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Separate measurements of the flexoelectric and surface polarization in a model nematic liquid crystal *p*-methoxybenzylidene-*p*′-butylaniline: Validity of the quadrupolar approach

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The temperature dependences of the surface polarization have been measured at the interface of a conductive glass with both the homogeneously and homeotropically oriented nematic liquid crystal *p*-methoxybenzylidene-*p*′-butylaniline. The polarization was found in the field-off regime from the pyroelectric response of a cell to a short laser pulse, absorbed in the bulk of the liquid crystal. The temperature increment was calculated from the measurements of the birefringence induced by the same light pulse. It has been shown that the surface polarization at the homeotropic (m_h) and planar (m_p) interfaces is directed from an interface into the bulk and from the bulk to an interface, respectively (with a magnitude $m_h \sim -0.3$ pC/m and $m_p \approx +0.2$ pC/m at 25 °C). The experimental data may be explained in terms of the quadrupole model of the order-electric polarization with account of some additional contribution from molecular dipoles. The same technique also allows for the measurements of the z component of the flexoelectric polarization using a pyroelectric response of a hybrid (homeoplanar) aligned nematic cell and proper subtracting of the surface contributions. The flexoelectric polarization has been shown to be opposite to the sum of the surface terms $m_h + m_p$ and directed from the planar to homeotropic interface. This means that the sum of the flexoelectric coefficients $e = (e_1 + e_3)$ is positive ($e \cong 1.7$ pC/m at 28 °C). The temperature dependence of e has been shown to involve a combination of both the quadrupolar and dipolar contributions.

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I. INTRODUCTION

The tensor of the orientational order parameter of a nematic liquid crystal has quadrupolar form

$$\mathbf{Q} = \tfrac{3}{2} S(\mathbf{nn} - \mathbf{I}/3), \tag{1}$$

where S is the order-parameter modulus, $\mathbf{n}$ is the director, and $\mathbf{I}$ is the unit tensor. Hence, the uniform nematic phase does not show spontaneous polarization although possesses large quadrupolar moment density $-q\mathbf{Q}$ (see [1,2] and references therein). However, both S and n_i can depend on coordinates and their spatial dependence results in the electric polarization

$$\mathbf{P} = -q \nabla \mathbf{Q}. \tag{2}$$

It can be a surface polarization [due to $S(\mathbf{r})$ dependence at the interface] or a flexoelectric one [due to $\mathbf{n}(\mathbf{r})$ dependence in the bulk].

In particular, at the interface with glass, the mirror symmetry of the nematic phase is broken and the surface polarization $\mathbf{m}_{\mathrm{surf}}$ (surface density of dipoles) arises [3–5] either perpendicular to the interface along the z axis (in case of the director parallel or perpendicular to it) or at some angle to the interface (in case of the tilted director orientation). The polarization is caused by a spatial dependence $S(z)$ in a thin bulk layer of thickness l, close to an interface and called order-electric polarization [6,7],

$$\mathbf{P}_s = \frac{3}{2} e_0 (\nabla S) \left(\mathbf{nn} - \frac{\mathbf{I}}{3} \right). \tag{3}$$

Here P_s is spatially dependent bulk macroscopic polarization $\langle \mathbf{P}_s \rangle = \mathbf{m}_{\mathrm{surf}}/l$ and e_0 is quadrupolar coefficient of a nematic with $S=1$. Note, that e_0 is a fundamental material constant [1] dependent on the molecular structure of a liquid crystal.

The value of $\mathbf{m}_{\mathrm{surf}}$ can also depend on other phenomena not as fundamental as that mentioned above, e.g., on different affinity of the two ends of a dipolar mesogenic molecule to a substrate or very slow processes of the ion adsorption from the bulk of a liquid crystal onto a solid substrate. This was studied in many experiments, see, e.g., [8–12].

The flexoelectric polarization $\mathbf{P}_f$ can be induced in the bulk by a bend or splay distortion of the director field. The most general form for $\mathbf{P}_f$ satisfying symmetry requirements is given by Meyer [13],

$$\mathbf{P}_f = e_1 \mathbf{n} \operatorname{div} \mathbf{n} - e_3 (\mathbf{n} \times \operatorname{curl} \mathbf{n}). \tag{4}$$

It includes splay and bend terms with corresponding flexoelectric coefficients e_1 and e_3. From the microscopic point of view [14], dense packing of dipolar banana- or pear-shaped molecules in a bent or splayed structure inevitably creates a dipole moment in a unit space. In a more general case, and, in particular, for nonpolar molecules, the flexoelectric effect originates from a gradient of the quadrupole moment density [2].

