

Temperature-Gradient-Induced Electric Polarization in a Liquid Crystal.

I. JÁNOSSY

Central Research Institute for Physics - H-1525 Budapest, P.O.Box 49, Hungary

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Abstract. - We measured the electric polarization induced by an alternating temperature gradient in the liquid crystal octyl-cyano-biphenyl. From the data the order-electric coefficient is estimated. It is found to be of the same order of magnitude as the flexoelectric coefficients, in accordance with the suggestions of Barbero *et al.*

The polarization properties of liquid crystals have been a subject of intense research for several years. For instance the coupling between the electric polarization and the distortion of the director field (flexoelectric effect) was investigated extensively in nematic and smectic A phases [1-3].

In a recent paper Barbero *et al.* [4] proposed a generalization of the flexoelectric effect by considering terms arising from the spatial variation of the nematic order parameter. The basic idea is that, while under homogeneous conditions polar molecules are oriented with equal probabilities parallel or antiparallel to any given direction, in the presence of a gradient of the order parameter this symmetry is broken. The number of permanent dipoles aligned parallel to the gradient is not equal to that of the antiparallel ones and as a result a macroscopic polarization develops. This polarization, P_0 , can be phenomenologically described as

$$P_0 = r_1(\mathbf{n} \cdot \text{grad} S) \mathbf{n} + r_2 \text{grad} S \quad (1)$$

Here S is the order parameter, \mathbf{n} is the nematic director. r_1 and r_2 are the order-electric coefficients which—according to the arguments of Barbero *et al.*—should be of the same order of magnitude as the flexoelectric coefficients (10^{-11} C/m). However, no direct measurement of these coefficients has yet been reported.

An obvious way of inducing a spatial variation in the order parameter is to apply a temperature gradient across the liquid crystal film. At constant pressure, uniform orientation ($\mathbf{n} = \text{constant}$) and moderate temperature gradients it can be assumed that the order parameter is a function of the local temperature only, $S = S(T)$. Hence the order-

polarization can be expressed in terms of $\text{grad} T$:

$$P_0 = k_1(\mathbf{n} \cdot \text{grad} T) \mathbf{n} + k_2 \text{grad} T \quad (2)$$

with

$$k_j = r_j / (dS/dT), \quad j = 1, 2. \quad (3)$$

Thus measuring the polarization generated by a temperature gradient the order-electric coefficients can be determined, provided dS/dT is known.

Motivated by the above considerations, we measured the electric voltage induced by an alternating temperature gradient in the liquid crystal octyl-cyano-biphenyl (8CB). In this letter we report the first results and compare these with the theoretical predictions. As we show our experimental results are consistent with the suggestions of Barbero *et al.* In addition, a pretransitional increase of the induced voltage was observed on approaching the nematic-isotropic transition point from the isotropic side. This fact suggests that the polar ordering of the molecules takes place in the «swarms» formed in the isotropic phase also.

The material used in the experiments, 8CB, was purchased from BDH and used without any further purification. The smectic *A*-nematic phase transition took place at 32 °C, the nematic-isotropic transition at 40 °C. The structure of the cell is shown in fig. 1. The glass

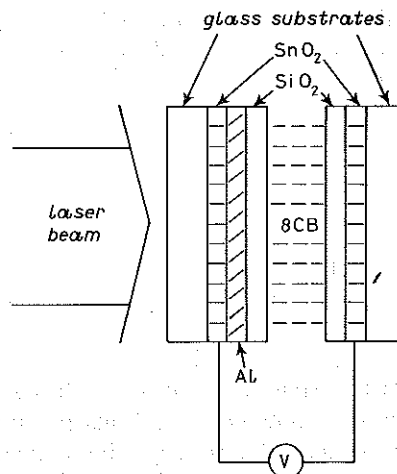


Fig. 1. - Experimental set-up.

substrates were coated with transparent electrodes; in addition a semi-transparent Al layer was evaporated onto one of the plates. Further 1000 Å thick SiO₂ layers were evaporated onto both plates, in order to prevent diffusion of the ions from the electrodes into the liquid crystal. Homeotropic orientation was ensured by coating the surfaces with octadecyl-triethoxy-silane. The thickness of the liquid-crystal film was approximately 50 μm. The cell was placed into a furnace by which its ambient temperature could be regulated. The temperature gradient was generated by illuminating the cell with an Ar ion laser at $\lambda = 514$ nm. 37% of the radiation was absorbed in the Al layer as deduced from transmission and reflection measurements.

