

# Kinetics of spontaneous polarization in a ferroelectric liquid crystal

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(Submitted 6 July 1978)

*Pis'ma Zh. Eksp. Teor. Fiz.* **28**, No. 6, 340–344 (20 September 1978)

The kinetics of the pyroelectric response of a liquid ferroelectric to a thermal pulse, with account taken of the finite relaxation time  $\tau$  of the spontaneous polarization, is considered. Direct measurements were made of the time  $\tau$  for a liquid crystal. A sharp increase of  $\tau$  was observed near the transition from smectic "C" to smectic "A."

PACS numbers: 61.30.Gd, 77.70. + a, 77.80.Bh

1. Progress in the study of ferroelectricity is connected to a considerable degree with the theoretical and experimental investigations of the dynamics of the crystal lattice. The behavior of the relaxation time of the ferroelectric soft mode near phase transitions yields valuable information on the nature of the spontaneous polarization in ferroelectrics and antiferroelectrics.<sup>1</sup> It is of fundamental interest to investigate the dynamics of spontaneous polarization in a new class of ferroelectrics—the recently discovered ferroelectric liquid crystals.<sup>2</sup>

We consider in this paper the kinetics of spontaneous polarization of a liquid crystal (LC), with account taken of the finite relaxation time, by starting from the kinetics of the pyroelectric current of an LC layer heated by a thermal pulse.

2. Let the pyroelectric be contained in a capacitor with electrode area  $S$  and capacitance  $C$ . In the short-circuit regime ( $R_L C \ll t_0$ , where  $R_L$  is the load resistance and  $t_0$  is the duration of the thermal pulse), the response voltage  $U$  of the pyroelectric is given by

$$U(t) = R_L S \frac{dP}{dt} \quad (1)$$

If the pulse is rectangular in form and the power density is  $W$ , then, neglecting the outgoing heat, the pyroelectric is given by

$$\frac{\partial T}{\partial t} = \begin{cases} \frac{W\eta}{c\rho d} & t < t_0 \\ 0 & t > t_0 \end{cases} \quad (2)$$

where  $\eta$  is the fraction of the absorbed power,  $c$  is the specific heat,  $\rho$  is the density, and  $d$  is the thickness of the pyroelectric layer.

In the simplest case, polarization relaxation with a finite (constant) time  $\tau$  can be described as follows:

$$\frac{dP}{dt} = - \frac{P - P_0(T)}{\tau} \quad , \quad (3)$$

Expanding the equilibrium polarization  $P_0(T)$  in a series (assuming the heat rise  $\Delta T(t)$  to be small), we obtain after integrating and taking (2) into account

$$U(t) = \frac{R_L W^* \eta}{c \rho d} \gamma \begin{cases} 1 - \exp(-t/\tau), & t < t_0 \\ [1 - \exp(-t_0/\tau)] \exp[-(t - t_0)/\tau], & t > t_0 \end{cases} \quad , \quad (4)$$

where  $\gamma = \gamma(T_0) = dP_0(T_0)/dT$  is the pyroelectric coefficient at the temperature  $T_0$ , and  $W^* = WS$  is the total power incident on the area  $S$ .

a) At  $\tau \ll t_0$ , Eq. (4) yields the customary formula for  $U_{\max}$  (Ref. 3):

$$U_{\max} \approx \gamma \frac{R_L W^* \eta}{c \rho d} \quad , \quad (5)$$

and the kinetics of  $U(t)$  reveals a leading front with a time constant  $\tau$ .

b) At  $\tau \gg t_0$  we have

$$U_{\max} \approx \gamma \frac{R_L W^* \eta}{c \rho d} \frac{t_0}{\tau} \quad , \quad (6)$$

i.e., the pyroelectric response decreases in proportion to the ratio of the relaxation time  $\tau$  to the duration  $t_0$  of the thermal pulse.

It follows from (6) and (5) that it is possible to estimate  $\tau$  from the known duration  $t_0$  of the thermal pulse and from the ratio of the pyroelectric coefficients measured by a stationary method (or from the pyroelectric response to a long thermal pulse with  $t_0 \gg \tau$ ), and with the aid of a short pulse  $t_0$ . In both cases, a) or b), the kinetics of the pyroelectric response is characterized at  $t > t_0$  by a decrease whose time constant equal to the relaxation time  $\tau$ , so that this time can also be determined from the level  $U(t)/e$ .

3. In earlier investigations of the pulsed pyroelectric effect in ferroelectric liquid crystals<sup>4</sup> we have considered the case when the duration of the thermal pulse is much less than the Debye relaxation time of the dipoles of the *LC*. Starting from the ratio of the stationary value of the pyroelectric coefficient expected from the temperature dependence of the polarization, as measured in Ref. 5, to the value of the dynamic pyroelectric coefficient measured by means of the pyroelectric response to a giant pulse, as well as from the pulse duration  $t_0 \sim 10^{-7}$  sec, we have estimated indirectly the

