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LETTER TO THE EDITOR

Pyroelectric properties of an antiferroelectric liquid crystal

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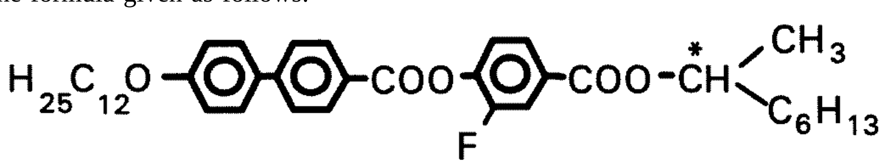
Abstract. The effects of temperature and applied voltage on the pyroelectric properties of an antiferroelectric liquid crystal are given. It has been found that the pyroelectric signal depends strongly on the bias voltage across the sample. The pyroelectric signal behaviour is interpreted with the aid of spontaneous polarization data and good agreement is found between the results from the pyroelectric and polarization techniques. The spontaneous polarization of the sample exhibits the temperature- and field-induced 'Devil's staircase' behaviour, as predicted by the Ising model.

The discovery of antiferroelectricity in some chiral liquid crystals [1] has regenerated enormous interest both in liquid crystal research [2] and in industrial applications [3]. Pyroelectricity is an intrinsic property of ferroelectric liquid crystals (FLC) and has been investigated previously by a number of research groups [4, 5]. Pyroelectric studies of some chiral smectic liquid crystals enabled Beresnev *et al* [4] to propose an initial model for the antiferroelectric liquid crystalline (AFLC) structure. Since this work we are unaware of any further pyroelectric investigations into antiferroelectric phases. In this paper we examine the pyroelectric properties that occur in AFLCs.

The sample to be investigated in this paper is AFLC (AS-573) synthesized at Hull with the formula given as follows:



This sample exhibits a variety of phases such as paraelectric (SmA), ferroelectric (SmC*), ferrielectric (SmC_γ) and antiferroelectric phases (SmC_A, AF). The phase transitions as determined by spontaneous polarization measurements are as follows: I $\rightarrow$ 105 °C $\rightarrow$ SmA $\rightarrow$ 93 °C $\rightarrow$ SmC* $\rightarrow$ 89 °C $\rightarrow$ FiLC (?) $\rightarrow$ 85 °C $\rightarrow$ AF $\rightarrow$ 83 °C $\rightarrow$ SmC_γ $\rightarrow$ 78 °C $\rightarrow$ SmC_A. The phases labelled AF and SmC_A correspond to the high- and low-temperature antiferroelectric phases which by definition have no net spontaneous polarization. The region labelled FiLC corresponds to a proposed high-temperature field-induced ferrielectric phase. The suggested molecular orderings in various phases are given in figure 1. The existence of the variety of phases observed can be explained by using the Ising model. The Ising model

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takes into consideration the competition between the attractive and repulsive interactions that stabilize a particular phase. This model can predict the temperature-induced 'Devil's staircase' [2]. The different structures allowed can be characterized by the parameter [2] $q_T = F/(A + F)$, which denotes the fraction of ferroelectric ordering (F) to the total ordering in a periodic structure. A is the number of antiferroelectric orderings and F is the number of ferroelectric orderings. The Ising model can also explain the field-induced Devil's staircase which can be described by a change in the structure parameter q_E with applied electric field. For this case the allowed structure is given by $q_E = R/(R+L)$, where R and L are the numbers of right- and left-tilting molecules. q_E increases monotonically with the applied field, as new structures are stabilized due to the interactions of molecular dipoles with the electric field. At a given temperature and applied bias, a particular phase will exist as a result of the competition between the temperature- and field-induced staircases.

