

Critical behavior of a liquid crystal near the phase transition between two ferroelectric phases

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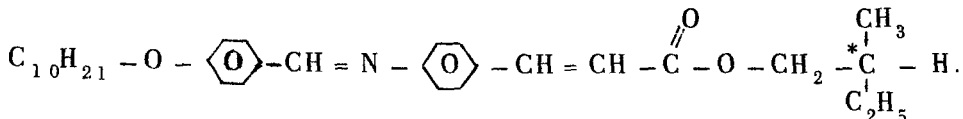
(Submitted 10 November 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 1, 37–41 (5 January 1980)

A critical slowing down of Debye relaxation of the spontaneous polarization in the neighborhood of the structural phase transition smectic H—smectic C was recorded in a liquid crystal.

PACS numbers: 64.70.Ew, 77.70. + a, 77.80.Bh

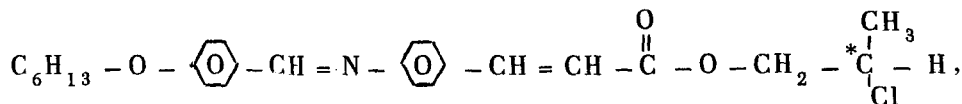
1. A critical behavior of crystals in the neighborhood of phase transitions provides valuable information about the nature of these transitions. In addition to this fundamental interest, their study also has great applied importance in view of the many radical properties of crystals and new effects occurring near the transitions. The liquid crystals with their many phases make a very convenient model. The smectic liquid crystals comprised of optically active (chiral) molecules are of particular interest. The presence of spontaneous polarization in the smectic layer at certain phases of these liquid crystals⁽¹⁾ allows us to study the critical behavior of a number of parameters by rather simple methods. Earlier, the critical behavior of dielectric susceptibility⁽²⁾ and the slowing down of spontaneous polarization relaxation⁽³⁾ near the transition point smectic C—smectic A were studied in the ferroelectric liquid crystal DOBAMBC:



2. In this paper we investigated for the first time the critical behavior of the relaxation time of spontaneous polarization τ in the region of structural phase transition chiral smectic H—chiral smectic C. The smectic H phase (SmH) appears in certain liquid crystals as the smectic C (SmC) phase is cooled. In contrast to SmC, in which the molecules have only a preferred direction or orientation for the long axes at specific angle to the normal of the layer, in each layer in SmH the molecules are packed hexagonally.⁽⁴⁾ Because of the specific viscous-elastic properties in the SmH phase, it is impossible to determine the spontaneous polarization P by methods of repolarization in a variable field⁽⁵⁾ or by using mechanical displacement.⁽⁶⁾ In the proposed work both the critical behavior of τ near the transition temperature T_{HC} and the spontaneous polarization P in the SmH phase (in which it has not been measured

before now) were studied by pyroelectric methods used by us earlier to study τ and P in DOBAMBC.^[3,7]

For the object of study we selected the ferroelectric liquid crystal *L*-II-hexyloxybenzylidene- Π' -amino-2-chlorpropyl-cinnamate (HOBACPC):



which has well-identified ferroelectric phases SmH and SmC.^[4] An important difference between the HOBACPC and DOBAMBC molecules is that the molecular dipole moment responsible for spontaneous polarization of the smectic layer is generated by the *C—Cl bond, which excludes the intermolecular rotations of this dipole group

