ ,  $\eta_s$ ,  $\eta_t$  with  $\eta_t = \eta_s$ . We characterize molecular reorientation by the two independent rotations  $\psi_l = \varphi \cos\theta + \beta$  and  $\psi_s = \varphi \sin\theta$  [around  $\mathbf{l}$  and  $\mathbf{s}$  respectively, as shown in Figs. 1(c)2 and 1(e)]. The electrostatic energy is  $U_E(\beta, \varphi, \theta) = -P_0 E (\cos\varphi \cos\beta - \sin\varphi \sin\beta \cos\theta)$  and the internal barrier energy taken to be  $U_b(\beta) = U_{\max}(\sin^2\beta + k \cos\beta)$ , where the first term in

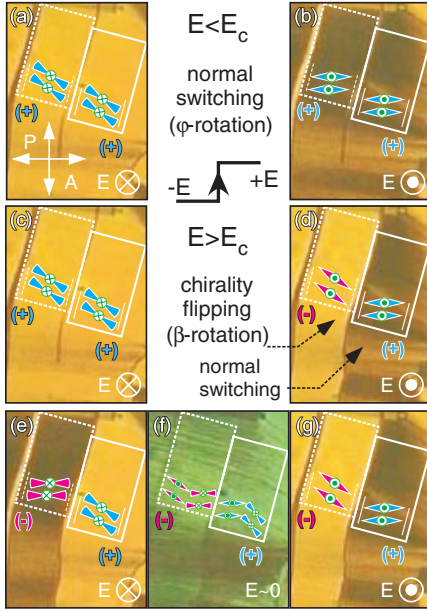


FIG. 2 (color online). Polarized optical microscope images of the electrooptic response of **H91** in the Sm-CP phase under application of a square wave electric field. From (a) to (b),  $E < E_c$  everywhere and the molecules in both regions (solid box and dashed box) switch around the tilt cone ( $\varphi$  rotation). From (c) to (d) is near the threshold for chirality flipping, the field reversals with  $E > E_c$  for the area in the dashed box, but  $E < E_c$  for the area in solid box. As a result, the handedness of layers in the dashed box flips but remains fixed in the solid box. On the other hand, the chirality of the layers is maintained under application of a low frequency triangular electric field (less than few hundred Hz). Upon reducing the initially positive field to  $E \sim 0$  [(e) to (f)] the antiferroelectric Sm- $C_A P_A$  state appears. Upon driving the field negative to  $-E < -E_c < -E_{th}$ , the Sm- $C_S P_F$  state reappears without changing the layer chirality, as shown in (f) to (g). The same switching process is observed upon increasing the field strength.

$U_b$  gives, for  $U_{max} > 0$ , the spontaneous symmetry breaking to degenerate chiral states (the case for a Sm-CP phase of achiral molecules), and the second term is present ( $k \neq 0$ ) if the system contains chiral molecules, making the energy different for a molecule with  $\beta = 0$  or  $\pi$  [the Sm- $C^*$  case, Fig. 1(e)]. In either case only the lowest order terms in the harmonic expansion of  $U_b(\beta)$  are kept.

To obtain the equations of motion, the rate of energy conversion to heat by change of  $\varphi$  or  $\beta$  is obtained from the Rayleigh dissipation function

$$D = \frac{1}{2}(\eta_l \dot{\psi}_l^2 + \eta_s \dot{\psi}_s^2) = \frac{1}{2}\eta_l(\dot{\varphi} \cos\theta + \dot{\beta})^2 + \frac{1}{2}\eta_s(\dot{\varphi} \sin\theta)^2, \quad (1)$$

where  $\eta_l$  and  $\eta_s$  are the orientational viscosities for rotation around  $l$  and  $s$ , respectively.  $\dot{\varphi}$  and  $\dot{\beta}$  are effectively terminal angular velocities, and we ignore inertial effects assumed to be fast on the time scale of molecular reorientation.  $D$  can be equated to the rate of internal energy

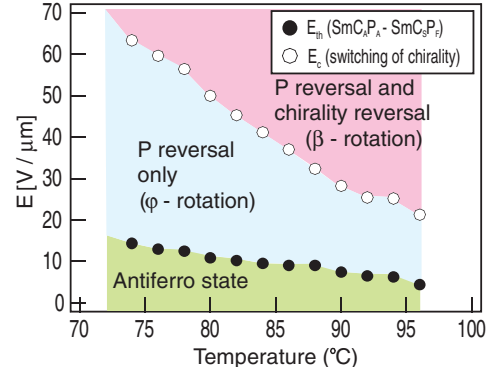


FIG. 3 (color online). Measured threshold fields  $E_{th}$  and  $E_c$  as a function of temperature in for the antiferroelectric Sm- $C_A P_A$  to field-induced ferroelectric Sm- $C_S P_F$  transition (●) and for the transition between normal switching  $\varphi$  rotation and chirality flipping  $\beta$  rotation (○) **H91**.

