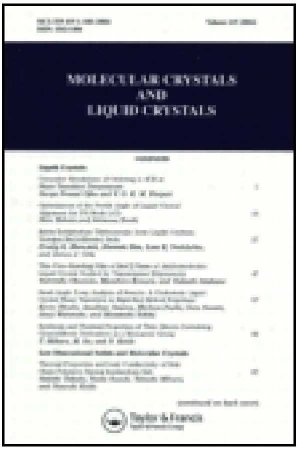

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Thermally Induced Depolarization Currents In a Palladium Containing Metallorganic Liquid Crystal

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In this paper we report the measurements of the thermally induced depolarization currents in a metallorganic liquid crystal. The depolarization current dependence on temperature has been interpreted in term of an internal electric field set up during the cooling down of the sample under a d.c. external applied voltage. The transition temperature shift verifies a Clausius-Clapeyron type equation also giving evidence of the saturation of the polarization. By analyzing the experimental data, we can hypothesize that there is a double order in the system: the nematic order, concerning the director **n** which behaves quite normally, and an electric order, concerning the electric dipoles. Whereas the first type of order induces a phase in the system (the nematic phase) it is doubtful that the second ones induces a real phase in the system.

Keywords: Liquid crystals; Dielectric properties; transitions in liquid crystals

1. INTRODUCTION

Usually, nematics are formed by rod-like organic molecules [1]. By symmetry reason nematic phases are not ferroelectric. A few years ago liquid crystals containing transition metals have been synthesized by different groups [2–4] in order to improve the electrical performances of possible devices [5].

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AZPAC [4,4′-Bis(hexiloxy)-azoxybenzene-palladium complex] is a palladium-containing metallorganic liquid crystal [6] whose formula is given in Fig.1. Some of its properties as a liquid crystal have been recently reported [7–11].

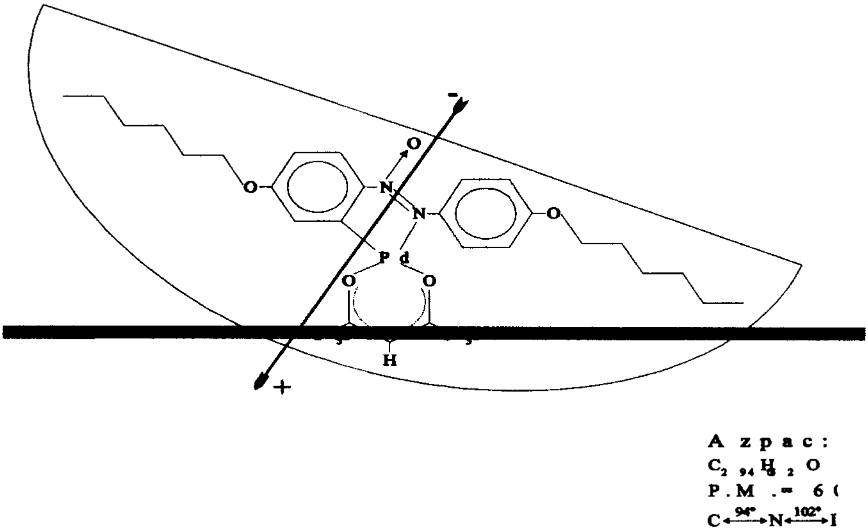

FIGURE 1 Schematic drawing of AZPAC molecule: its specific molecular form, i.e.. not rod like as usual nematics but semidiscotic, which prevents a free rotation about the long molecular axis, is emphasized. The physical direction of the molecular dipole is shown by the large arrow

In recent papers [12,13] we discussed the aggregation-assisted induced electric order in the nematic phase of AZPAC. We have interpreted the somewhat contradictory measurements on AZPAC in terms of its specific molecular form, i.e. not rod like as usual nematics but semidiscotic, which prevents a free rotation about the long molecular axis. Also, the possibility of Pd---O(N) interactions leads to the formation of polar multimers which are responsible of a transitory ferroelectric order in a direction orthogonal to the molecular director, that it could still exist after the nematic ordering is totally destroyed (still being normal to the plane of the sample).

