

## FLEXOELECTRIC POLARIZATION IN NEMATIC LIQUID CRYSTALS MEASURED BY FIELD ON-OFF PYROELECTRIC TECHNIQUE

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A novel, pyroelectric effect based technique was developed for the direct measurements of flexoelectric polarization  $\mathbf{P}_f$  in hybrid aligned nematic cells. The pyroelectric response is measured, first, in the field off regime, and then with the bias field applied. The latter allows a direct comparison of  $\mathbf{P}_f$  with the field induced polarization over the whole range of the nematic phase of a standard compound 5CB. The sum of the flexoelectric coefficients ( $e_1 + e_3$ ) was shown to be negative and its dependence on the nematic order parameter does not follow a simple law (linear or quadratic) as was predicted theoretically. Dynamics of  $\mathbf{P}_f$  is discussed in terms of the order parameter fluctuations.

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Nematic liquid crystals are uniaxial media with a preferable direction of molecular axes  $\mathbf{n}$  called the director. The states of the director  $\mathbf{n}$  and  $-\mathbf{n}$  are indistinguishable (no polar axis) and the nematic phase does not show spontaneous polarization. However, a macroscopic polarization may be induced by deformation, namely, by a bend or splay distortion of the director field [1, 2]

$$\mathbf{P}_f = e_1 \mathbf{n} \operatorname{div} \mathbf{n} - e_3 (\mathbf{n} \times \operatorname{curl} \mathbf{n}) \quad (1)$$

consists of two terms with correspondent flexoelectric coefficients  $e_1$  and  $e_3$  related to the splay and bend distortions.

Despite the fact, that the flexoelectric effects often manifest themselves in electrooptical phenomena, defect formation, structural instabilities, etc.[3], accurate measurements of  $\mathbf{P}_f$  are still a challenge to researchers because the polarization is, as a rule, screened by free charge carriers and there is no simple way to switch it and observe repolarization currents as it is routinely being done in case of ferroelectric liquid crystals. What is usually measured is the converse effect: when an electric field is applied an alignment of a liquid crystal becomes distorted. Since pioneer work [4] different techniques have been suggested to measure flexoelectric coefficients [5–8], but, in fact, the accuracy of those measurements is influenced by a number of parameters involved (dielectric anisotropy  $\epsilon_a$ , birefringence, elastic moduli, field inhomogeneity, etc.) and additional problems arise with determination of sign of the effect (for collection of data see Ref.[10]).

The aim of the present paper is to show how the temperature dependence of the flexoelectric polarization may be measured directly with a high accuracy in hybrid aligned nematic (HAN) sandwich cells often used in electrooptical experiments. The experiment has been carried out by a modified pyroelectric technique on a standard compound 4-pentyl-4'-cyanobiphenyl (5CB) for which, at present, no reliable experimental data are

available [10]. For 5CB  $\epsilon_a \gg 0$  and the sum  $(e_1 + e_3)$  is especially difficult to be found from a converse flexoelectric effect due to competing action of a strong dielectric torque. In addition, our technique allows the measurements of  $P_f$  dynamics on both sides of the nematic-isotropic liquid phase transition.

In a HAN cell the director is oriented homeotropically (along the layer normal  $z$ ) at one of two opposite limiting plates and homogeneously (along the  $x$ -axis) at the other. Therefore,  $\mathbf{n} = (\sin \vartheta, 0, \cos \vartheta)$  with  $\vartheta_0 = 0$  at  $z = 0$  and  $\vartheta_d = \pi/2$  at  $z = d$  where  $\vartheta(z)$  is an angle the director forms with the normal ( $z$ ) to the plates and  $d$  is layer thickness. In this case, from Eq.(1) we have:

$$P_x = (-e_1 \sin^2 \vartheta + e_3 \cos^2 \vartheta) \frac{d\vartheta}{dz}, \quad (2)$$

$$P_z = -\frac{1}{2}(e_1 + e_3) \sin 2\vartheta \frac{d\vartheta}{dz}. \quad (3)$$

