Direct measurement of the flexoelectric polarization of nematic liquid crystals

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The flexoelectric polarization in the nematic liquid crystals MBBA and 5CB has been measured for the first time. The temperature dependence has been found for the flexoelectric coefficient e_{11} for 5CB, and that for the sum of coefficients $e_{11} + e_{33}$ has been found for MBBA.

According to Ref. 1, the flexoelectric polarization is a function of the spatial derivatives of the director **n** of a nematic liquid crystal:

$$P_f = e_{11} \, \mathbf{n} \, \text{div} \, \mathbf{n} + e_{33} \, \text{rot} \, \mathbf{n} \times \mathbf{n}, \tag{1}$$

where e_{11} and e_{33} are flexoelectric coefficients. The first term in (1) is associated with transverse-bending S-deformation. The coefficient e_{11} is large if the molecules can be regarded as pear-shaped with a longitudinal dipole moment. The second term results from a transverse-bending B-deformation and is large for banana-shaped molecules with a large transverse dipole moment.

There have been no previous direct measurements of the value of p_f caused by a deformation of the field of the director **n**. The coefficient e_{33} is usually evaluated from the inverse flexoelectric effect,[2] i.e., from the appearance of a B-deformation induced by an external electric field. The only attempt which has been made to determine the coefficients e_{33} from the direct effect was that made in Ref. 3, but there the deformation was caused by a hydrodynamic flow in an extremely special geometry, so that a calculation of the flexoelectric coefficient e_{33} required many reservations. The literature reveals no data at all on the coefficient e_{11}, since measurements of the inverse flexoelectric effect are usually hindered by the positive dielectric anisotropy of a nematic liquid crystal, $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ (the subscripts $\parallel$ and $\perp$ refer to the directions of **n**) with longitudinal molecular dipoles.

In this letter we take a fundamentally new approach to a direct determination of the flexoelectric polarization itself, for a deformation state specified by boundary conditions. The magnitude of the polarization is determined by integrating the temperature dependence of the pyroelectric coefficient of the deformation structure, and it is not particularly sensitive to the sign of ϵ_a. This method can accordingly be used to measure both the flexoelectric coefficients, for any nematic liquid crystal. In the present letter we report data on two classical substances, which differ in the sign of ϵ_a, specifically, 5CB (p-pentylcyanobiphenyl) and MBBA (p-methoxy benzylidene p'-butylaniline).

Here is the experimental procedure. For the measurement, we fabricated a cell with a "hybrid" or mixed homeotropic-planar orientation. A thin layer of the nematic liquid crystal (its thickness was varied from 4 to 20 μm) lay between two glass plates, on which SnO_2 electrodes, which have a definite optical transmission in the visible and near-IR regions, were deposited beforehand. The electrode surfaces were treated in such a way that the molecules of the liquid crystal were oriented homeotropically, i.e., perpendicular to the substrate, on one of the electrodes (this surface was processed with chromium distearylchloride). The molecules at the other surface were in a planar orientation, i.e., parallel to the substrate (we used a method of rubbing over a layer of polyvinylketal, deposited beforehand on the electrode). Figure 1 shows the corresponding distribution of the director in the sample. In this homeotropic-planar structure, a B-deformation (near the upper electrode) is combined with an S-deformation (near the lower electrode). According to (1), the layer has an electric polarization whose sign depends on the signs of e_{11} and e_{33}.

A light pulse from an Nd:YAG laser, with a wavelength $\lambda = 1.06\,\mu$m and a pulse length $t_p = 100\,\mu$s, is incident on the cell. This light is absorbed in the electrodes, and its heats the thin layer of the liquid crystal almost instantaneously ($\tau \ll t_p$). The value of p_f changes, since the coefficients e_{11} and e_{33} depend on the temperature. The voltage of the pyroelectric effect appears across the electrodes. This voltage is proportional to the pyroelectric coefficient

$$\gamma(T) = dP_f(T)\,/\,dT. \tag{2}$$

Since the polarization p_f and the pyroelectric signal are observed only in the nematic phase, the value of $p_f(T)$ can be determined by integrating $\gamma(T)$ over the temperature from the point (T_{NI}) of the transition to the isotropic phase to any required temperature in the nematic phase. We had used this procedure previously for a ferroelectric liquid crystal.[4] In the case at hand, an absolute calibration of the measurements was
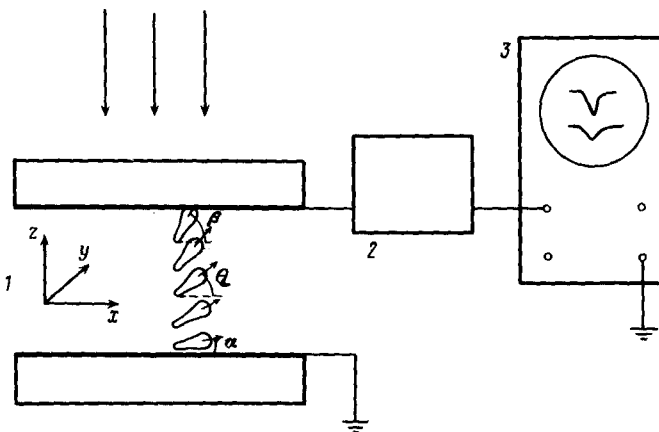

FIG. 1. The experimental layout. 1—Cell with a sample in a homeotropic-planar orientation; 2—UZ-29 amplifier; 3—S8-11 oscilloscope.

achieved by comparing the pyroelectric coefficients of the deformed structures of ne-
matic liquid crystals with the pyroelectric coefficient of the classical ferroelectric
DBC.[4]