At steady-state conditions the polarization induced by any external perturbation is screened by the mobile ions contained in the material. For this reason in the experiments

the heating was modulated with a frequency significantly higher than the inverse of the relaxation time of the space charges in the liquid crystal. The relaxation time, $\tau = \epsilon_0 \epsilon_{\parallel} / \sigma_{\parallel}$ (ϵ_{\parallel} and σ_{\parallel} are the parallel component of the dielectric constant and conductivity, respectively) was estimated from resistivity and capacity measurements. Its inverse increased from 250 s^{-1} in the smectic A phase to 600 s^{-1} above the clearing point. The modulation was realized by mechanical chopping of the laser beam at the frequency $f = 1.8 \text{ kHz}$. The alternating part of the electric signal induced between the two electrodes was detected by a lock-in-amplifier.

In order to find the connection between the measured signal and the coefficients k_j the temperature change caused by the laser has to be determined. This change can be decomposed into a constant part and a superposed alternating part with zero average. Due to the lock-in technique used in the measurements the signal is only sensitive to the latter component, hence we calculate this part. It is useful to consider the thermal diffusion lengths of the liquid crystal and the substrate defined as $l_{\parallel} = \sqrt{2D_{\parallel}/\omega}$, $l_s = \sqrt{2D_s/\omega}$, respectively. Here $\omega = 2\pi f$; D_s is the heat diffusivity of the substrate, D_{\parallel} is the parallel component of that in the liquid crystal. In our experimental situation both l_s and l_{\parallel} were of the order of few μm -s (see later) thus very small compared to the laser spot size (2 cm). Furthermore, l_{\parallel} was small compared to the film thickness L . In this limit the temperature modulation can be readily obtained from the heat flow equation. Assuming a sinusoidal time variation for the alternating part of the input laser power, we obtain for the temperature modulation

$$\Delta T(\mathbf{r}, z, t) = T_0(\mathbf{r}, z) \exp[i\omega t] \quad (4)$$

with

$$T_0(\mathbf{r}, z) = \alpha W_0(\mathbf{r}) \exp[-kz] \exp[i\pi/4],$$

where

$$1/\alpha = \sqrt{2(K_{\parallel}/l_{\parallel} + K_s/l_s)}; \quad k = l_{\parallel} \exp[i\pi/4]. \quad (5)$$

Here K_s and K_{\parallel} are the thermal conductivities of the substrate and the liquid crystal, respectively. $W_0(\mathbf{r})$ is the amplitude of the alternating component of the dissipated laser energy/unit area and time in the Al layer at the position \mathbf{r} ; z is the distance from this layer.

The temperature gradient is essentially normal to the liquid crystal layer. In this case, for a homeotropic cell, the induced polarization can be written as (see eq. (2))

$$P_0 = (k_1 + k_2) dT/dz. \quad (6)$$

To calculate the voltage induced between the two electrodes, we divide mentally the plates into small regions, each being large compared to the cell thickness, but small enough to neglect the variation of $W_0(\mathbf{r})$ within them. The amplitude of the voltage induced in an isolated region at \mathbf{r} is

$$v_0 = \frac{1}{\epsilon_0 \epsilon_{\parallel}} \int_0^L P_0 dz \approx \frac{k_1 + k_2}{\epsilon_0 \epsilon_{\parallel}} T_0(\mathbf{r}, 0) = -\frac{k_1 + k_2}{\epsilon_0 \epsilon_{\parallel}} \alpha W_0(\mathbf{r}) \exp[i\pi/4], \quad (7)$$

where it is taken into account that $L \gg l_{\parallel}$. The factor $1/\epsilon_{\parallel}$ describes the screening effect of the dielectric polarization. The superposed effect of all regions is obtained by considering these as parallel capacitors. The resulting voltage amplitude is the mean value of the v_0 's:

$$V_0 = \frac{1}{F} \int v_0 d^2\mathbf{r} = -\frac{k_1 + k_2}{\epsilon_0 \epsilon_{\parallel} F} \alpha Q_0 \exp[i\pi/4], \quad (8)$$

where F is the cell area, Q_0 is the amplitude of the total absorbed power/unit time in the Al layer. Equation (8) can be used to evaluate the parameter $k_1 + k_2$ from the measured data.