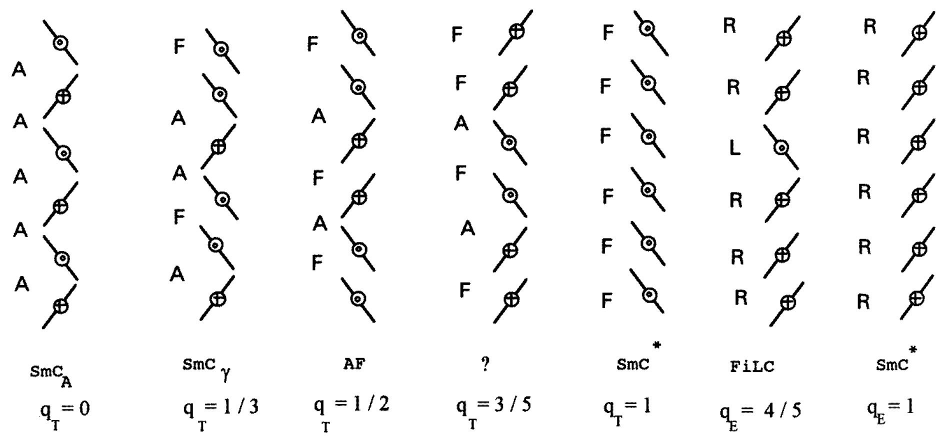

Figure 1. The suggested molecular orderings described by parameter q_T of phases occurring on the temperature-induced staircase. The symbols ○ and + represent the direction of the molecular dipole, into and out of the plane of the page, respectively.

An automated version of the pyroelectric technique devised by Glass *et al* [5] is used to examine the pyroelectric properties of FLCs. This technique involves dynamic heating of an FLC cell using a chopped light source with a modulation frequency of 125 Hz and subsequent detection of the pyroelectric signal using a lock-in amplifier. The cells consisted of two glass plates (20×14 mm^2), coated with a thin layer of indium tin oxide (ITO) with an active electrode region of dimension 8×8 mm^2. A polyvinyl alcohol (PVA) coating was spun onto the ITO electrodes. Mylar thin-film spacers of 8 μm thickness were used to achieve the required cell spacing. The cells were filled in the isotropic phase at 160 °C and allowed to cool slowly to room temperature. Homogeneous alignment of the sample was obtained and this was verified using a polarizing microscope. The sample was subsequently heated at a rate of 0.2 °C min^{-1}. The spontaneous polarization measurements made for different applied voltages were obtained using the integral current reversal technique [7].

The pyroelectric coefficient (γ) by definition is as follows

$$\gamma = \frac{\mathrm{d}P_s}{\mathrm{d}T} \tag{1}$$

where P_s is the local spontaneous polarization due to one layer and dT is the change in temperature of the sample caused by its heating due to the light source.

In our recent paper [6], we showed that the pyroelectric properties of FLCs not only depend on the rate of change of P_s as in (1), but are also strongly dependent on the structure of the material within the cell. Under certain experimental conditions, the director (representing the average molecular position in a layer) possesses a helical structure over a series of layers. The macroscopic spontaneous polarization P_s^* is therefore equal to zero. Application of an electric field leads to a distortion of the helix which then results in a non-zero macroscopic polarization P_s^*. For the case where the director structure is arranged on a helix, the measured pyroelectric signal, I, using a lock-in amplifier is written [6] as:

$$I(f) = K\frac{\mathrm{d}P_s^*}{\mathrm{d}T} = K\frac{\mathrm{d}P_s}{\mathrm{d}T}\int_0^{p_0}\cos\varphi(z,\ E)\ \mathrm{d}z. \tag{2}$$

Here $K = A\,\mathrm{d}T/\mathrm{d}t$; A is the electrode area, $\mathrm{d}T/\mathrm{d}t$ is the rate at which the sample is heated, p_0 is the pitch of the helix, φ is the azimuthal angle, z lies along the axis of the helix. In such a cell, the pyroelectric signal given by I depends not only on the basic function $\mathrm{d}P_s/\mathrm{d}T$ but also on the structural parameters given in the integral of (2).