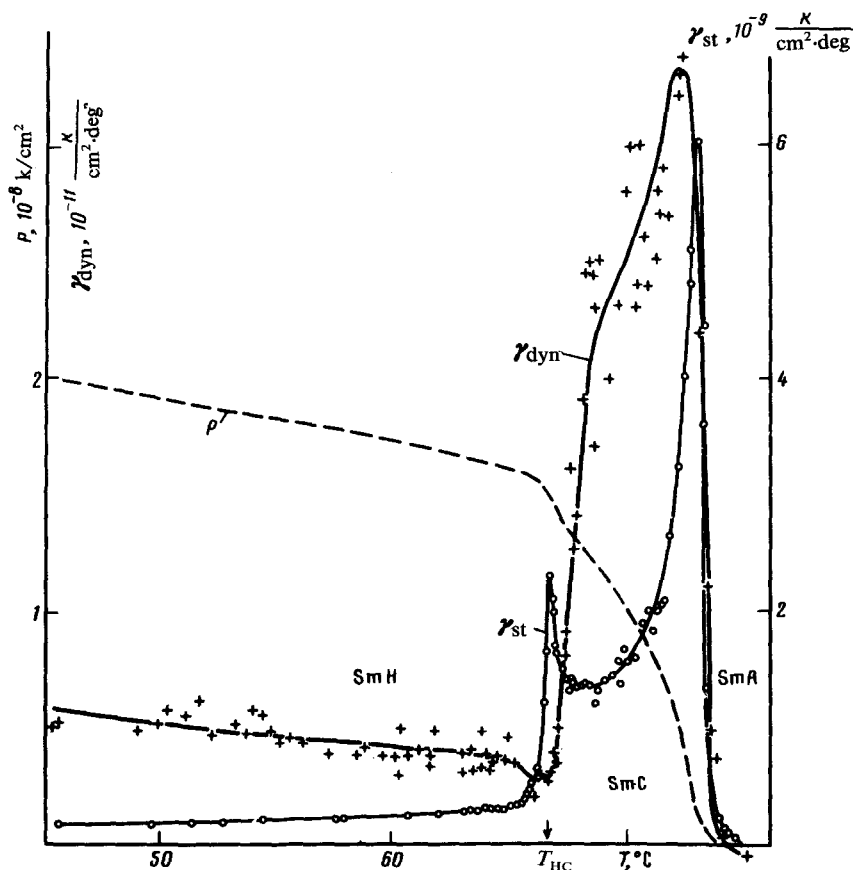


FIG. 1. Temperature dependences of the stationary (γ_{st}) and dynamic (γ_{dyn}) pyroelectric coefficients and of the spontaneous polarization (P) for *L*-II-hexyloxybenzylidene- Π' -amino-2-chlorpropylcinnamate (HOBACPC): γ_{st} and γ_{dyn} are obtained from the pyroelectric response to laser pulses of duration, 3×10^{-4} and 3×10^{-8} sec, respectively.

relative to the chiral fragment, and leads to a significant increase of polarization of the smectic layer in comparison with DOBAMBC, where the dipole moment produced by the C=O bond is not rigidly bound to the asymmetric carbon atom *C.

The relaxation time of the spontaneous polarization τ was determined according to Ref. 3 from the equation:

$$\tau(T) = t_0 \gamma_{st}(T) / \gamma_{dyn}(T) \quad (1)$$

Here, $\gamma_{st}(T) = dP/dT$ is the stationary pyroelectric coefficient measured analogously to that in Ref. 7, from the pyroelectric response at a sufficiently long (in comparison with τ) thermal pulse from a free-running neodymium laser with an envelope duration of 3×10^{-4} sec.

Also, $\gamma_{dyn}(T)$ is a dynamic pyroelectric coefficient measured in the same way as in Ref. 7, from the pyroelectric response to a giant pulse with a width at half-height $t_0 = 3 \times 10^{-8}$ sec.

3. In Fig. 1 the temperature dependence of the pyroelectric coefficients $\gamma_{st}(T)$ and $\gamma_{dyn}(T)$ is given for HOBACPC, and also for the spontaneous polarization $P(T)$ obtained by integrating γ_{st} with respect to the temperature curve. Near the phase transitions $SmH \rightarrow SmC$ and $SmC \rightarrow SmA$, the $\gamma_{st}(T)$ curve has sharp maxima. Moreover, near T_{CA} the pyroelectric coefficient reaches 6×10^{-9} k/cm²·deg, and in the range 67–73 °C it is about 2×10^{-9} k/cm²·deg which, in principle, makes it possible to use this type of liquid crystal materials in pyroelectric transducers. The maximum polarization $P \approx 2 \times 10^{-8}$ k/cm² in the SmC phase is in agreement with the data of Ref. 6. It is larger in HOBACPC than in DOBAMBC⁽⁷⁾ by a factor of 5–6.