Besides the alternating temperature gradient a static gradient is present in the sample too. This is caused partly by the constant part of the dissipation, partly by imperfect thermostation. Observation of the nematic-isotropic transition gives information on the magnitude of this effect. We found that at the power levels used in the experiments and expanding the laser beam to a spot size comparable to the sample area (2 cm^2), the static gradient was fully due to inhomogeneous thermostation. The temperature interval from the appearance of an isotropic part to the complete melting of the film was 1°C . Therefore, the measured signal represents an average over a temperature range of 1°C .

The experimentally detected voltage is shown in fig. 2a) as a function of the ambient temperature of the cell. In fig. 2b) the phase relative to the laser modulation is displayed.

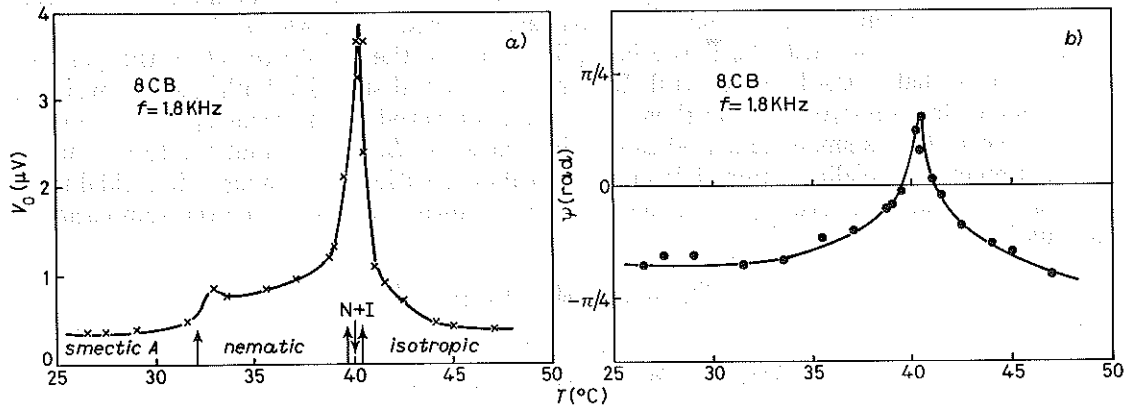


Fig. 2. — The absolute value (a)) and the phase (b)) of V_0 as a function of the temperature. Laser power 150 mW; the first Fourier component of the dissipated power (Q_0) 35 mW.

As it can be seen from fig. 2, the absolute value of V_0 as well as its phase are almost the same in the smectic A state and in the isotropic state well above the clearing point. This fact suggests that there is a «background» not related to order-electricity. This background may arise from the ionic double layers which form at the liquid crystal-solid interfaces or from the thermoelectric power generated in the electrodes by the heating. Furthermore, we cannot exclude a contribution from photoionization. We assume, however, that the difference between the measured voltage and the background originates from order electricity.

This interpretation is supported by the comparison of the temperature dependence of V_0 with that of dS/dT . The latter is displayed in fig. 3 for 8CB based on the measurements by Horn [5]. The main features of the two curves are similar; namely both curves exhibit maxima near the phase transitions and are slowly increasing within the nematic phase. This similar behaviour is expected if it is assumed that the order electric coefficients—like the flexoelectric ones—are not strongly temperature dependent.

From the above data it is possible to estimate the numerical value of the order-electric coefficient $r_1 + r_2$. We carry out this estimation for $T_c - T = 3^\circ\text{C}$, where the influence of temperature inhomogeneities in the sample are not important. Unfortunately the thermal data, $D_{||}$ and $K_{||}$ are not known for 8CB, therefore, we replace these parameters by typical values measured for other liquid crystals: $D_{||} = 1.2 \cdot 10^{-7} \text{ m}^2 \text{ s}$ [6]; $K_{||} = 0.25 \text{ W/m}^\circ\text{C}$ [7]. For the glass substrates $D_s = 1.8 \cdot 10^{-6} \text{ m}^2 \text{ s}$; $K_s = 1 \text{ W/m}^\circ\text{C}$. For 8CB $\epsilon_{||} = 14$ [8]. In the experiments we had $Q_0 = 35 \text{ mW}$; $F = 2 \text{ cm}^2$. At 3°C below the clearing point the measured