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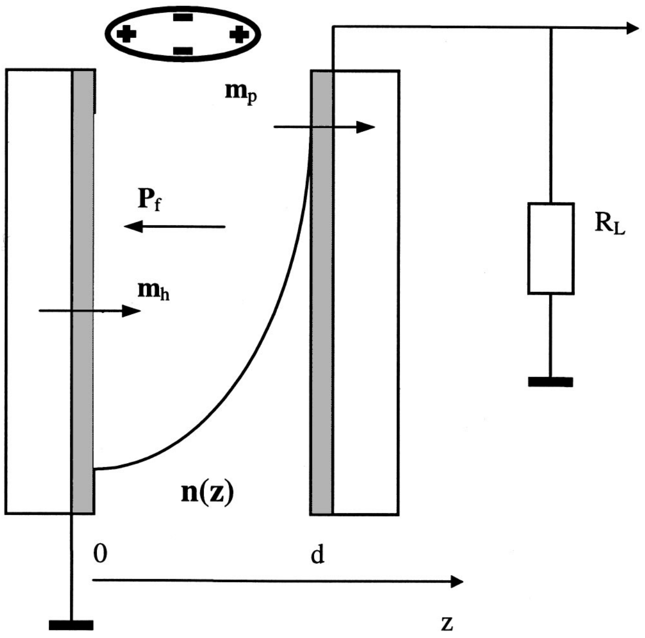

FIG. 1. An MBBA hybrid cell with the director profile and found directions of surface and flexoelectric polarization. The structure of a "molecular" quadrupole is shown on the top.

There is a general relationship [15] (see also [6]) between the quadrupolar coefficient in Eq. (3), and the sum of the flexoelectric coefficients from Eq. (4):

$$e_0 = \frac{e_1 + e_3}{3S}. \tag{5}$$

The nonzero difference $e^* = (e_1 - e_3) \sim S^2$ was shown [6,15] to appear due only to a higher order term in the polarization expansion over *S*. Thus, it is the sum $e = (e_1 + e_3)$ that is the most fundamental characteristic of the flexoelectric effect as has been underlined earlier [1].

Equation (5) allows for the determination of the fundamental coefficient e_0 of a nematic liquid crystal from the measurement of the *z* component of the flexoelectric polarization in a hybrid nematic cell. In such a cell, see Fig. 1, $\mathbf{n} = (\sin\vartheta, 0, \cos\vartheta)$ with $\vartheta_0 = 0$ at $z = 0$ (homeotropic interface) and $\vartheta_d = \pi/2$ at $z = d$ (planar interface), where $\vartheta(z)$ is an angle the director forms with the normal (*z*) to the plates and *d* is layer thickness. Thus, from Eq. (4), with ϑ_0 and ϑ_d assumed to be constant, we have

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

$$= -\frac{e_1 + e_3}{2d}. \tag{6}$$

Generally speaking, in a hybrid cell we have three contributions to the total *z* component of polarization to be treated separately, namely, one from the bulk (P_f) and two from the planar and homeotropic interfaces, P_{sp} and P_{sh}:

$$P_{\mathrm{total}} = P_f + P_{\mathrm{sp}} + P_{\mathrm{sh}}. \tag{7}$$

MBBA (*p*-methoxybenzylidene-*p′*-butylaniline) is a classical nematic liquid crystal and its surface and flexoelectric properties have been studied in a number of papers, see [16,17]. The experimental data on the sign and magnitude of *e* are very controversial, because, mostly, the converse flexoelectric effect was studied by an electro-optical technique. The latter requires either knowledge of anchoring conditions or the electric field gradient (or both), and in all cases, the flexoelectric polarization is not separated from the surface one. The latter is also true for early polarization measurements on a hybrid cell by a pyroelectric technique. In addition, all the electro-optic techniques suffer from the significant influence of polarization screening effects.

Recently we have developed a powerful technique for separate measurements of the surface and flexoelectric polarization of a liquid crystal as a function of temperature [18–20]. It is based on the pyroelectric method and does not use an external electric field. By measuring the pyroresponse of different cells (planar, homeotropic, and hybrid) to a heating laser pulse the surface polarization and the sum of flexoelectric coefficients $e(T)$ can be studied separately [18]. In combination with the "optical thermometer method" for determination of the temperature increment, the flexoelectric and surface polarization has been measured with good precision [19,20] for such model liquid crystals as 4-pentyl- and 4-octyloxy-4′-cyanobiphenyl (5CB and 8OCB).

The aim of the present paper is to measure separately the surface polarization for the planar and homeotropic orientations and the sum of flexoelectric coefficients $e(T)$ for MBBA over the whole range of the nematic phase. These data are necessary to verify the validity of the underlying quadrupolar models and also for calculation of the fundamental parameter of the nematic phase, the quadrupolar coefficient e_0.