Moreover, by measuring AZPAC molecular dipole moment, and also the average dipole moment which gave rise to the observed paraelectric behavior of the substance, we have brought about new evidence to our assumption that, apart from the nematic order and orthogonal to the direction of the nematic director, there is an electric order due, in part, to a process of aggregation [12].

In this paper we present the measurements of the thermostimulated depolarization current of homogeneously planar aligned AZPAC cells, linking the observed temperature shift to a Clausius-Clapeyron type equation.

Our paper is organized as follows: in section 2 the used experimental set-up is described. The obtained results are reported and discussed in section 3. Finally, the main conclusion of our investigations is stressed in section 4.

2. EXPERIMENTAL DETAILS

The AZPAC has been derived from cyclopalladation of 4–4′-dihexiloxyazoxybenzene (HOAB) with $[(PhCN)_2PDCl_2]$, followed by halo-bridge cleavage with substituted acetylacetonate salt. The HOAB shows a nematic phase between 80 and 126°C.

The transition temperatures of AZPAC are: T_{KN} =94°C; T_{NI} =102°C (where K stands for crystalline solid, N for nematic and I for isotropic).

The sample cell consists of two parallel square (L ≅ 10 mm) glass plates spaced by two Mylar strips (d ≅ 36 μm). Both surfaces of the glass plates are coated with indium tin oxide (ITO) transparent electrodes.

The planar orientation of AZPAC was achieved by coating clean glass plates with the ACM-72 (Atomergic Chemetals Corp.) polymer, a surface aligning material which ensures planar alignment with a small pretilt (approximately 2°).

The experimental set-up is presented in Fig. 2. The cell was placed in a thermally insulated oven whose temperature could vary slowly by a HAAKE F3 liquid bath thermostat. The temperature was measured by a 500 Ω platinum resistor, sampled by a digital multimeter interfaced to a PC.

The oven was placed in a metal box to avoid external electric influence on the measurements.

The sample was first heated beyond the nematic-isotropic transition temperature and then let to cool down, from the isotropic phase to the glassy state of AZPAC, in an applied d.c. voltage of different values in the range between 0 and 30 V. We point out the fact that AZPAC usually does not undergo immediately a liquid crystal to solid state transition, but it remains in a supercooled "glassy" state for some hundred of hours [12].

In this way, a macroscopic polarization remained frozen in, so in the subsequent heating without any applied voltage, the decay of it close to the nematic-isotropic transition was recorded as a depolarization current.

The current was sampled by a digital picoamperometer, interfaced with the PC.