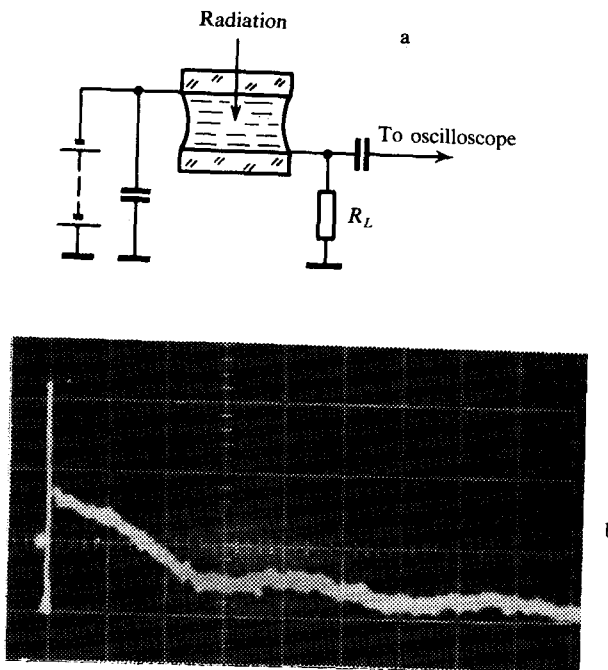


FIG. 1. a)—setup for the registration of the pyroelectric response of a liquid crystal cell to a laser pulse of duration  $t_0 = 3 \times 10^{-8}$  sec; b)—oscillogram of pyroelectric response. Sweep 1 microsecond per division, each vertical division equals 2 mV.

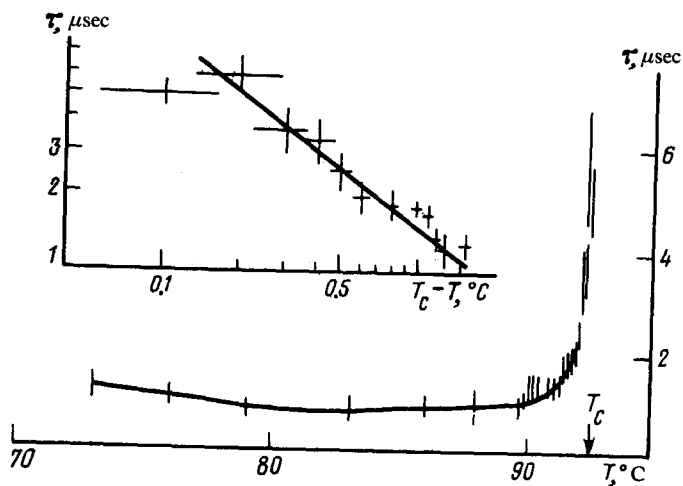


FIG. 2. Temperature dependence of the relaxation time for the DOBAMBC liquid crystal.

Debye-relaxation time of the dipoles for the best known ferroelectric crystal, *l-p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate (DOBAMBC),  $\tau \approx 10^{-5} - 10^{-6}$  sec.

In the present study we measured directly, for the first time ever, the relaxation time of the polarization of DOBAMBC by means of the kinetics of the decrease of the pyroelectric signal of a liquid-crystal layer heated by a giant pulse from a neodymium laser. The experimental procedure is similar to that of Ref. 4 (the measurement setup is illustrated in Fig. 1a). The total power of the thermal pulse with duration  $t_0 \approx 3 \times 10^{-8}$  sec at half-height was 50 kW, and in this case the 200  $\mu\text{m}$  liquid-crystal layer was heated by not more than 0.1 °C. The electric time constant of the cell together with the amplifier input did not exceed 15 nsec. The sharp peak at the start of the oscillogram typical of this experiment (Fig. 1b), a peak whose shape duplicates the giant pulse, is due to the "fast" component of the change of the polarization of the liquid crystal (it is possibly connected with the rotation of the DOBAMBC molecules around their long axes). The slow decrease of the pyroelectric signal is characterized by a time constant  $\tau$  of several microseconds and is due to the "slow" component of the variation of  $\bar{P}$ , which is apparently connected with the rotation of the molecules about their short axes. The value of  $\tau$  agrees with the estimate given in Ref. 4 for the Debye relaxation time in accordance with formula (6), and also with the presence of a frequency dispersion of the dielectric constant, observed in the frequency region  $10^4$ – $10^6$  Hz (Ref. 6). The temperature dependence of the relaxation time of the pyroelectric effect of DOBAMBC, shown in Fig. 2, reveals a fast growth of  $\tau$  near the smectic "C"—smectic "A" transition. The critical exponent  $\alpha$  in the relation

$$\tau^{-1} \sim (T_c - T)^\alpha \quad (7)$$

amounted to  $0.67 \pm 0.10$ . We note that the large error in the measurement of  $\tau$  is connected with the oscillatory character of the decrease of the pyroelectric signal. The oscillations are due to the piezoelectric effect in the ferroelectric liquid crystal, and their frequency is determined by the natural frequency of the mechanical oscillations of the liquid-crystal cell.

4. We have thus observed singularities of the pyroelectric effect in liquid ferroelectric systems with slow relaxation of the polarization. Near the smectic "C"—smectic "A" phase transition we observed an increase in the relaxation time, similar to the behavior of the ferroelectric soft mode in solid ferroelectrics near the Curie point.<sup>1</sup>

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