The  $P_z$  value averaged over cell thickness

$$\langle P_f^z \rangle = \frac{1}{d} \int_0^d P_f^z dz = \frac{e_1 + e_3}{4d} (\cos 2\vartheta_d - \cos 2\vartheta_0) = -\frac{e_1 + e_3}{2d} \quad (4)$$

might be measured by a pyroelectric technique if the opposite plates are made of conductive glasses. Indeed, by definition, the pyroelectric coefficient is  $\gamma = dP_s/dT$  where  $P_s$  is spontaneous polarization and  $T$  is temperature. For a HAN cell  $P_f$  takes the place of  $P_s$  and, since the flexoelectric polarization vanishes in the isotropic (I) phase (like  $P_s$  of a ferroelectric vanishes in a paraelectric phase), its temperature dependence in the nematic (N) phase may be found by integrating the pyroelectric coefficient starting from a certain temperature  $T_i$  well above the N - I transition

$$P_f(T) = \int_{T_i}^T \gamma(T) dT. \quad (5)$$

In order to measure  $\gamma(T)$  we have to change temperature by a small amount  $\Delta T$  and record a pyroelectric response, in the form, e.g., of the voltage  $U_p$  across the load resistor  $R$  shunted by input capacitance  $C$ . The most convenient, dynamic regime of measurements is based on heating the sample of area  $A$  by absorbed light of a pulse laser [11 - 13]. For very fast (in comparison with  $RC$ ) jump of temperature, to the end of a laser pulse  $t_p$  the pyroelectric voltage reaches the magnitude  $A\Delta T\gamma/C$  and then decay with  $RC$  time constant:

$$U_p = -\frac{A\Delta T\gamma}{C} \exp\left(-\frac{t}{RC}\right). \quad (6)$$

On a longer time scale,  $U_p$  changes sign and, being much smaller, slowly decays with a thermal time constant.

For  $\gamma(T)$  measurements, the main difficulty comes from uncertainty in determination of  $\Delta T$  that depends on absorbed light intensity and heat capacity of the liquid crystal layer. The latter problem is especially serious when one works in vicinity of the first order N - I phase transition (our case). In order to solve it we have developed a novel procedure based on comparison of the pyroelectric response originated from  $P_f$  with

that resulting from the field induced polarization, the latter serves as an internal label for calibration. Indeed, when an external d.c. field is applied to a sample, the field induced polarization  $P_i = \epsilon_0 \chi E$  is added to the flexoelectric polarization. The induced polarization is temperature dependent due to temperature dependence of susceptibility  $\chi(T)$  and contributes to a total, field dependent pyroelectric coefficient:

$$\gamma(T, E) = \frac{d(P_f + P_i)}{dT} = \gamma + \gamma_i = \gamma + \epsilon_0 E \frac{d\chi}{dT}. \quad (7)$$

In our case, even for small fields (e.g.,  $1 \text{ V}/\mu\text{m}$ )  $\gamma_i \gg \gamma$  and the measurements of the field induced response are very easy. The derivative  $d\chi/dT = d\epsilon/dT$  is obtained from the independently measured dielectric permittivity. It is important, that  $\epsilon(T)$  has to be measured on the same cell with the same voltage as was applied during the pyroelectric measurements.

In our experiments, we used  $10.2 \mu\text{m}$  and  $20.5 \mu\text{m}$  thick HAN cells, prepared from ITO covered quartz plates. The opposite electrodes were covered with polyimide (unidirectionally rubbed) and silane layers for the homogeneous and homeotropic orientation, respectively. The cells were placed in a thermal jacket and irradiated by pulses of a Nd-YAG laser (Spectron Laser System) operating in the continuous wave regime (wavelength  $1.064 \mu\text{m}$ , pulse duration  $t_p = 100 \mu\text{s}$ , frequency  $5 \text{ Hz}$ , average incident power  $40 \text{ mW}$ , spot of  $5 \text{ mm}$  diameter completely covering the  $3 \times 3.5 \text{ mm}$  cell area). Much shorter pulses ( $Q$ -switched regime,  $t_p = 20 \text{ ns}$ ) were used to observe the kinetics of the response. The light was partially absorbed (about 38%) by both ITO electrodes providing temperature increment in the bulk about  $0.05 \text{ K}$ . The pyroelectric response was measured with zero and  $-9 \text{ V}$  bias voltage by a digital oscilloscope ( $R = 800 \text{ k}\Omega$ ). Dielectric measurements were made in the same jacket with the same bias voltage using an Impedance Analyser (Yokogawa-HP, model 4192A).