In FLCs for small applied voltages the pyroelectric signal is found to be linearly dependent on applied electric field [6]. For AFLCs extra considerations such as the temperature and field-induced 'Devil's staircase' should be taken into account [2]. In figure 2 the measured spontaneous polarization P_s^* is normalized with respect to the spontaneous polarization for an unwound SmC* phase, P_s. The spontaneous polarization in the region $T = 79$–$82\,^\circ$C for an applied voltage of less than 7 V is approximately $P_s^* = \frac{1}{3}P_s$, which corresponds to the normal ferrielectric SmC$_\gamma$ phase, with structure parameter $q_T = \frac{1}{3}$. For $V_{app} = 1$ V the spontaneous polarization exhibits a maximum with $P_s^* = \frac{3}{5}P_s$ at $T = 85\,^\circ$C. The peak represents a high-temperature ferrielectric phase FiLC. This region [9] labelled as FiLC has a polarization exactly the same as that allowed for a phase with $q_E = \frac{4}{5}$. For applied voltages $V \geqslant 2$ V at the temperature within $T = 84$–$87\,^\circ$C, the spontaneous polarization increases further and this is due to a combination of the field-induced transition from FiLC to SmC* and distortion of the SmC* helix. The polarization measurements also show that a voltage $V \leqslant 5$ V is not sufficient to destroy the antiferroelectric ordering of the high-temperature AF phase.

The temperature dependence of pyroelectric signal (I), its integrated value (S), and measured spontaneous polarization (P_s^*), for a bias voltage of 0.5 V are shown in figure 3: two negative and one positive pyroelectric peaks are observed. At a higher voltage bias voltage of 1 V (see figure 4), the low-temperature positive peak disappears and two peaks of the same polarity are obtained. Good qualitative agreement was found between the integrated pyroelectric signal and the polarization measurements over a temperature range 93–83 °C that includes the SmA–SmC*–FiLC–SmC* phases. However, the value for the integral of pyroelectric signal does not go to zero as P_s^* does at a temperature of 83 °C. At lower temperatures the discrepancies between the integrated pyroelectric signal (S) and spontaneous polarization increase.

For a direct bias voltage of 0.5 V, the pyroelectric signal exhibits three pyroelectric peaks, two negative peaks and one positive peak. These are shown in figure 3. The pyroelectric signal is proportional to the pyroelectric coefficient, as mentioned earlier. We analyse the pyroelectric data on cooling from the SmA phase. At $T = 93\,^\circ$C, a sharp negative pyroelectric peak occurs which signifies that the spontaneous polarization is increasing with decreasing temperature. This peak corresponds to the SmA–SmC* phase transition, as is observed in a ferroelectric liquid crystal. Below 93 °C, a region occurs where the pyroelectric signal goes to zero and the signal is stable over 2 °C: this indicates that there is a stable ferroelectric (SmC*) region where the polarization is almost independent

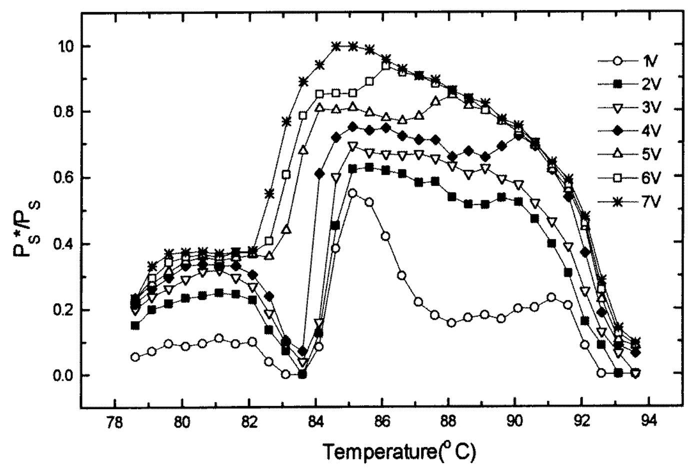

Figure 2. P_s^*/P_s is the normalized spontaneous polarization and P_s is the spontaneous polarization of the unwound SmC* phase i.e. the maximum spontaneous polarization. P_s^* is the measured macroscopic spontaneous polarization.