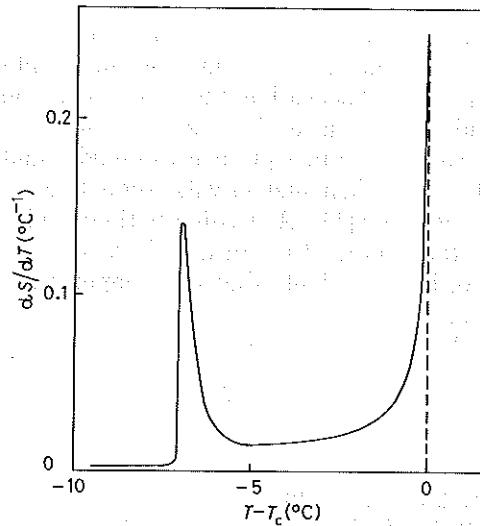


Fig. 3. $-dS/dT$ as a function of the temperature, based on the data published in ref. [5].

voltage (after subtracting the background) is $V_0 = 0.56 \mu\text{V}$. With these numbers we get from eq. (8)

$$k_1 + k_2 = 0.62 \cdot 10^{-13} \text{ C/m } ^\circ\text{C}.$$

From Horn's data at the same temperature $dS/dT = 0.02 \text{ } ^\circ\text{C}^{-1}$, hence

$$r_1 + r_2 = (k_1 + k_2)/(dS/dT) = 0.31 \cdot 10^{-11} \text{ C/m}.$$

A typical value of a flexoelectric coefficient is $3 \cdot 10^{-4}$ c.g.s. units $= 10^{-11}$ C/m. Dozov *et al.* [3] measured the bulk flexoelectric coefficient for 8CB. According to their data at $2.7 \text{ } ^\circ\text{C}$ below the clearing point $e_b = e_1 - e_3 = 0.3 \cdot 10^{-11}$ C/m (e_1 and e_3 are the splay and bend flexoelectric coefficients, respectively). This value agrees well with the estimated value of $r_1 + r_2$. Therefore, our result confirms the assumption that order-electric and flexoelectric coefficients are of the same order of magnitude.

In connection with the phase of the measured signal we note that according to eq. (4) the phase of the temperature variation is shifted by $\pi/4$ with respect to that of the dissipation. If the induced polarization followed adiabatically the temperature gradient a similar phase shift should have been found in the voltage. As it can be seen from fig. 2a) the measured phase was much less than $\pi/4$ and approached this value only near the clearing point. (Subtraction of the background does not change this picture qualitatively.) A possible interpretation of this fact is that the induced polarization has a rather long relaxation time (say 10 ms) which becomes shorter near the phase transition. The measurement of the effect throughout a wide frequency range could help to clarify this point.

The data obtained around the nematic-isotropic phase transition are obviously influenced by the relatively large temperature variation in the sample. Nevertheless, it was observed unambiguously that the induced voltage began to increase drastically already at temperatures at which there was no isotropic part in the film yet. Similarly, on cooling the sample from the isotropic phase the signal increased sharply already before nematic droplets were formed. From these facts we conclude that the peak cannot be merely attributed to the presence of a nematic-isotropic interface. (According to ref. [4] the interface is polarized and its motion could contribute to the induced voltage.)

The pretransitional increase of the signal in the isotropic phase must be connected with the formation of nematiclike «swarms», *i.e.* the increase of orientational short-range order near the clearing point [9]. Our observation indicates that the polar ordering of the molecules takes place already in a swarm if there is a temperature gradient across it.

Finally we note that polar ordering takes place at the solid-liquid crystal interface also, in the first molecular layer [10]. This phenomenon was studied recently by Guyot-Sionnest *et al.* using second-harmonic generation [11]. According to their findings the polar order at this interface is independent of the temperature in a wide temperature range, including the range we studied. Therefore, it is not likely that the temperature modulation of this layer had an effect on our results.

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