

Piezoelectricity of a ferroelectric liquid crystal with a glass transitionA. Jákli,^{1,*} T. Tóth-Katona,^{1,*†} T. Scharf,² M. Schadt,³ and A. Saupe¹¹*Liquid Crystal Institute, Kent State University, Kent, Ohio 44242*²*Institute of Microtechnology, University Neuchatel, Neuchatel, Switzerland*³*Rolic Research Limited, Gewerbestrasse 18, CH-4123 Allschwil, Switzerland*

(Received 18 June 2001; revised manuscript received 29 April 2002; published 15 July 2002)

Pressure-electric (hydrostatic piezoelectric) measurements are reported on bookshelf textures of a ferroelectric smectic-*C* (*Sm C**) liquid crystal with a glass transition. The continuous variation of a partially fluid state to the solid glass enables one to trace how the piezoelectric effect depends on the consistency of the material. It was observed that in the *Sm C** samples with poled glass the piezoelectric constants are comparable to conventional piezoelectric crystals and poled piezoelectric polymers. This implies their application possibilities. The magnitude of the piezoelectric constant in the glassy state depends very much on the poling conditions. The studies indicate that there are two counteracting effects, which cancel each other out in the *Sm C** phase near the glass transition. Our analysis indicates that the pressure-induced director tilt change has a dominating effect both in the fluid and the glassy *Sm C** states.

DOI: 10.1103/PhysRevE.66.011701

PACS number(s): 83.80.Xz, 77.65.-j, 77.84.-s, 64.70.Md

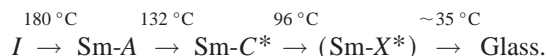
I. INTRODUCTION

Piezoelectricity is one of the basic properties of condensed materials. The prefix “piezo” is derived from the Greek word “press” reflecting the nature of the first piezoelectric effects observed in crystals by the Curie brothers [1]. The converse piezoelectric effect was predicted by Lippmann [2] on the basis of thermodynamic principles and experimentally verified by the Curie brothers. The piezoelectricity had been regarded as curiosity until Langevin mentioned the first practical application of this effect in 1918 [3]. Discoveries of new piezoelectric materials started a new boom in research in the 1940s when strongly piezoelectric ferroelectric ceramics [4] were observed. Synthetic polymer films can also show strong piezoelectric effects if they are subjected to strong dc electric fields at elevated temperatures [5]. Due to their flexibility and the possibility to prepare films of large area, these materials opened up new applications and device concepts that could not have been realized with conventional crystalline piezoelectric substances. The best-known and commercially most attractive example is polyvinylidene fluoride (PVDF), which has been utilized as an active element in many applications ranging from infrared detector technology to loudspeakers [6]. Today piezoelectric devices are found in television sets, radios, wristwatches, small computer games, automobiles, etc. Many communication and navigation systems use piezoelectric resonators for frequency control, generation, and selection. In spite of the more than a century long history the study of piezoelectricity is still in an accelerating stage [7].

By symmetry, piezoelectric materials have to be noninvariant under inversion. Chiral ferroelectric [such as smectic-*C* (*Sm C**)] liquid crystals [8] have C_2 symmetry and sat-

isfy this requirement [9]. Liquid crystals are fluid in some directions, so they cannot always maintain elastic restoring forces. Accordingly, without generalization of the definition of strain, linear electromechanical effects can be regarded piezoelectric only in directions where the material is elastic (e.g., in the direction normal to the layers in smectic phases [10], and in the plane normal to the columns in columnar liquid crystals [11]). One may also observe the “real” piezoelectric behavior of liquid crystals, for example, when the molecules are cross linked (e.g., in elastomers) [12,13], or when their structure is frozen in a glassy state. This motivated us to study the behavior of the pressure electricity during the transition from a partially fluid state to a rigid glassy state.

In this paper rheological and piezoelectric studies on a liquid crystalline material RO46-4912 from ROLIC Research Ltd. [14] will be reported. The phase sequence of the material in cooling is [14]



Note that the *Sm-X** phase in the parentheses is monotropic and the in heating glassy state directly melts to the *Sm C** phase at $\sim 85^\circ\text{C}$.