II. EXPERIMENT

In a typical symmetric sandwich cell with two limiting boundaries, the $\mathbf{P}_s$ vectors at the two interfaces cancel each other. To measure $\mathbf{P}_s$ one has to deal only with one surface or provide a certain asymmetry of a liquid crystal cell. Our main idea is to use the pyroelectric response of a cell to a spatially dependent temperature increment in order to separate the contributions to the macroscopic polarization coming from the surfaces and from the bulk. In general, the pyroelectric coefficient is $\gamma = dP^*/dT$, where P^* is any macroscopic polarization and *T* is temperature. If we are interested only in the polarization originated from the orientational order we should subtract the "isotropic" contribution to γ and calculate $P^*(T)$ in the nematic phase by the integration of $\gamma(T)$ starting from a certain temperature T_i above the *N-I* transition.

$$P^*(T) = \int_{T_i}^{T} \gamma(T)dT. \tag{8}$$

In order to measure $\gamma(T)$ we slightly change temperature of the liquid crystal (by ΔT) using an absorption of a short laser pulse and record a pyroelectric response in the form of voltage U_p across the load resistor R. The latter is shunted by input capacitance and cell capacitance $(C=C_{\mathrm{in}}+C_{\mathrm{cell}})$. For a very fast (in comparison with RC) jump of temperature, to the end of a laser pulse t_p the pyroelectric voltage reaches the maximum magnitude $A\gamma\Delta T/C$ and then decay with RC time constant [21]:

$$U_p=-\frac{A\Delta T\gamma}{C}\exp\left(-\frac{t}{RC}\right). \tag{9}$$

Expressions (8) and (9) are valid for the measurements of both the flexoelectric polarization in a hybrid (HP) cell and the surface polarization in planar (PP) and homeotropic (HH) cells. The difference is only in determination of the temperature increment. One should use the increment $\langle \Delta T\rangle$ averaged over cell thickness for an HP cell (due to bulk P_f) and the increment ΔT_0 at the illuminated interfaces for PP and HH cells.

For the $\gamma(T)$ measurements, two problems must be solved. First of all, in order to suppress any contribution from the rear interface and to deal only with the front one, a gradient of increment $\Delta T(z)$ along the cell normal has to be provided. It has been done by doping MBBA with a dye that provides almost complete absorption of light in the bulk of our cells at laser beam wavelength $\lambda=532$ nm.

The second problem is determination of the absolute magnitude of temperature increment created by a laser pulse. The average value $\langle \Delta T\rangle$ over the cell thickness d can be measured by monitoring laser-induced birefringence at $\lambda=632.8$ nm of the planar cell used for pyroelectric measurements. This, "optical thermometer" technique is described in detail in [19]. The increment at a surface ΔT_0, to the end of a laser pulse, is calculated from $\langle \Delta T\rangle$ and a light absorption profile with known absorbance D at $\lambda=532$ nm as $\Delta T(z)=\Delta T_0\exp(-Dz/d)$, hence,

$$\Delta T_0=\langle \Delta T\rangle D/(1-e^{-D}). \tag{10}$$

We used sandwich HP, PP, and HH cells consisting of two parallel glass plates covered by ITO conductive layers (with electrode overlapping areas $A\cong 0.37\pm 0.01$ cm^2) and separated by 55 μm teflon stripes. For planar orientation we used unidirectionally buffed polyimide layer, the homeotropic orientation was achieved spontaneously on clean ITO. All the cells were filled with MBBA (Tokyo Kasei Kogyo) doped with 0.5 wt % of a bis-azodye (KD184, NIOPIK). The dye has maximum absorption at $\lambda=525$ nm and shows no absorption at $\lambda=623$ nm [19]. The clearing point of freshly made cells was $T_{\mathrm{NI}}=44\,°\mathrm{C}$, but a decrease of T_{NI} down to 40 °C was observed within a week, therefore, all the temperature dependences below were fitted to the initial temperature. The dye provides almost the same optical absorbance of our three cells for an ordinary polarized light at 532 nm (e.g., $D_o=1.18\pm 0.02$ and 1.98 ± 0.02 at $T=25$ and 46 °C, respectively, for all the cells), therefore, only the temperature dependence of D_o for the homeotropic cell is shown in Fig. 2. The coincidence of the absorption curves is very important for comparison of the pyroelectric response of the three cells because, only in this case, the temperature increment $\langle \Delta T\rangle$ is the same in all of them for a fixed laser pulse energy.