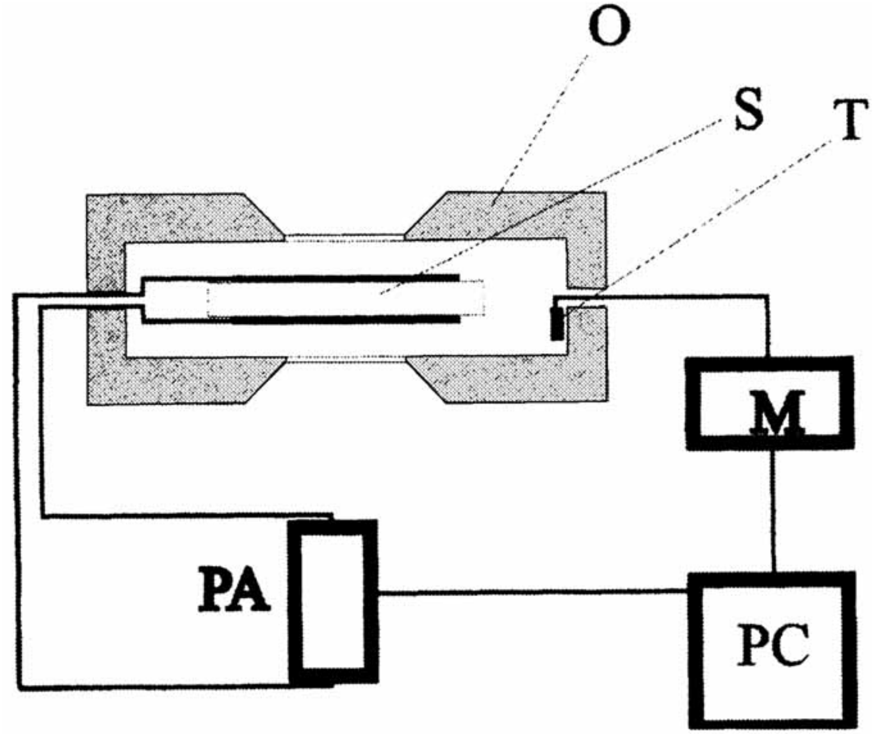

FIGURE 2 Experimental set-up: **O** = thermally insulated oven, the temperature of which could be varied slowly by a HAAKE F3 liquid bath thermostat. The oven was placed in a metal box to avoid external influence on the measurements. **S** = Liquid crystal sample. **T** = 500Ω platinum resistor. **M** = digital multimeter. **PA** = digital picoamperometer. **PC** = Personal computer

Keeping constant the rate of temperature increase, that in our case was 0. 1 K/s, the thermostimulated depolarization current is proportional to the amount of polarization which had been frozen in.

3. RESULTS AND DISCUSSION

In Fig. 3 we report a set of typical curves of the thermostimulated depolarization current recorded with the technique presented in the previous section. Previous measurements made by us on AZPAC's ligand [i.e. 4–4′-dihexiloxyazoxybenzene] have shown a sharp depolarization peak, which does not appear, at the nematic-isotropic transition temperature but at the crystal-nematic point. A set of these records is presented in Fig. 4.

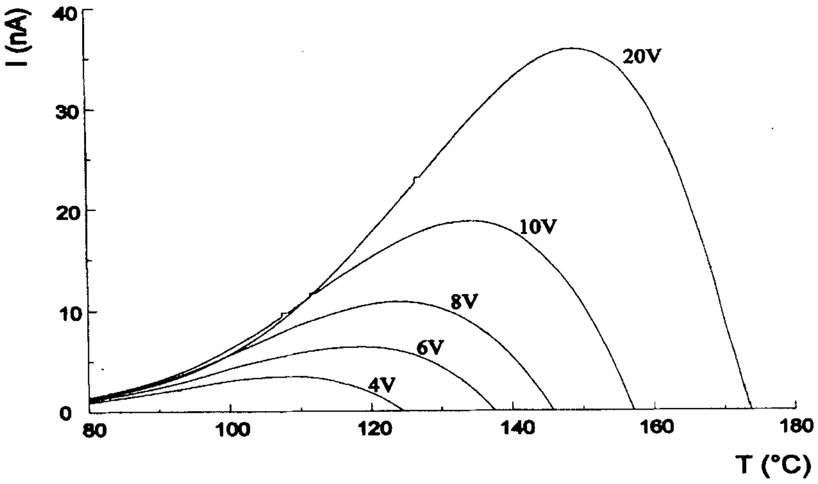

FIGURE 3 A set of typical curves of the thermostimulated depolarization current obtained when heating up the AZPAC cell