II. EXPERIMENTS**A. Sample preparation**

The liquid crystal was sandwiched between two glass plates with transparent electrode layers of indium tin oxide (ITO) in their inner surfaces. The film thickness was set to $D=8\ \mu\text{m}$ by polyimide spacers. The smectic layers were aligned uniformly in the *Sm-A* phase by shifting the top plate periodically (1–10 Hz) with an amplitude of about 0.1 mm. The mechanical shear was applied by a loudspeaker or piezoelectric actuator of the experimental setup used also for the rheological measurements [see Fig. 1(a)]. The resulting alignment was checked by a polarizing microscope and it

*On leave from the Research Institute for Solid State Physics and Optics, Budapest, Hungary.

†Present address: Physics Department, Kent State University, P.O. Box 5190, Kent, OH 44242.

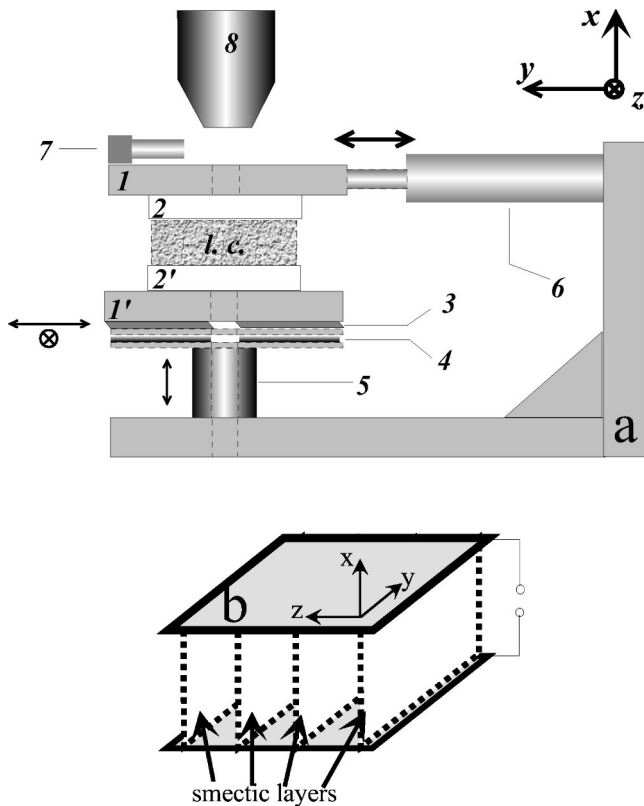


FIG. 1. (a) Experimental setup used for alignment and the rheological studies. The liquid crystal (l.c.) is sandwiched between two glasses (2 and 2'), which are fixed to hot plates (1) and (1'). The piezoceramic elements (3, 4, and 5) are sensitive in y , z , and x directions, respectively. The upper plate is driven either by a loudspeaker or by a piezoelectric actuator (6). The motion of the top plate is measured by a piezoelectric accelerometer (7) (BK 4375 from Bruel & Kjaer, sensitivity 0.1 mm/s^2). The textures can be observed by a polarizing microscope (8). (b) Schematic representation of the smectic layer structure.

was verified that the sample has a “bookshelf” structure where the smectic layers are parallel to the shear and are normal to the cover plates. The layer structure is illustrated in Fig. 1(b). Cooling the material to the Sm-C* phase a helical structure forms. The pitch of the helix has a maximum of $L_0 \sim 1\text{--}2 \mu\text{m}$ at $T \sim 120^\circ\text{C}$ [14]. We could not see any zigzag defect in the whole temperature range studied, which indicates that the bookshelf alignment remained basically undistorted. Under sufficiently strong electric fields the helix becomes unwound with the spontaneous polarization uniformly parallel to the electric field. The uniform structure could be frozen in the glassy phase when the material was cooled in low frequency electric field of $2 \text{ V}/\mu\text{m}$. The pressure electric measurements were carried out in the aligned uniform bookshelf textures.

B. Rheological studies

The transition from the ferroelectric liquid crystal to the solid glassy state was studied by rheological measurements. The measurement setup corresponds to that reported in Ref. [15] and sketched in Fig. 1.