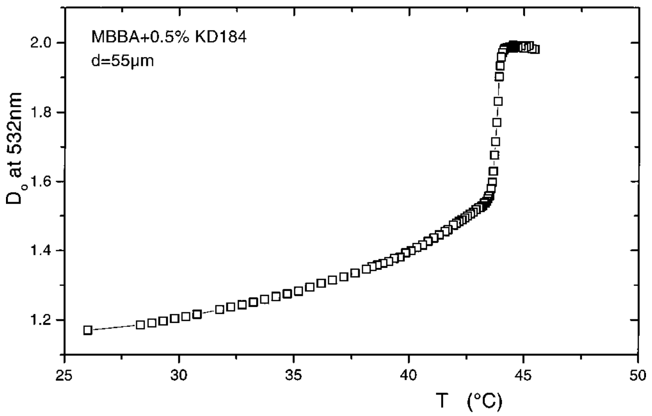

FIG. 2. Temperature dependent absorbance of homeotropic cell (o-polarized light, $\lambda=532$ nm).

The thermal jacket had two optical windows that allowed the irradiation of the samples by pulses of a Nd-YAG (yttrium aluminum garnet) laser consequently from the front and rear sides. The laser operated with pulse duration $t_p\approx 100$ ns at $\lambda=532$ nm (light electric vector $\mathbf{e}$ was in the horizontal plane perpendicular to the director $\mathbf{n}$ in all cells). The pulse frequency was $f=1$ Hz, spot diameter 7 mm, and pulse energy $W_p=8$ mJ. The pyrovoltage was measured by a digital oscilloscope.

In our previous papers [19,20] we reported on detailed measurements of increment $\langle \Delta T\rangle$ (averaged over cell thickness) by the "optical thermometer method." The latter is based on the optical transmission of a polarized He-Ne laser beam under simultaneous irradiation of a planar cell by YAG laser pulses. Evidently, $\langle \Delta T\rangle$ depends only on incident light power, optical absorbance, and specific heat of the liquid crystal. We have applied this technique to liquid crystals 5CB and 8OCB doped with the same dye and established that, at a fixed laser pulse energy, the temperature dependence of $\langle \Delta T\rangle$ is surprisingly weak due to mutual compensation of the absorbance and specific heat influence (e.g., $\langle \Delta T\rangle$ varied only from 1 to 2 K over the whole range of the nematic and smectic A phases of 8OCB [20] and was 1.5 ± 0.3 K over the nematic phase of 5CB [19]. Since the YAG laser produces the same pulses as in our previous experiments, and the absorption of MBBA cells almost coincides with that of the 5CB cells, we used the data on $\langle \Delta T\rangle$ obtained earlier for 5CB with a small correction on the difference in absorbance and specific heat for the two materials (MBBA [22], 5CB [23]). From this procedure we have obtained $\langle \Delta T\rangle$ (MBBA)$=1.7\pm 0.3$ K over the whole temperature range. Afterwards, the increment at the surface (ΔT_0) strongly dependent on absorbance was calculated using Eq. (10).

III. RESULTS

The pyroelectric response of the homeotropic and planar cells, both irradiated from the front (grounded) electrode is

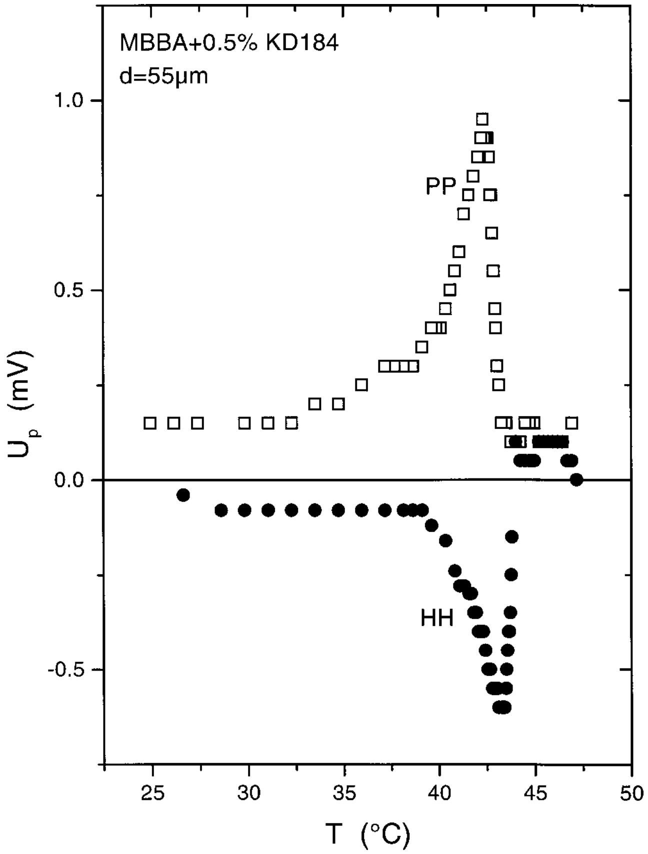

FIG. 3. Pyroelectric response vs temperature for homeotropic (HH, filled circles) and planar (PP, open squares) cells both irradiated from the front (grounded) interface.