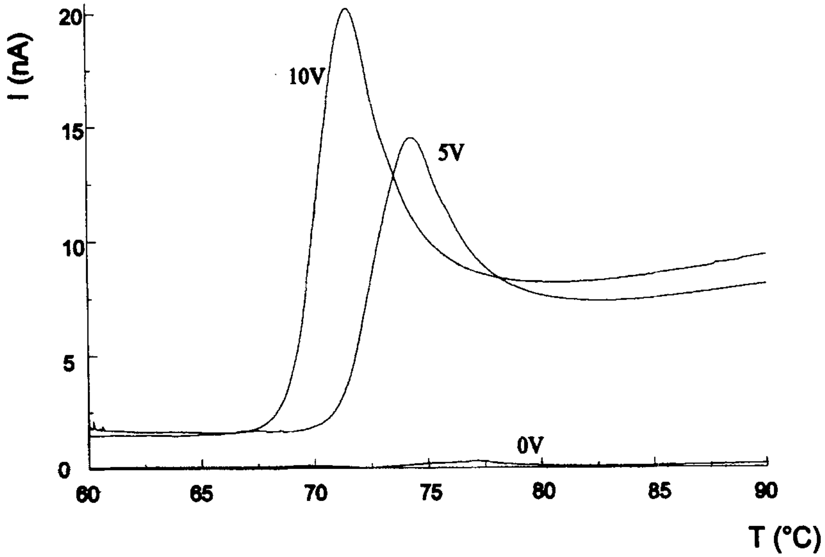

FIGURE 4 A set of typical curves of the thermostimulated depolarization current obtained when heating up the AZPAC's ligand (HOAB) cell

From the saturation curve in Fig. 3, corresponding to 20 V applied voltage, we estimated a total charge Q of 8000 nC which could come from the orientation of 1 % of the AZPAC's dipoles. The measured electric dipole moment of AZPAC was found to be 3.54 Debye [13].

Other nematic materials show an increase of the thermocurrent even starting from the solid phase (10 to 15 degrees ahead of crystal-nematic transition temperature). Even when the temperature has been kept constant for tens of seconds, the sample being in the solid phase, the thermocurrent still went up for a while.

Fig. 5 shows the behavior of the maximum value of the current vs. the voltage applied during the cool down. It is interesting to stress that a saturation value is reached for a value of the applied voltage of about 20 V, corresponding to an applied electric field of about 5.5 kV/cm.

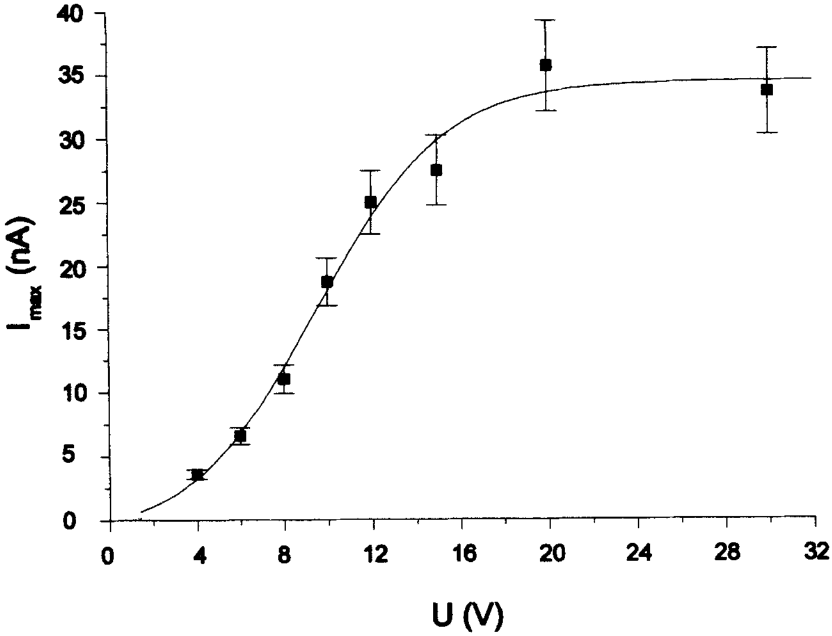

FIGURE 5 The maximum value of the current versus the voltage applied during the cool down. It is interesting to stress that a saturation value is reached for a value of the applied voltage of about 20 V, corresponding to an applied electric field of about 5.5 kV/cm

The temperatures corresponding to the maxima of the current's values versus the applied voltage are shown in Fig. 6.