released by changes in  $\varphi$  or  $\beta$ , as follows

$$-\frac{\partial U_E}{\partial \varphi} = \frac{\partial D}{\partial \dot{\varphi}}, \quad -\frac{\partial U_E}{\partial \beta} - \frac{\partial U_b}{\partial \beta} = \frac{\partial D}{\partial \dot{\beta}},$$

from which we obtain the coupled equations of motion for the terminal angular velocities  $\dot{\varphi}$  and  $\dot{\beta}$ , using rotational viscosities for the  $\varphi$  rotation and  $\beta$  rotation given by  $\eta_\varphi = \eta_s \sin^2\theta + \eta_l \cos^2\theta$  and  $\eta_\beta = \eta_l$ , respectively,

$$\frac{d\varphi}{dt} = \frac{P_0 E \sin\varphi \cos\beta \sin^2\theta + (dU_b/d\beta) \cos\theta}{\eta_\varphi - \eta_\beta \cos^2\theta} \quad (2a)$$

$$\frac{d\beta}{dt} = \frac{P_0 E (\cos\varphi \sin\beta + \sin\varphi \cos\beta \cos\theta) - (dU_b/d\beta)}{\eta_\beta} - \frac{d\varphi}{dt} \cos\theta. \quad (2b)$$

Numerical solutions to these differential equations were obtained by the Euler-Cauchy method.

Key results of the model are shown in Fig. 4, for the case of the response of a spontaneously chiral Sm-CP phase ( $k = 0$  in  $U_b$ ) responding to a field step  $E$  at  $t = 0$ . At low field, polarization reversal via a  $\pi$  rotation of  $\varphi$  is induced, with a transient pulse in  $\beta$  that peaks when the torque on  $\mathbf{P}$  is the largest. The magnitude of the transient pulse increases with increasing  $E$ . At the flipping threshold field  $E_c$ , both  $\varphi(t)$  and  $\beta(t)$  have evolved into nearly identical  $\pi/2$  steps, and above the threshold, reversal via a  $\pi$  rotation in  $\beta$  occurs, with a transient pulselike response now in  $\varphi$ . Figure 4(e) presents the field dependence calculated from the model of the 10%–90% reorientation time for  $\varphi(t)$  when  $E < E_c$  and for  $\beta(t)$  when  $E > E_c$ , indicating a  $1/E$  dependence, continuous through  $E_c$ . Measurement of the 10%–90% electro-optical response time in the Sm-CP phase of **H91**, plotted in Fig. 4(f), shows  $1/E$  behavior in the field dependence, through the transition from nonflipping to flipping response. Figure 5 gives the calculated dependence of  $E_c$  on barrier height  $U_{max}$ , and on viscosity anisotropy  $\eta_\beta/\eta_\varphi$ . The flipping threshold  $E_c$



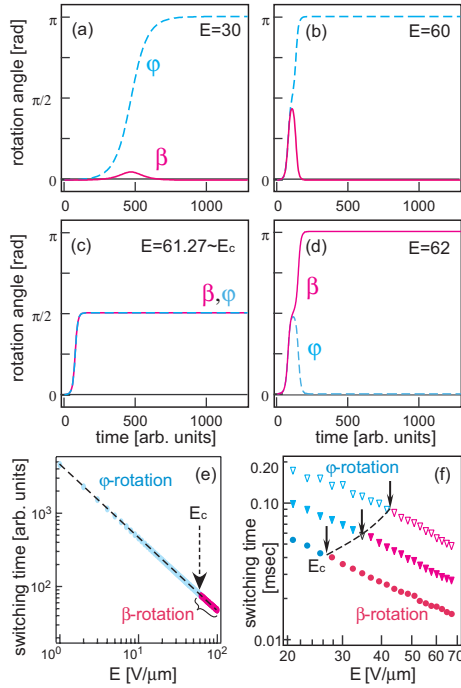


FIG. 4 (color online). Switching dynamics under field reversal: (a) to (e) Model results for  $\eta_\beta/\eta_\varphi = 0.96$ ,  $P = 400$ ,  $\theta = 15^\circ$ , and  $U_{\max} = 10\,000$ , with (a)–(d) showing  $\varphi(t)$  (dashed line) and  $\beta(t)$  (solid line) for fields of increasing amplitude. (a), (b) For  $E < E_c$ , the molecules rotate through  $\pi$  around the tilt cone ( $\varphi$  rotation), which maintains the layer chirality. (d) For  $E > E_c$ , the molecules rotate around their long axis ( $\beta$  rotation), flipping the handedness of the layer chirality. (e) The model gives a switching time  $\tau \propto 1/E$ , continuous through the chirality reversal transition, a prediction that matches the experimental **H91** data well. (f) Measured 10%–90% reorientation times of **H91** at  $T = 75^\circ\text{C}$  (open triangles),  $T = 80^\circ\text{C}$  (closed triangles), and  $T = 85^\circ\text{C}$  (closed circles).