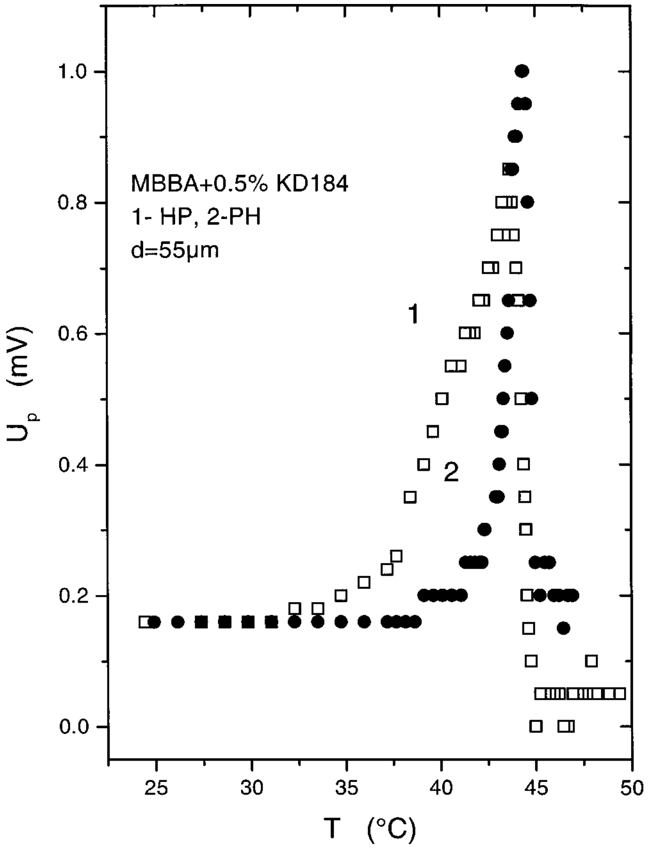

FIG. 4. Pyroelectric response vs temperature for hybrid (HP) cell irradiated from either the front (homeotropic and grounded) electrode (curve 1) or rear (planar) electrode (curve 2).

presented in Fig. 3. As expected, all the data change their sign if the same cells are irradiated from the rear (signal) electrode. In the isotropic phase there is small background signal, not relevant to the posed problem and it will be subtracted later on. There is a dramatic difference between the pyroelectric response in the nematic phase for MBBA and 5CB [19]: for homeotropic orientation the signal from MBBA is negative, but from 5CB positive; for the planar orientation, on the contrary, positive signal is observed from MBBA, negative from 5CB. For 8OCB we observe a mixed case [20]. From the sign of the pyroeffect we have found (as explained in [19]) that, *in MBBA, at the homeotropic interface (without any surfactant) the surface polarization is directed from the interface into the bulk of the liquid crystal and the surface polarization at the planar interface with rubbed polyimide layer is directed from the bulk to the interface*. In a hybrid cell the two polarizations are summed as shown in Fig. 1.

The pyroelectric response of our hybrid cell irradiated from the front (homeotropic grounded) and rear (planar, not grounded) electrodes is presented in Fig. 4. This signal corresponds to a sum of both flexoelectric and surface polarization and, for any irradiation direction, is positive (in the case of 5CB the signal was negative). We can find the intrinsic flexoelectric pyroresponse of MBBA by two alternative procedures, namely, either by *subtracting from curve 1* the contribution of the homeotropic interface (curve HH in Fig. 3), or by *adding to curve 2* the contribution from the planar interface (curve PP in Fig. 3) because for the rear irradiation a response of the planar cell is inverted. However, since each of the contribution is proportional to its own temperature increment, first we should find corresponding ΔT_0 values from Eq. (10) and data of Fig. 2 (for fixed value of $\langle \Delta T \rangle = 1.7\,\mathrm{K}$). The result is as follows: on cooling from the isotropic phase to 25 °C the value of ΔT_0 decreases from 3.4 to 2.5 K due to an increase in the light absorption depth at the same absorbed energy.

Now, using the $\Delta T_0(T)$ data for both HH and PP cells and Eq. (9) (for $t=0$), we find the absolute magnitude of the "surface" pyroelectric coefficient γ_s for the planar and homeotropic interfaces (from data of Fig. 3). The permanent total capacitance $C=142$ pF has been taken for all the cells (in fact, it is determined by the input circuit and varies only within 2%). After subtracting the isotropic background and integrating γ_s, we obtain the absolute magnitude of the surface polarization m_h and m_p for the two interfaces over the whole temperature range. The results are shown in Fig. 5.