At lower applied voltages, the behavior exhibited is a second-power dependence. At higher values of the applied voltage, the temperatures corresponding to the maxima of the currents tend to a saturation value. This one is reached at the same value of the applied voltage for which the current's maximum values also saturate.

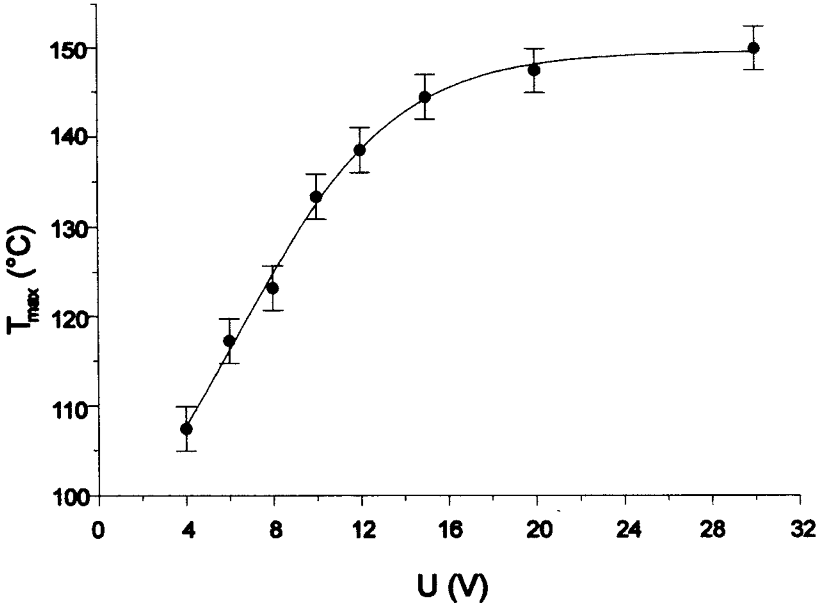

FIGURE 6 The temperatures corresponding to the maxima of the current's values versus the applied voltage. At lower applied voltage, the behavior exhibited is a second-power dependence. At higher value of the applied voltage, the temperatures corresponding to the current's maximum values tend to a saturation value that is reached at the same value of the applied voltage at which the current's maximum values saturate

In the paper [14], following the work of Bahr et al. [15], we derived a Clausius-Clapeyron type equation for the dependence of the transition temperatures on the applied electric field.

Starting with the equality of the chemical potential anywhere on an equilibrium curve, using the Gibbs free energy variation

$$dG_i = -S_i dT + \mu_i dM_i - V_i D_i dE$$

where i is for 1 or 2, we obtain:

$$\frac{\Delta T}{\Delta E} = -V\frac{D_2 - D_1}{S_2 - S_1} = -V\frac{P_2 - P_1}{S_2 - S_1} \tag{1}$$

For a fixed electric field D_2-D_1=P_2-P_1, where D_2 and D_1 are the electric displacements in the two phases, P_2 and P_1 are the polarizations and S_2 and S_1 are the entropies in the same two phases evaluated for the amount of material contained in a volume V.

This formula has been verified by Bahr [15], in the case of smectic C – smectic A transition, showing an increase of the transition temperatures with the applied field E. Moreover, we verified the formula in the case of chiral smectic C – isotropic transition which exhibit an opposite trend [14].

Of course, the amount of order in the nematic phase (phase 1) is greater than in the isotropic phase (phase 2), accordingly, we get S_2-S_1>0.

As far as the difference P_2-P_1 is concerned, we have to take into account the fact that AZPAC has negative anisotropy [10], i.e. it possesses a transverse electric dipole component greater than the longitudinal one. When the director **n** is parallel to the cell plates, a d.c. external applied electric field may easily orient the electric dipoles as this supposes only rotations around the molecular long axis.