The zero bias pyroelectric response of a  $20.5 \mu\text{m}$  HAN cell to a heating laser pulse has a shape predicted by Eq.(6). The Inset to Fig.1 shows the temperature dependence of the pulse amplitude (squares). On cooling, at the I - N phase transition, the response increases from some background value, shows a sharp maximum and then decreases. The signal is independent of the direction of irradiation (either from the front or rear electrode) and positive when a homogeneously orienting electrode is grounded. It means, that positive free charges compensating for a light induced decrease in the flexoelectric polarization are flowing through the load from the homogeneous to homeotropic electrode. Therefore,  $P_f$  is directed from the homeotropic to homogeneous electrode and the sum ( $e_1 + e_3$ ) is negative, opposite to the results of Ref.[9]. The response of a reference cell with two homeotropically orienting electrodes is considerably weaker (also shown in the same Inset by triangles) and changes sign from negative to positive (in the nematic phase) when the direction of light beam is reversed. Evidently, there is a certain contribution to the response from the so-called surface polarization which is also responsible for the background response in the isotropic phase. The existence of a surface polarization has been discussing for many years [6, 14], and the pyroelectric technique proves to be a powerful tool for its investigation.

After subtracting the background and integrating the pyroelectric response over temperature we obtain the flexoelectric polarization, shown in the main plot of Fig.1. A sharp increase is consistent with the first order phase transition. The absolute value of  $P_f$  was found with the help of Fig.2 which shows the pyroelectric response of the same cell with

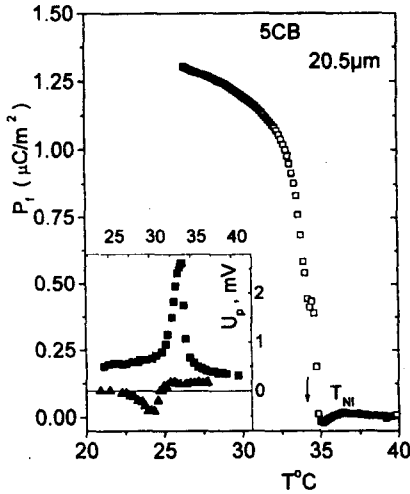


Fig.1. Inset: Temperature dependence of the zero bias pyroelectric response of a 20.5  $\mu\text{m}$  HAN cell (filled squares) and 20  $\mu\text{m}$  homeotropic cell (filled triangles). Main plot: flexoelectric polarization of the same HAN cell

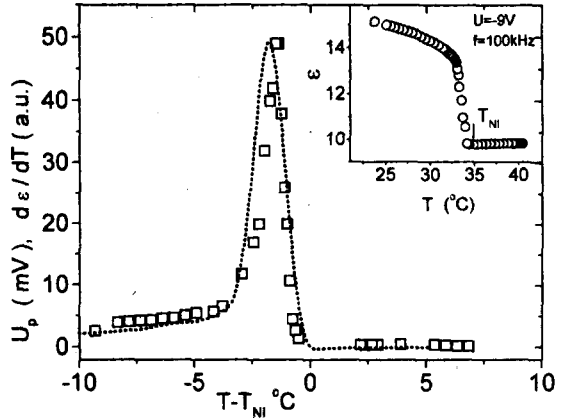


Fig.2. Inset: temperature dependence of dielectric constant at frequency 100k Hz of the same 20.5  $\mu\text{m}$  HAN cell with bias voltage  $-9\text{V}$  applied. Main plot: pyroelectric response with the bias voltage  $-9\text{V}$  (open squares) and derivative  $d\epsilon/dT$  scaled to compare it with the pyroelectric data (dotted line)