For the hybrid cell, first we find pure flexoelectric response by subtracting the surface contributions to the total pyroelectric response (for front and rear irradiation) and then calculate the pyroelectric coefficient from Eq. (9) (related solely to flexoelectricity) using the bulk increment $\langle \Delta T \rangle$. The genuine coefficient γ is shown in Fig. 6 for the HP cell irradiated from each side. From Fig. 6 it is clear that the

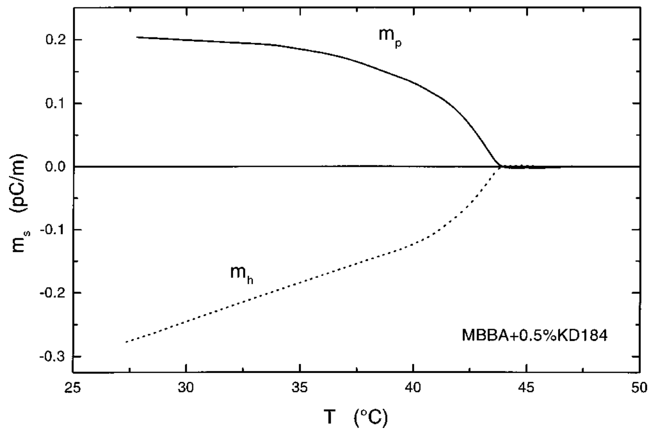

FIG. 5. Magnitude of the surface polarization m_h and m_p for homeotropic and planar interfaces as a function of temperature.

flexoelectric polarization in MBBA is directed from the planar to homeotropic interface (as in 8OCB, and opposite to the case of 5CB). After integrating over temperature we find the z component of P_f, and using Eq. (6) obtain two curves for the apparent sum of flexoelectric coefficients $e(T)$ shown by the dotted and dashed lines in Fig. 7. The difference between the two curves seems to be considerable and needs an explanation.

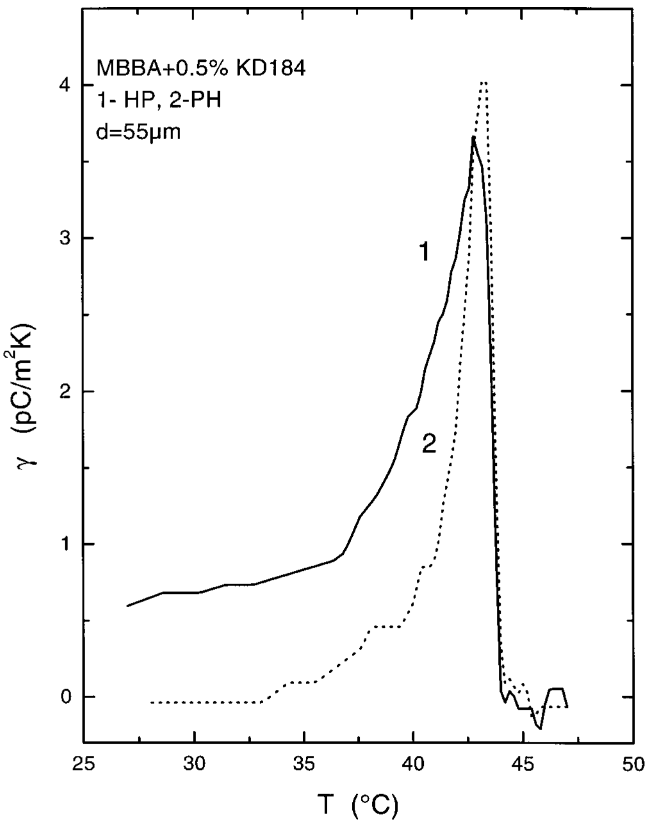

FIG. 6. Pyroelectric coefficient, related solely to the flexoelectric polarization due to the director curvature in the HP cell. The hybrid cell was irradiated from either the grounded homeotropic interface (curve 1) or planar interface (curve 2).

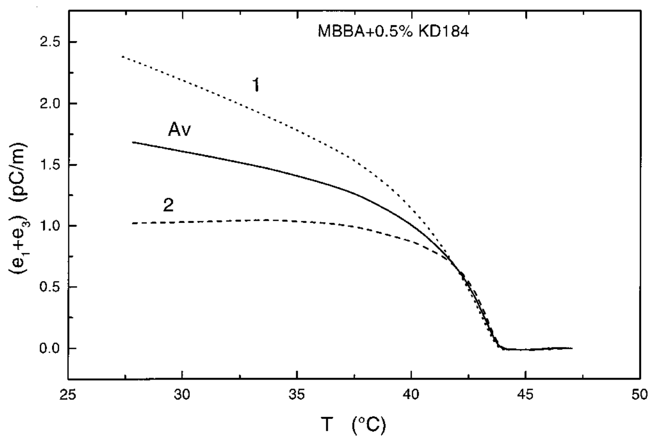

FIG. 7. Temperature dependence of the sum of flexoelectric coefficients $e=(e_1+e_3)$. The hybrid cell was irradiated from either the grounded homeotropic interface (dotted curve) or planar interface (dashed curve). The solid curve is the average of the two.