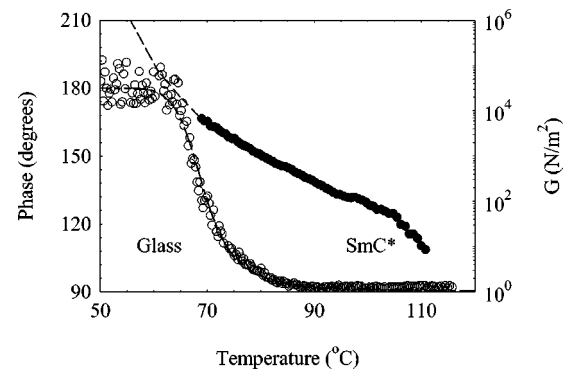


FIG. 2. Temperature dependence of the effective elastic constant G (●) and the phase shift (○) between the force applied on the top plate and transmitted to the bottom one. The measurements were carried out in cooling from the glassy smectic phase.

We applied periodic horizontal force to the top plate and measured the amplitude and phase of the force transmitted by the liquid crystal medium to the bottom plate. The shear was supplied by a loudspeaker above 70°C , and at lower temperatures by a piezoelectric actuator (PSt 500/10/5 from Piezomechanik GmbH), which has a stiffness of $1.6 \times 10^8 \text{ N/m}$ (data given by the producer).

The temperature dependence of the effective elastic constant and the phase shift indicates that the Sm-C* phase behaves as a Newtonian fluid along the smectic layers, and behaves basically like elastic solid below about 60°C (see Fig. 2). In between a viscoelastic behavior is observed. X-ray measurements show that in the viscous and viscoelastic range the smectic layer spacing decreases corresponding to the temperature behavior of the director tilt angle. The temperature dependences of the smectic layer spacing and the permanent polarization are shown in Fig. 3.

C. Pressure-electric measurements

To avoid flow effects in the partially fluid Sm-C* phase the samples were placed in a cell in which the pressure was periodically varied. The induced electric current (pressure electricity) was determined using the experimental setup sketched in Fig. 4.

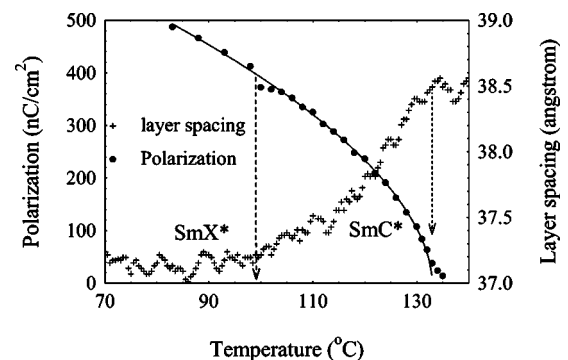


FIG. 3. Temperature dependences of the spontaneous polarization (●) and of the layer spacing (+). The measurements were carried out in cooling from the isotropic phase at rate $-1^\circ\text{C}/\text{min}$.

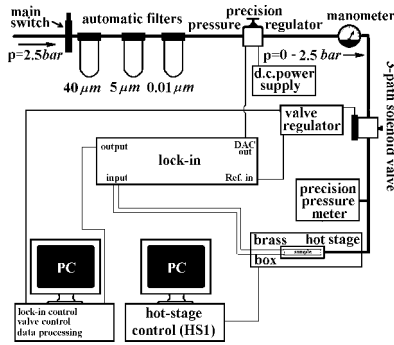


FIG. 4. Experimental setup used for pressure-electricity measurements.

The pressure dependence of the piezoelectric current I_p and the phase difference Φ between the periodic pressure and the electric current are measured in the glassy state both in unpoled and poled cells.

It is seen that the piezoelectric signal increases by more than an order of magnitude after poling. The poling was achieved by cooling the sample to room temperature meanwhile $U=20V_{p-p}$, $f_U=2$ Hz periodic voltage was applied. The pressure dependences of I_p and Φ at room temperature are plotted for the poled cell in Fig. 5. In comparison I_p is also shown for the nonpoled cell.

The magnitude of the hydrostatic coupling constant d_h can be calculated from the current I_p and the pressure p as $d_h = I_p / 2\pi f p A$, where A is the electrode area. The frequency dependence of the piezoelectric constant is shown in Fig. 6. The apparent decrease at higher frequencies is probably due to the valve regulator system that does not allow fast switching of the pressure.

Both d_h and the phase Φ were measured by applying periodic pressures between 0 to 2.4 bars above atmospheric pressure. The periodic pressure-induced electric currents were measured at various temperatures as the function of the amplitude and frequency of pressure oscillations.