In the isotropic phase, the thermal movement hinders the alignment of the molecules so the macroscopic polarization is less than in the nematic phase: ΔT/ΔE should be positive.

In our experiment, when the sample is cooling down from isotropic to nematic to glassy phase, a certain polarization sets up which is frozen-in the glassy state. Therefore, in the case presented in this paper, ΔE is not the external applied electric field but an internal electric field induced by the frozen-in polarization.

As Fig. 5 shows, the polarization (also the internal electric field) goes to saturation at a certain applied voltage. In the isotropic phase the polarization goes to zero (there is no electric field). So P_2 is zero and P_1 is proportional to U (the voltage) for small values of it, and afterwards remains constant. ΔE is also proportional to P_1, so

$$\Delta T \propto V \frac{P^2}{\Delta S} > 0 \tag{2}$$

when U is small, P is proportional to U and we get

$$\Delta T \propto \frac{V}{\Delta S} U^2 \tag{3}$$

that is a second power dependence.

At larger values of U, P is constant, i.e. $P_{saturation}$, so

$$\Delta T \propto \frac{V}{\Delta S} P^2_{saturation} \tag{4}$$

and does not depends on the value of U.

The data displayed in Fig. 6 are in good agreement with this interpretation.

In Fig. 7 we report the configuration in the nematic temperature range. The director **n** is in the plane of the sample at 45° to the crossed polarizers and many multimers, if not all of them, are in the polar state oriented perpendicular to the sample plane. When the temperature reaches the clearing value, the nematic order disappears but the multimers can still exist and the polarization does not vanish suddenly. It is important to stress that the direction of the nematic director and the direction of the polarization are weakly related, but rather orthogonal to each other.

Of course, the temperature increase destroys the polar multimers, then a transition towards a complete nonpolar state takes place, but as this transition spans quite a large temperature interval one cannot speak of a well-defined ferroelectric “phase”.

Even at a fixed temperature the relaxation towards the state of zero polarization goes on, yet slowly.

4. CONCLUSIONS

The depolarization current dependence on temperature has been interpreted in terms of an internal electric field that sets up during the cooling down of the sample under a d.c. external applied voltage.

The transition temperature shift verifies a Clausius-Clapeyron type equation, also giving evidence of the saturation of the polarization.

What might be special about AZPAC is the fact that the molecule does possess three different principal inertia moments: the molecule having thus the form of a drawing ruler. In the nematic phase with planar orientation [9], the transversal electric dipole – which is larger, AZPAC having negative anisotropy – can be oriented in the same direction by an external electric field. Yet, this specific form of AZPAC hinders the rotation about the long axis and the electric dipoles stay aligned for a longer time.

Reference [9] also shows two quite similar relaxation times of the order of 10^{-6} s, both obeying an Arrhenius-type temperature dependence with an activation energy of the order of 1 eV. So, rotation about the long axis does not seem to be much easier than about the other two.

Also, the possibility of Pd---O(N) interactions leads to the formation of polar multimers which are responsible of a transitory ferroelectric order in a direction orthogonal to the molecular director, that could still exist after the nematic ordering is totally destroyed (still being normal to the plane of the sample).

One important point should be emphasized. Why is the temperature shift so large?