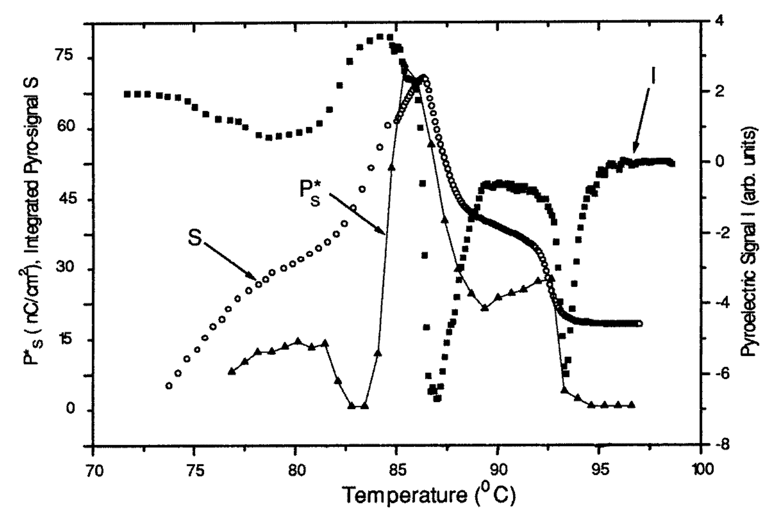

Figure 3. The pyroelectric signal, I, the integrated pyroelectric signal, S, and the measured spontaneous polarization, P_s^*, are given at an applied voltage of $V_{app} = 0.5$ V dc.

of temperature. This is also observed in the spontaneous polarization data. However a voltage of 0.5 V is not sufficient to completely unwind the helix and hence the spontaneous polarization is lower than the maximum for an unwound structure. At $T = 87\,^{\circ}$C another sharp negative peak occurs, indicating a further increase in the spontaneous polarization which is consistent with that of a high-temperature field-induced ferrielectric phase. This phase may be formed by the field-induced distortion of a high-temperature ferrielectric phase with $q_T = \frac{3}{5}$ and $P_s^* = \frac{1}{5}P_s$ (see figure 1). Since a phase with $q_T = \frac{3}{5}$ is unstable, the phase structure could easily be modified by a small bias voltage. The region of high spontaneous

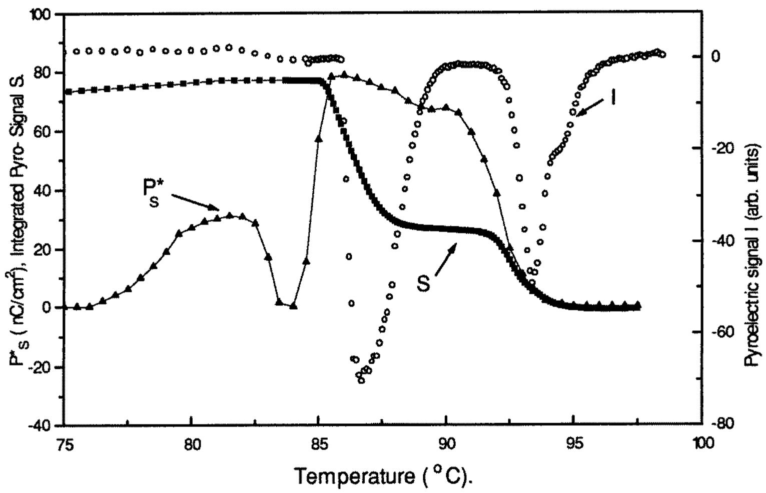

Figure 4. The pyroelectric signal, I, the integrated pyroelectric signal, S, and the measured spontaneous polarization, P_s^*, are given at an applied voltage of $V_{app} = 1$ V dc.

polarization may therefore represent a high-temperature field-induced ferrielectric phase FiLC with $q_E = \frac{4}{5}$ and $P_s^* = \frac{3}{5} P_s$. At $T = 86\,^\circ$C, the sign of the pyroelectric signal changes, becoming positive. This is significant as it indicates that the spontaneous polarization is decreasing with decreasing temperature. This is consistent with the observation of a high-temperature antiferroelectric phase AF, with $q_T = \frac{1}{2}$, in the range 83–84 °C, found from the P_s measurements where the spontaneous polarization goes to zero. At lower temperatures the pyroelectric signal is still positive. This implies that the polarization continues to decrease and the AF–SmC_γ phase transition is not being detected.