depends linearly on  $U_{\max}$  but diverges rapidly as viscous isotropy is approached at  $\eta_\beta/\eta_\varphi \approx 0.95$ . Thus the reason why the chirality flipping ( $\beta$  rotation) has not been observed often is that the chiral Sm-C or achiral Sm-CP system usually has either high  $U_{\max}$  or  $\eta_\beta/\eta_\varphi$  close to 1.

Spontaneous polarization reversal of tilted polar smectic phases under application of an electric field typically occurs by rotation around the tilt cone ( $\varphi$  rotation). This

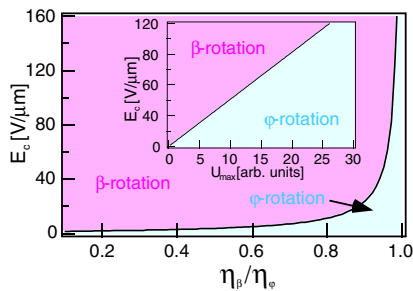


FIG. 5 (color online). Calculated critical field  $E_c$  vs the anisotropy in the rotational viscosities  $\eta_\varphi$  and  $\eta_\beta$ , and vs the barrier height  $U_{\max}$ .

process is well understood both experimentally and theoretically. However, as we have demonstrated, anisotropy of the rotational viscosity changes the molecular reorientation process from  $\varphi$  rotation, which keeps the layer handedness, to  $\beta$  rotation, which flips the layer handedness at high field. This leads us to speculate that calamitic chiral Sm-C phases will respond initially to high field steps in a fashion similar to **H91**, i.e., exhibit a transient chirality reversal at fixed  $\varphi$  via  $\beta$  reorientation about the long molecular axis, followed by a readjustment of both  $\beta$  and  $\varphi$  to end up, in the usual way, with the handedness of the initial state but with  $\varphi = \pi$ . This effect could occur, for example, in the calamitic Sm-C phase of bent-core molecules. Such behavior would be manifested by polarization reversal current bumps in the absence of optic axis reorientation. We believe that in bent-core materials the existence of the Sm-A or Sm-C phases is indicative of a relatively small  $U_{\max}$  and thus of the potential to exhibit chirality flipping in the Sm-CP phase [8–10]. Also, our model should be applicable to the switching dynamics in the  $B_{\text{tilt}}$  phase [11] by taking into account the interaction of the director with the column domain boundaries.

We thank Dr. Gerhard Pelzl and Dr. David M. Walba for useful discussions. This work was supported by NSF MRSEC Grant No. DMR 02139198 and NSF Grant No. DMR-0302060.

- [1] L. Pasteur, C R Acad Sci URSS, Ser A (1925-1933)/Doklady Akademii Nauk SSSR, Seriya A **26**, 535 (1848).
- [2] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996).
- [3] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblova, and D. M. Walba, Science **278**, 1924 (1997).
- [4] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. Lett. (Paris) **36**, L69 (1975).
- [5] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1993).
- [6] W. Weissflog, H. Nadasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, and H. Kresse, J. Mater. Chem. **11**, 2748 (2001).
- [7] A. Eremin, H. Nadasi, G. Pelzl, S. Diele, H. Kresse, W. Weissflog, and S. Grande, Phys. Chem. Chem. Phys. **6**, 1290 (2004).
- [8] M. W. Schröder, S. Diele, G. Pelzl, and W. Weissflog, Chem. Phys. Chem. **5**, 99 (2004).
- [9] R. A. Reddy, M. W. Schröder, M. Bodyagin, H. Kresse, S. Diele, G. Pelzl, and W. Weissflog, Angew. Chem. **117**, 784 (2005).
- [10] W. Weissflog, U. Dunemann, M. W. Schröder, S. Diele, G. Pelzl, H. Kresse, and S. Grande, J. Mater. Chem. **15**, 939 (2005).
- [11] J. Szydłowska, J. Mieczkowski, J. Maraszek, D. W. Bruce, E. Gorecka, D. Pociecha, and D. Guillon, Phys. Rev. E **67**, 031702 (2003).
- [12] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, H. T. Nguyen, and M. F. Achard, Phys. Rev. E **69**, 061702 (2004).