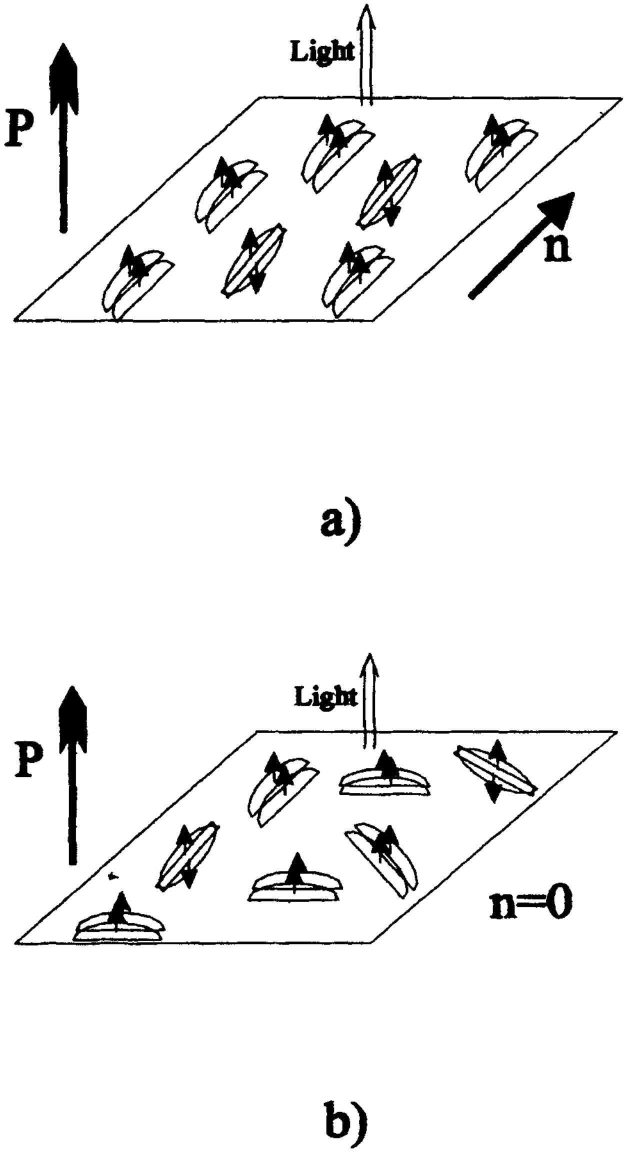

FIGURE 7 **a)** The nematic temperature range. The director **n** is in the plane of the sample at 45° to the crossed polarizers and many multimers, if not all of them, are in the polar state oriented perpendicular to the sample plane. **b)** When the temperature reaches the clearing value, the nematic order disappears but the multimers can still exist and the polarization does not vanish suddenly. It is important to stress that nematic and polar ordering are weakly related and orthogonal to each other

If we consider equation (2) we note that ΔT is larger either if P is large or ΔS is small. Recent observations of pulsed laser stimulated pyroelectricity of AZPAC [16] also showed that AZPAC's ferroelectric properties are not so large as for a normal ferroelectric chiral smectic C. Instead, ΔS could be quite small because the temperatures presented in Fig. 6 do not indicate transition from nematic to isotropic phase (transition accompanied by a latent heat, i.e. $\Delta S \neq 0$) but transition from electrically ordered molecules (multimers) to electrically disordered molecules. This behavior is justified by other measurements [12] which show that the shift of the transition temperatures with increasing electric field is within the error bars when we take into account the "classical approach" of the phase transition, i.e. looking at the sample through crossed polarizers.

We can say that there is a double order in the system: the nematic order, concerning the director **n**, which behaves quite normally, and an electric order, concerning the electric dipoles. Whereas the first type of order induces a phase in the system (the nematic phase) it is doubtful that the second ones induces a real phase in the system.

Contrary to the nematic order, which stays on indefinitely, the electric order decays in time even when the temperature is kept constant. Nevertheless, the system can be in the isotropic phase and still have an electric order, i.e. when dipoles stay perpendicular to the electrodes the long axes of the molecules can take any orientation in a plane, more or less parallel to the electrodes. The nematic phase is partly destroyed, but the electric order could still stay on.