Upon heating from the poled glassy state d_h increases until melting to the fluid Sm-C*. Above it the response drops to almost zero in the range of 95–100 °C, then increasing and reaching a maximum again at 120 °C (see Fig. 7). It

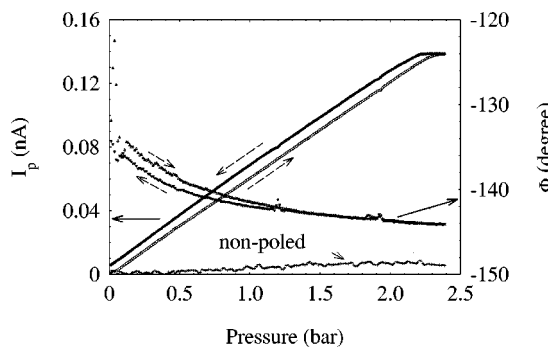


FIG. 5. Pressure dependence of the piezo current I_p and the phase shift Φ as a function of the amplitude of the periodic pressure ($f=1$ Hz) at room temperature.

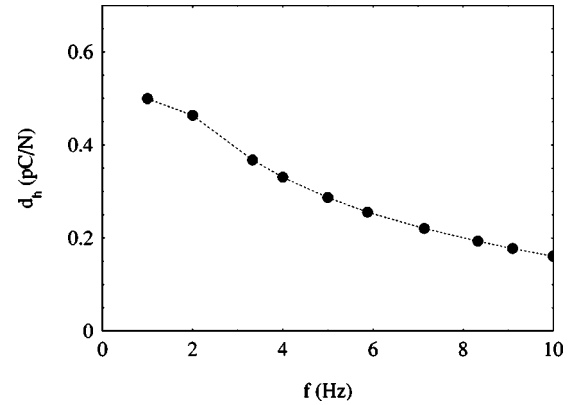


FIG. 6. Frequency dependence of the apparent piezoelectric coupling constant d_h in the glassy state at room temperature.

is remarkable that the phase shift is basically constant ($\sim -150^\circ$) in the glassy state, then it jumps to about 0 at melting to Sm-C* and stays constant in the whole Sm-C* range. Under cooling a different temperature dependence was observed: the response shows no significant change at the Sm-C*→Sm-X* transition, but there is peak at the Sm-X*→Glass transition. This is due to the appearance of the Sm-X* phase instead of the glassy state, which forms gradually only below 50 °C. The overall response in cooling is much smaller than in heating from the poled glassy state, since in cooling no poling was applied. Apart from the slight decrease shown in Fig. 6 the temperature dependence of the hydrostatic piezoelectric constant was basically frequency independent up to 10 Hz.

III. DISCUSSION

The most significant observation is the nearly 180° phase shift at the Glass→Sm-C* phase transition. This means that the piezoelectric coupling has different signs indicating counteracting effects in the glassy and the fluid Sm-C* phases.

In the fluid Sm-C* phase the smectic layers are compressible and the smectic layer distance decreases proportional to the pressure [16]. This is due to the pressure-

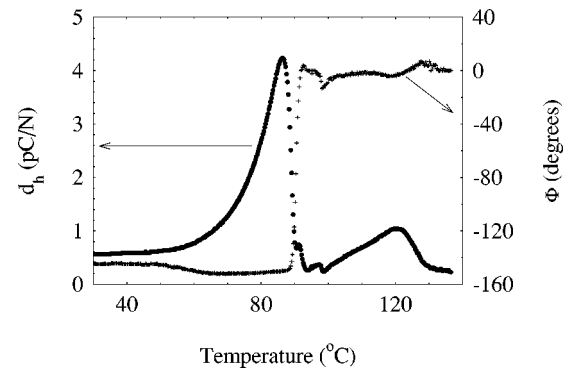


FIG. 7. Temperature dependence of the piezoelectric constant d_h and the phase shift Φ in heating from the poled glassy state in 1 °C/min rate. Frequency of the pressure vibration is $f=1$ Hz.

induced change of the tilt angle. Due to the coupling between the polarization P and the tilt angle θ this has a contribution to the piezoelectric effect. Additional contributions may arise from the pressure-induced shift of the Sm-A \rightarrow Sm-C* phase transition temperature (T_{AC}) and from the pressure dependence of the actual temperature of the material (T). We estimate that the latter effect is very weak and the applied pressure-induced heating is less than 10^{-4} °C, which is about two orders of magnitude smaller than the shift of T_{AC} [16]. Accordingly, we will consider isothermal behavior and we can define the relative temperature $t = T_{AC} - T$, which increases with the pressure. As P is increasing both with θ and t , their contribution has the same sign.