It is an elementary matter to find a theoretical expression for P_f^z for a homeotro-
pic-planar cell with boundary values of the angles α and β which do not depend on the
temperature. From (1) we find

$$P_f^z = (e_{11} + e_{33})\sin\theta\cos\theta\,\frac{\partial\theta}{\partial z}\,,\tag{3}$$

$$\langle P_f^z \rangle = \frac{\int_0^d P_f^z\,dz}{d} = \frac{e_{11} + e_{33}}{4}(\cos 2\alpha - \cos 2\beta).\tag{4}$$

Using (4), we can easily find the sum of the flexoelectric coefficients, $(e_{11} + \epsilon_{33})(T)$,
from the value of the polarization $P_f^z(T)$ and the boundary conditions $\alpha = 0$ and
$\beta = \pi/2$.

Figure 2 shows the temperature dependence of the measured pyroelectric coeffi-
cient for a 5CB layer $d = 16\,\mu$m thick. Also shown here is the temperature dependence
of the flexoelectric polarization P_f^z. The calculated behavior of the flexoelectric coeffi-
cient e_{11} (under the assumption $e_{33} = 0$, by virtue of the cylindrical symmetry of the
5CB molecule and the absence of a transverse component of the dipole moment in the
case of this molecule) is shown by curve 1 in Fig. 3. For a cell of thickness $d = 9\,\mu$m,
the measured values of e_{11} for 5CB are precisely the same, although a further reduc-
tion of the thickness to $4\,\mu$m results in a decrease in the calculated values of e_{11},
apparently because the angles α and β do not remain constant.

For MBBA, the curves of $\gamma(T)$ and $P_f(T)$ are qualitatively the same as those in
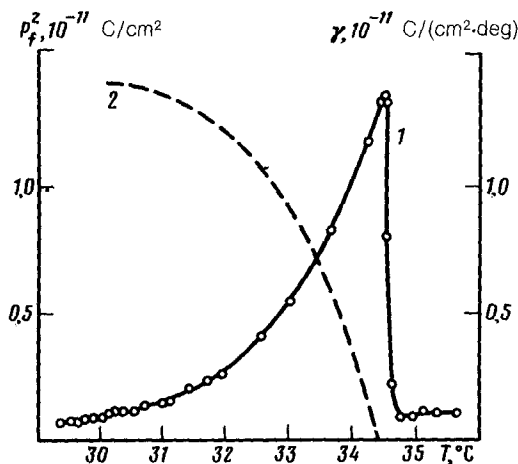Fig. 2. Curve 2 in Fig. 3 shows the sum of flexoelectric coefficients $e_{11} + e_{33}$. The value

FIG. 2. Temperature dependence of (1)
the pyroelectric coefficient and (2) the
flexoelectric polarization for a 5CB sample
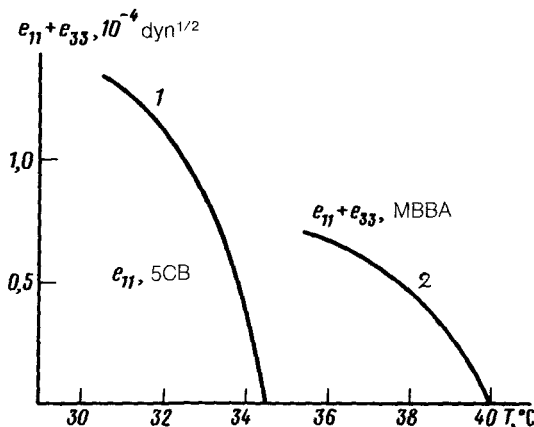in a homeotropic-planar orientation.

FIG. 3. Temperature dependence of (1) the flexoelectric coefficient e_{11} for 5CB and (2) the sum of flexoelectric coefficients $e_{11} + e_{33}$ for MBBA.

of $e_{11} + e_{33}$ for MBBA at room temperature $[e_{11} + e_{33} = (7 - 8) \times 10^{-5} \, \text{dyn}^{1/2}]$ agrees with the values found for e_{33} from the inverse flexoelectric effect. This agreement is evidence that the value of e_{11} is small because of a small longitudinal dipole moment. For 5CB, we have the value $e_{11} = 1.5 \times 10^{-4} \, \text{dyn}^{1/2}$, and (as mentioned above) this is the first determination of this quantity. The dipole moment of 5CB (because of the polar group $-C \equiv N$) is larger than that of MBBA, so that it is not surprising that the flexoelectric coefficient turns out to be significantly larger.

The method described above can be used to study not only the flexoelectric polarization caused by a bulk deformation of the director but also effects of a surface polarization. In Fig. 2, for example, we see that a small "pyroelectric coefficient" persists even in the isotropic phase. The change in the direction along which the cell is illuminated indicates that this small signal travels along the side of the surface of the cell where the orientation is homeotropic. This conclusion is supported by the observation of small signals (an order of magnitude smaller than in the homeotropic-planar cells) from cells with a purely homeotropic orientation, in which there should be no flexoelectric effect, because of the relation $\alpha = \beta = \pi/2$. This conclusion is also supported by the complete absence of signals from purely planar cells. Our experimental results thus agree with the assertion that homeotropically oriented layers of 5CB have a temperature-independent surface polarization, which Guyot-Sionnest[5] made on the basis of experiments on the generation of the second optical harmonic form a surface layer. Unfortunately, we are not able to carry out an absolute determination of the value of P_s is this case, because we lack a starting point for the integration of $\gamma(T)$.

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