We also want to say some words with respect to using this type of Clausius-Clapeyron derivation. In the papers already mentioned [14,15] the electric field is external and at the transition temperature – i.e. smectic to isotropic – there is a true equilibrium between the two phases. In AZPAC's case, we may consider two thermodynamic systems, loosely connected, one of them concerning the direction of the long axis characterized by the nematic order parameters n and

$$S = \frac{1}{2}\langle 3n_i n_j - \delta_{ij}\rangle \tag{5}$$

and another concerning the dipoles and characterized by the electric parameter P, i.e. the macroscopic polarization. The concept of two thermodynamic systems considered separately is not new in physics; we only have to remember the so-called spin-lattice relaxation phenomena in EPR and NMR [17]. Here the nematic order can be compared to lattice vibrations which also act as a thermal bath, whereas the electric order to the spin system.

Actually, we applied the Clausius-Clapeyron type formula to the electric system, so the rather large temperature shift, AT, has little to do with the nematic-isotropic transition point, but characterizes the temperature at which the electric order decays. On the other hand, when the electric order has not decayed enough we cannot speak of a 100% isotropic phase. The reason is related to the distribution of the molecular long axes, which is isotropic only with respect to the direction perpendicular to the glass plates. It is worth to take into account that the probability to find the molecular long axes parallel to the plates is greater than perpendicular to them. In other words, the long axis distribution function has a cylindrical symmetry about the normal to the plates instead of a spherical one. It is this partial anisotropy that is responsible for the apparent lack of shift in the transition temperature when the sample is viewed through crossed polarizers along the perpendicular to the cell.

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References

(1) See for example: P. G. De Gennes and J. Prost, The Physics of Liquid Crystals, Oxford Science Publications, (1993).

(2) D. W. Bruce, S. C. Davis, D. A. Dunmur, S. A. Hudson, P. M. Maitlis, P. Styring, Mol. Cryst. Liq. Cryst. **215**, 1 (1992).

(3) S. A. Hudson, P. M. Maitlis, Chem. Rev. **93**, 861 (1993).

(4) P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, Coordination Chemistry Reviews, **117**, 215 (1992).

(5) A. M. Levelut, Mol. Cryst. Liq. Cryst., **215**, 31 (1992).

(6) M. Ghedini, D. Pucci, S. Armentano, R. Bartolino, C. Versace, G. Cipparrone, N. Scaramuzza, Italian patent No VE92000003 (1992).

(7) C. Versace, G. Cipparrone, D. Lucchetta, D. Pucci, M. Ghedini, Mol. Cryst. Liq. Cryst., **212**, 313 (1992).

(8) G. Cipparrone, C. Versace, D. Duca, D. Pucci, M. Ghedini, C. Umeton, Mol. Cryst. Liq. Cryst., **212**, 217 (1992).

(9) T. Beica, A. L. Alexe-Ionescu, A. Th. Ionescu, E. Miraldi, D. Pucci, and M. Rajteri, Mol. Cryst. Liq. Cryst. **270**, 91 (1995).

(10) N. Scaramuzza, D. Pucci, M. C. Pagnotta, Mol. Cryst. Liq. Cryst., **239**, 195 (1994).

(11) N. Scaramuzza, M. C. Pagnotta, Mol. Cryst. Liq. Cryst., **239**, 263 (1994).

(12) A. Th. Ionescu, D. Pucci, N. Scaramuzza, C. Versace, A. G. Petrov, R. Bartolino, J. Chem. Phys. **103**, 5144 (1995).

(13) A. Th. Ionescu, N. Scaramuzza, C. Versace, J. Phys. Chem. **101**, 8438 (1997).

(14) I. Cuculescu, G. Barbero, A. L. Alexe-Ionescu, A. Th. Ionescu, R. Bena, C. Ghizdeanu, V. Stoian, Mod. Phys. Lett. B **9**, 791 (1995).

(15) C. Bahr, G. Heppke, B. Sabaschus, Liq. Cryst. **11**, 41 (1992).

(16) L. M. Blinov, A. Th. Ionescu, unpublished.

(17) J. H. Van Vleck, Phys. Rev. **57**, 426 (1940); R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).