For the present material a helix forms in the fluid Sm-C* phase. The presence of the helix inside the film results in a much smaller effective polarization than P_0 (P_0 is the polarization of the uniform structure). It is known [17] that the width of the unwound regions near the surfaces is about half of the pitch. Consequently, the effective polarization that contributes to the piezoelectric response can be approximated as $P = P_0 L_0 / D$ ($D = 8 \mu\text{m}$ is the film thickness and $L_0 \sim 1 \mu\text{m}$ is the helical pitch at atmospheric pressure). It is reasonable to suppose that the number of layers over which the polarization rotates by 2π remains constant under pressure. Accordingly, the helical pitch L and the electric polarization P decrease proportional to the pressure-induced compression of the smectic layers. This counteracts with the effect of phase transition shift and with the director clinic. We note that a polarization may be induced by bend or splay deformation of the director field (flexoelectric effect). In the helical ranges of the sample both director splay and bend are present. However, the flexoelectric polarization is a linear function of the director deformation, so it is also helical and will be averaged out.

We see, therefore, that in bookshelf texture the polarization depends on three factors: the reduced temperature t ; the director tilt angle θ ; and the helical pitch L . Taking these into account, the hydrostatic coupling constant can be written as

$$d_h^{\text{Sm-C}^*} = \frac{dP}{dp} = \frac{\partial P}{\partial t} \frac{\partial t}{\partial p} + \frac{\partial P}{\partial \theta} \frac{\partial \theta}{\partial p} + \frac{\partial P}{\partial L} \frac{\partial L}{\partial p}. \quad (3.1)$$

The compression of the layers is determined by the hydrostatic layer compression modulus B as

$$-\frac{\Delta d}{d} \equiv \delta = \Delta p B. \quad (3.2)$$

With this, the pitch can be expressed as $L = L_0(1 - \delta) = L_0[1 - (\Delta p/B)]$, which gives that

$$\frac{\partial P}{\partial L} \frac{\partial L}{\partial p} = -\frac{P_0}{D} \frac{L_0}{B}. \quad (3.3)$$

Assuming rigid molecules the layer compression δ and the director clinic $\Delta\theta$ are related as

$$-\delta = \frac{\cos(\theta + \Delta\theta) - \cos\theta}{\cos\theta} = -\Delta\theta \tan\theta = -\frac{\Delta p}{B}. \quad (3.4)$$

Denoting the slope of the polarization as $\gamma = (1/P)(\partial P/\partial t)$, Eq. (3.1) can be rewritten as

$$d_h^{\text{Sm-C}^*} = \frac{L_0}{D} P_0 \left(\gamma \frac{\partial t}{\partial p} + \frac{\gamma}{\partial\theta/\partial t} \frac{1}{B \tan\theta} - \frac{1}{B} \right). \quad (3.5)$$

In this expression each parameter is measured except the layer compression modulus B and the shift of the transition temperature. From the measurements of Guillon *et al.* [16] we estimate that $B \sim 10^9 \text{ N/m}^2$ and $\partial t/\partial p \sim 10^{-7} \text{ }^\circ\text{C m}^2/\text{N}$. Furthermore, from our measurements we get that $P_0 = 2.3 \times 10^{-3} \text{ C/m}^2$, $L_0 = 1.5 \mu\text{m}$, $\gamma = 2.5 \times 10^{-2}$, $\theta = 15^\circ$ and $d\theta/dt = 10^{-2}$. These suggest that the pressure-induced tilt angle increase has the largest contribution to the piezoelectric constant, which comes out to be $d_h \sim 5 \text{ pC/N}$ at $T = 120^\circ\text{C}$. This value is about five times larger than the measured one, probably due to surface effects. The decrease of the layer spacing cannot take place uniformly, since this would require molecular motion even at the surfaces. The surface anchoring, however, prohibits this and a buckling of the layers may happen, which would reduce the effect of the pressure-induced tilt-angle change, but would not decrease the effect coming from the pitch variation.