the bias voltage  $-9\text{V}$  applied. Now the amplitude of the signal is approximately 20 times higher. The signal comes from the temperature dependent field induced polarization due to  $d\epsilon/dT$ , see Eqn.(7). The temperature dependence of dielectric constant shown in the Inset to Fig.2. The properly scaled derivative  $d\epsilon/dT$  is shown in Fig.2 by the dotted line. The latter is close to the pyroelectric response and the ratio of the two gives a calibration curve that takes into account all unknown temperature dependent factors mentioned above. With this calibration curve the  $P_f(T)$  dependence shown in Fig.1 has been found. The maximum value of  $P_f$  is  $1.27\ \mu\text{C}/\text{m}^2$ . For another cell of thickness  $10.2\ \mu\text{m}$ ,  $P_f$  value found by the same procedure is  $2.2\ \mu\text{C}/\text{m}^2$ . The corresponding flexo-coefficients  $(e_1 + e_3)$  at  $25^\circ\text{C}$  for the two cells are  $-53\ \text{pC}/\text{m}$  ( $1.6 \cdot 10^{-3}\ \text{StatV}$ ) and  $-45.6\ \text{pC}/\text{m}$  ( $1.4 \cdot 10^{-3}\ \text{StatV}$ ), respectively. For the second (thinner) cell, a decrease in  $(e_1 + e_3)$  may be accounted for by a certain decrease in the difference of the two director angles at the boundaries,  $\vartheta_d - \vartheta_0 < \pi/2$ , due to a finite anchoring energy. Generally speaking, the accuracy of  $P_f$  and  $(e_1 + e_3)$  measurements (about 20%) is mainly determined by a proper account of the surface polarization background.

The sign of  $(e_1 + e_3)$  corresponds to that found earlier [13], however, the present absolute value is almost one order of magnitude higher. The reason seems to be in different calibration procedure. The earlier calibration was based on a comparison with a ferroelectric liquid crystal which, under a bias voltage applied, might show a polarization screening effect, and also had a different optical texture, resulting in additional light scattering and quite different thermal properties (new calibration is free of those disadvantages). Now we can also recalculate the flexoelectric coefficients for another standard nematic MBBA from the earlier pyroelectric measurements [13]:  $(e_1 + e_3) = -24\ \text{pC}/\text{m}$ . The negative sign and the magnitude correspond to the best data on MBBA from in the literature [10].

In order to shed more light on the mechanism of flexoelectricity we have plotted the flexoelectric coefficients as a function of the orientational order parameter  $S$ . The linear and quadratic dependencies were predicted for the quadrupolar [2] and dipolar [15] mechanisms. We have taken the data on order parameter from [16] and plotted in Fig.3 the  $(e_1 + e_3)$  values for our  $20.5 \mu\text{m}$  cell (from Fig.1) as a function of  $S$ . The linear dependence may be seen only well below the N - I transition. Closer to the transition the slope increases dramatically. Such a complicated behaviour is not surprising [17] if we remember that 5CB molecules have flexible tails and forms dimers due to cyano-group interaction. Qualitatively same results were obtained with data on  $S$  taken from [18, 19].

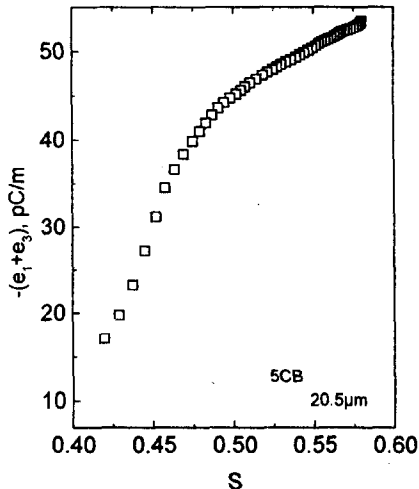


Fig.3. Sum of flexoelectric coefficients  $(e_1 + e_3)$  as a function of the orientational order parameter

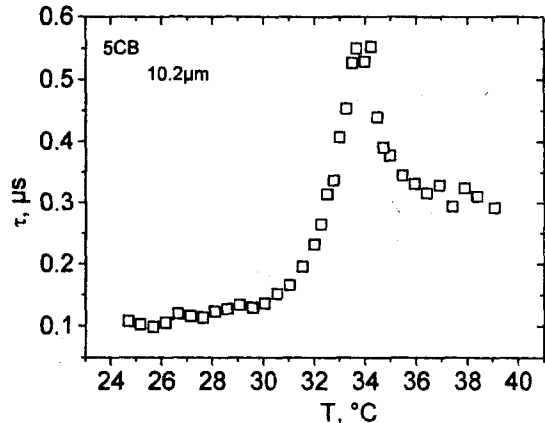


Fig.4. Temperature dependencies of the rise time of the pyroelectric response to a 20 ns laser pulse