Now we discuss the pyroelectric results for a bias voltage of 1 V, which are shown in figure 4. The pyroelectric signal exhibits two negative peaks, one centred at 93 °C and the other at 87 °C. The lower-temperature positive peak at $T = 85\,^\circ$C (see figure 3) is not observed. The negative peak at 93 °C represents the SmA–SmC* transition. In the temperature range $T = 89$–92 °C, the pyroelectric signal is almost zero. This implies that in this temperature interval the polarization does not change much with temperature. This is consistent with an SmC* phase, which was also the case for a lower bias voltage of 0.5 V. The second negative peak at $T = 87\,^\circ$C of figure 4 occurs at the same temperature as that of figure 3. The negative peak at 87 °C also signifies an increase in the spontaneous polarization with a decrease in temperature which is due to the existence of an FiLC phase. In this case it is interesting to note that the pyroelectric signal allows detection of the SmC*–FiLC phase transition, which is not clear from the corresponding spontaneous polarization measurements. Further cooling gives rise to an almost-zero pyroelectric signal which corresponds to a temperature-independent spontaneous polarization. The SmC_γ–SmC_A transition was not shown by the pyroelectric measurements for the reasons given below.

The discrepancies between the integral (S) of the pyroelectric signal (I) in the AF ($q_T = \frac{1}{2}$) and SmC_A ($q_T = 0$) phases and the spontaneous polarization measurements (P_s^*) could be explained by taking into account the results obtained by Ema *et al* [8]. They showed that the relaxation time (τ_{AF}) between antiferroelectric and ferrielectric phases is of the order of tens of seconds. The modulation frequency of heat signal in our experiment ($\mathrm{d}T/\mathrm{d}t$) is 125 Hz. The relaxation time τ_{AF} is greater than the period, 8 ms, of the heat signal and this leads to inaccuracy in the detection of the antiferroelectric–ferrielectric phase transition by the pyroelectric technique. Another important reason arises from the fact that there is quite a large hysteresis in transition temperatures between ferrielectric and antiferroelectric phases [8]. Values of temperature hysteresis for these phase transitions vary from 0.05 to 0.22 °C. These are considerably larger than temperature changes caused by the light source during pyroelectric measurements. Thus a small variation of the temperature around the transition temperature may not induce these phase transitions.

The pyroelectric properties of a antiferroelectric liquid crystal are studied. The strong dependence of pyroelectric signal on temperature and applied voltage has been reported. The pyroelectric signal allows us to detect the following phase transitions at a bias voltage of 0.5 V: SmA–SmC*, SmC*–FiLC, and FiLC–AF in agreement with the polarization measurements. At a bias voltage of 1 V, two phase transitions, SmA–SmC* and SmC*–FiLC are detected by the pyroelectric technique. In this case, the pyroelectric signal behaviour detects the SmC*–FiLC phase transition which is unclear from the corresponding spontaneous polarization measurements. For the SmC_γ–SmC_A phase transition, the integrated pyroelectric signal does not follow the temperature dependence of spontaneous polarization. The main reason for this discrepancy is the large relaxation times of the antiferroelectric and ferrielectric phases. The unusual behaviour within the SmC* temperature region indicated by a negative peak at 87 °C for bias voltages of 0.5 V and 1 V could be explained by the coexistence of a high-temperature ferrielectric phase with $q_T = \frac{3}{5}$ and the SmC* phase with $q_T = 1$.

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