It is well known that a response of a linear pyroelectric crystal is independent of the absorbed energy distribution and, in that case, the result would be the same for the two irradiation regimes. Our case is more complicated. The observed difference between two measurements can appear for several reasons. The most important is the time instability of MBBA that strongly influences the surface polarization. Indeed, when, in the course of the present work, we used an aged sample of MBBA with clearing point about 32 °C and respectively smaller order parameter, we observed solely the contribution from the surface polarization and the signal from a hybrid cell was negative (like in old paper [24] where the surface contribution has not been taken into account). That is why all our present pyroelectric measurements were made within two days on newly made samples of MBBA just bought from the Tokyo Kasei Kogyo company. Nevertheless, our results may still suffer of MBBA temporal instability.

The discrepancy may also appear if, e.g., at one, most probably, planar interface (with polyimide), during irradiation by a laser pulse, the director angle slightly changes, $\vartheta_d < \pi/2$. Then the magnitude of the flexoelectric polarization will be reduced by irradiation [see Eq. (6)] and curve 2 in Fig. 7 will be lower than curve 1.

Some discrepancy may also originate from the inhomogeneous distribution of the flexoelectric polarization in a hybrid cell along the z axis (e.g., due to a difference in elastic moduli $K_{11} \neq K_{33}$ and corresponding spatial variation of the director curvature) or from some difference in the thermal conductivity at the planar and homeotropic sides.

In any case, our two curves show two extreme cases and the correct curve must be in between the two. Their average shown by the solid curve in Fig. 7 seems to be the most reasonable solution. The value of the sum e at room temperature is 1.7 ± 0.7 pC/m. For such material as MBBA this inaccuracy can be accepted.

IV. DISCUSSION

Our principal experimental results to be considered are shown in Figs. 5 and 7. Let us discuss first a simpler case of

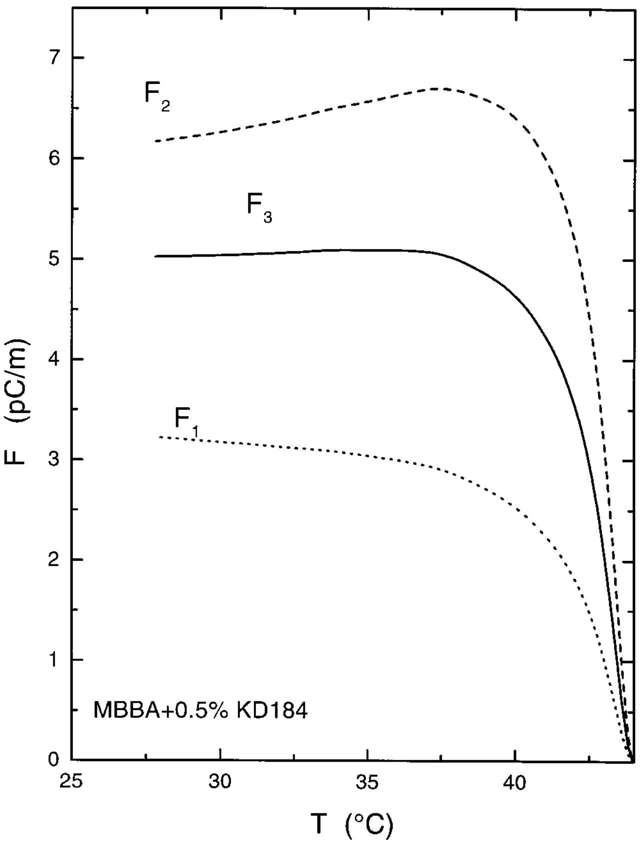

FIG. 8. Temperature dependence of fitting functions F (see the text).

the flexoelectric polarization. From Fig. 7 it can be seen that $e>0$ and small in comparison with literature data which vary [17,25] from -25 to $+10$ pC/m. In a hybrid cell the direction of P_f is opposite to that of the sum of the surface polarizations. The latter has a smaller but still significant magnitude. We believe that the discrepancy with literature data comes mostly from the surface effects, especially important in MBBA, in which the flexoelectric polarization is, indeed, very small. In some cases described in literature, e.g., in an aged material with bulk impurities, or due to a surfactant used for homeotropic orientation the surface polarization may even exceed P_f and must have been treated separately.