Fig.4 shows a rise time  $\tau$  of the pyroelectric response to a 20 ns pulse of laser. In full analogy with a discussion of the soft mode relaxation times for ferroelectric liquid crystals [20]  $\tau$  may be referred to as an intrinsic dynamic time of the substance. Under assumption that angles  $\vartheta_0$  and  $\vartheta_d$  are temperature independent (0 and  $\pi/2$ ) the response time should correspond to the dynamics of the flexoelectric coefficient dependent solely on nematic order parameter. Indeed, the Kerr effect measurements in the isotropic phase of 5CB near the I - N transition [21] show almost the same pretransitional behaviour. In our case, the dynamics of the order parameter is easily measured on the nematic side of the transition what is difficult to do with other techniques. The inverse time  $\tau^{-1}$  manifests a Curie type behaviour with slope  $-1.6 \cdot 10^6 \text{ (sK)}^{-1}$  in the range of  $T_c - T = 2 \text{ K}$ .

To conclude, we have developed a novel, pyroelectric effect based technique for the direct measurements of the flexoelectric polarization in HAN cells. It is essential that, in calculations of the polarization and flexoelectric coefficients, only two easily measurable physical parameters are involved, the pyroelectric response, and the dielectric permittivity of the substance. The accurate determination of sign and the absolute value of the polarization has been performed on a standard nematic liquid crystal 5CB; the sum of the flexoelectric coefficients  $(e_1 + e_3)$  was shown to be negative ( $-53 \text{ pC/m}$  at  $25^\circ\text{C}$ ) with a sharp temperature dependence. The kinetics of the response reveals the dynamic of the order parameter fluctuations on both sides of the N - I transition.

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1. R.B.Meyer, Phys. Rev. Lett. **22**, 918 (1969).
  2. J.Prost and J.P.Marcerou, J. Phys. (Paris) **38**, 315 (1977).
  3. L.M.Blinov and V.G.Chigrinov, *Electrooptic Effects in Liquid Crystal Materials*, Springer Verlag, New York, 1993.
  4. D.Schmidt, M.Schadt and W.Helfrich, Z. Naturforsch. **A27**, 277 (1972).
  5. J.P.Marcerou and J.Prost, Mol. Cryst. Liq. Cryst. **58**, 259 (1980).
  6. A.Derzhanski, A.Petrov and M.Mitov, J. Phys. (Paris) **39**, 273 (1978).
  7. I.Dofov, I.Penchev, Ph.Martinot-Lagarde and G.Durand, Ferroelectrics Lett. **2**, 135 (1984).
  8. P.R.Maheswara Murthy, V.A.Raghunatan, and N.V.Madhusudana, Liq. Cryst. **14**, 483 (1993).
  9. S.R.Warrier and N.V.Madhusudana, J. Phys. II (France) **7**, 1789 (1997).
  10. A.Petrov, in: *Physical Properties of Liquid Crystals*, Eds. D.Dunmur, A.Fukuda and G.Luckhurst, EMIS Datareviews Series, 1999.
  11. J.Cooper, Rev. Sci. Instr. **33**, 92 (1962).
  12. M.Simphony and S.Shaulov, J. Appl. Phys. **42**, 3741 (1971).
  13. L.A.Beresnev, L.M.Blinov, S.A.Davidyan et al., Pis'ma ZhETF **45**, 592 (1987).
  14. P.Guyot-Sionnest, H.Hsiung and Y.R.Shen, Phys. Rev. Lett. **57**, 2963 (1986).
  15. J.P.Straley, Phys. Rev. **A14**, 1835 (1976).
  16. E.M.Aver'yanov, V.A.Zhuikov, V.Ya.Zyryanov, and V.F.Shabanov, ZhETF **86**, 2111 (1984).
  17. M.A.Osipov, Sov. Phys. JETF **58**, 1167 (1984).
  18. J.W.Emsley, G.R.Luckhurst and C.P.Stockley, Mol. Phys. **44**, 565 (1981).
  19. A.Buka and W.H.de Jeu, J. Phys.(Paris) **43**, 361 (1982).
  20. L.M.Blinov, S.Okazaki, M. Ozaki, and K.Yoshino, Mol. Mats. **9**, 163 (1998).
  21. V.N.Tsvetkov and E.I.Ryumtsev, Mol. Cryst. Liq. Cryst. **133**, 125 (1986).