In the poled glassy state the polarization is uniform and is normal to the electrodes. As the glass was frozen in from the Sm-X* phase, which has a tilted layer structure with in-plane order, the main effect of the pressure is the tilt-angle change. The experimental results imply that in the glassy state the pressure induces an increase of the layer spacing, i.e., leads to a decrease of the polarization. It is obvious that pressure-dependent x-ray measurements are needed in the glassy state to verify this point.

It is remarkable that the magnitude of the piezoelectric constant is comparable to conventional poled piezoelectric polymer PVDF. It has to be emphasized that in the case of surface stabilized Sm-C* cells, where the pitch is larger than the film thickness, the effective polarization and the piezoelectric effect could be as large as 50 pC/N. Taking into account the ease of preparing aligned thin films of these materials and their simultaneous optical responses a number of practical applications could be available for liquid crystal piezoelectric materials.

ACKNOWLEDGMENTS

This work was supported by the NSF ALCOM Center under Grant No. DMR 89-20147 and by the Hungarian National Fund OTKA 023102. Some of the experiments were carried out at the Max Planck Research Group for Liquid Crystals of the Martin Luther University, Halle, Germany.

- [1] J. Curie and P. Curie, *Bull. Soc. Fr. Mineral.* **3**, 90 (1880).
- [2] G. Lippmann, *C. R. Hebd. Seances Acad. Sci.* **92**, 1049 (1881).
- [3] P. Langevin, French Patent No. 505 (17 September 1918), p. 703.
- [4] B.M. Wul and I.M. Goldman, *Akad. Nauk.* **49**, 179 (1945); A. Von Hippel, R.G. Breckenridge, F.G. Chesley, and L. Tisza, *Ind. Eng. Chem.* **38**, 1097 (1946); S. Roberts, *Phys. Rev.* **71**, 890 (1947).
- [5] H. Kaway, *Jpn. J. Appl. Phys.* **8**, 975 (1970).
- [6] T.T. Wang, J.M. Herbert, and A.M. Glass, *Application of Ferroelectric Polymers* (Chapman and Hall, New York, 1988).
- [7] X. Geng and Q.M. Zhang, *J. Appl. Phys.* **85**, 1342 (1999); A.E. Glazounov and Q.M. Zhang, *Appl. Phys. Lett.* **72**, 2526 (1998).
- [8] R.B. Meyer, L. Liebert, L. Strelecki, and P. Keller, *J. Phys. (France) Lett.* **36**, L69 (1975).
- [9] P. Pieranski, E. Guyon, and P. Keller, *J. Phys. (France)* **36**, 1005 (1975); A. Jákli, L. Bata, Á. Buka, N. Éber, and I. Jánossy, *J. Phys. (France) Lett.* **46**, L759 (1985); A. Jákli and L. Bata, *Mol. Cryst. Liq. Cryst.* **201**, 115 (1991).
- [10] A. Jákli and N. Éber, in *Modern Topics in Liquid Crystals*, edited by Á. Buka (World Scientific, Singapore, 1993), pp. 235–256.
- [11] A. Jákli, M. Müller, D. Krüerke, and G. Heppke, *Liq. Cryst.* **24**, 467 (1998).
- [12] S.U. Vallerien, F. Kremer, and E.W. Fischer, *Makromol. Chem., Rapid Commun.* **11**, 593 (1990); W. Lehmann, L. Hartmann, F. Kremer, P. Stein, H. Finkelmann, H. Kruth, and S. Diele, *J. Appl. Phys.* **86**, 1647 (1999).
- [13] C.-C. Chang, L.-C. Chien, and R.B. Meyer, *Phys. Rev. E* **55**, 534 (1997); E.M. Terentjev and M. Warner, *Eur. Phys. J. B* **8**, 595 (1999).
- [14] K. Schmitt, R.-P. Herr, M. Schadt, J. Funfschilling, R. Buchecker, X.H. Chen, and C. Benecke, *Liq. Cryst.* **14**, 1735 (1993).
- [15] A. Jákli, M. Müller, and G. Heppke, *Liq. Cryst.* **26**, 945 (1999).
- [16] D. Guillon, J. Stamatoff, and P.E. Cladis, *J. Chem. Phys.* **76**, 2056 (1982).
- [17] M. Brunet and C.T. Williams, *Ann. Phys. (Paris)* **3**, 237 (1978); M. Glogarova, L. Lejcek, J. Pavel, V. Janovec, and J. Fousek, *Mol. Cryst. Liq. Cryst.* **91**, 309 (1983).