The structure of a "molecular" quadrupole responsible for the positive sum $e=(e_1+e_3)$ is shown in Fig. 1. The distribution of positive and negative charges is the same as in the case of 8OCB (and opposite to 5CB). It is not surprising because in both cases (MBBA and 8OCB) the transverse dipole of an alkoxy group (averaged over time) contributes to the structure of the quadrupole. However, our results on order parameter dependence of e cannot be explained in terms of the sole quadrupolar model. In Fig. 8 (dotted curve) we have plotted the temperature dependence of the ratio $F_1=e/S$ [data on $S(T)$ are taken from [26]]. Let us disregard a region about 4 °C below the phase transition, where the accuracy of our measurements may be influenced by an anomaly in the specific heat, latent heat, an appearance of the two-phase region and thermal gradients, and consider only the low-temperature part of the curve. We see that the ratio is not constant as expected from Eq. (5) but slightly increases with decreasing temperature. On the contrary, the ratio $F_2=e/S^2$ (dash curve) decreases in the same range. The temperature independent plateau (solid curve) corresponds to the fitting ratio $F_3=e/(0.25S+0.75S^2)\cong 5$ pC/m. From this and Eq. (5) we can estimate the quadrupolar coefficient $e_0\cong +0.42$ pC/m. This value is, indeed, very small in comparison with the nematic phase of 8OCB (+4 pC/m) and 5CB (-11 pC/m). The term in F_3 proportional to S^2 implies that higher order terms in the expansion of polarization over order parameter [6,15] should be taken into account. For example, such a dependence is expected for the dipolar contribution to the flexoelectricity. Since e_0 is small, it is not surprising that the dipolar contribution becomes important.

Having e_0 found, we can discuss the results on the surface polarization. Consider first the quadrupole model [6]. From Eq. (3), with the gradient ∇S directed along the z axis, after integrating over z, we have the following expressions for the planar and homeotropic orientation:

$$m_p=-(1/2)e_0\Delta S_p \quad \text{and} \quad m_h=e_0\Delta S_h. \tag{11}$$

Here $\Delta S_{p,h}=S_{p,h}-S$ is the difference between the surface and bulk order parameters both assumed to be temperature dependent. Different signs in two formulas (11) are related to different orientation of molecular quadrupoles at the planar and homeotropic interfaces. In case of MBBA $m_h<0$ and $m_p>0$, see Fig. 5, therefore, ΔS in Eq. (11) should have the same sign for the two interfaces. With the structure of a molecular quadrupole shown in Fig. 1, we arrive at the following conclusion: at both the planar (polyimide) and homeotropic (clean ITO) interfaces the magnitude of the orientational order parameter at the surface is lower, than that in the bulk, $S_p, S_h<S$, $\Delta S_{p,h}<0$. The situation is the same as in 5CB [19] where all the signs of relevant parameters are inverted (for m_p, m_h as well as for e_0). This is also in accord with the results obtained for cyanobiphenyl mixture E7 [25]. The quantitative estimations of $\Delta S_{p,h}$ from Fig. 5 and solely quadrupole model with $e_0\cong +0.42$ pC/m would give us too large values, $\Delta S_p\cong 1$, $\Delta S_h\cong 0.75$ (instead of expected 0.2–0.5 as in 5CB and 8CB [19,20]), pointed again to the importance of the additional, most probably, dipolar contribution to the surface polarization of MBBA [27].

V. CONCLUSION

In conclusion, the temperature dependence of the z component of the electric polarization has been measured for MBBA in a homeotropic, planar, and hybrid aligned nematic cells. In a hybrid cell the total polarization includes two surface polarizations and the bulk, flexoelectric one. The polarization was found in the field-off regime from the pyroelectric response of cells to a short laser pulse; the light at $\lambda=532$ nm was strongly absorbed by a small amount of a dye. The temperature increment was calculated from the measurements of the light pulse induced birefringence. As a result, the temperature dependences of both surface polarizations (for a planar and homeotropic interface) and the flexoelectric one were found separately. The sum of the flexoelectric coefficients e was shown to be positive (and small), opposite to the case of 5CB. On the molecular scale, the difference is accounted for by different distribution of electric charges in molecular quadrupoles formed in the nematic phase of MBBA and 5CB. The sign of the surface polarization is also explained in terms of the quadrupolar model of the order-electric polarization. However, due to smallness of quadrupolar coefficient e_0 in MBBA, the temperature dependence of the flexoelectric coefficient and the absolute magnitude of the surface polarization include some dipolar contribution to the polarization that is of the same order of magnitude as the quadrupolar one.

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