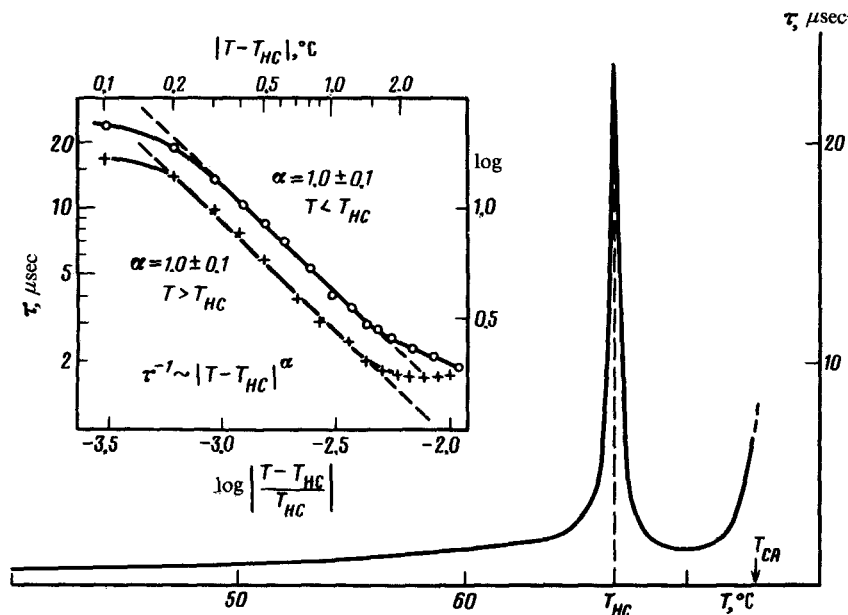


FIG. 2. Temperature dependence of the relaxation time τ of the spontaneous polarization in the SmH and SmC phases of HOBACPC.

4. Of greatest interest is the structural phase transition between the ferroelectric phases SmH and SmC, for which $\gamma_{st}(T)$ exhibits a sharp maximum, and $\gamma_{dyn}(T)$ has a dip.

Figure 2 shows the temperature dependence of the relaxation time for spontaneous polarization $\tau(T)$ calculated from the $\gamma_{st}(T)$ and $\gamma_{dyn}(T)$ curves by using Eq. (1). The time $\tau(T)$, measured in the same way as in Ref. 3 from the kinetics of the pyroelectric response to a giant pulse, is identical to that in Fig. 2. However, in this case the accuracy of $\tau(T)$ is somewhat lower. Near T_{CA} , a sharp increase in τ is similar to that for DOBAMBC.⁽³⁾

The distinctive feature of the SmH \rightarrow SmC transition is that the spontaneous polarization occurs in both phases, and the pyroelectric procedure allows us to determine $\tau(T)$ from both sides of the T_{HC} point. Assuming that the temperature T_{HC} corresponds to a sharp maximum in τ , we can determine its position with high accuracy; in our experiment, $T_{HC} = 66.8 \pm 0.05$ °C.

In the range 0.1 °C $< |T - T_{HC}| < 1.5$ °C, the behavior of $\tau(T)$ can be accurately described by the expression

$$\tau^{-1} \sim |T - T_{HC}|^{\alpha}, \quad (2)$$

in which the critical index α is 1.0 ± 0.1 on both sides of T_{HC} .

The liberation dynamics of the molecular dipoles with the temperature dependence of the relaxation time, illustrated in Fig. 2, is characteristic of the relaxation-type soft modes, produced as a result of continuous phase transitions.⁽⁸⁾ Thus, it follows from our dynamic experiments that the SmC \rightarrow SmH phase transition has a composite nature. The ordering of the rigid molecular frame into a hexagonal structure is a first-order transition that releases heat of transition.⁽⁴⁾ At the same time, the ordering of flexible chiral fragments of the molecules (carrying dipoles responsible for spontaneous polarization) has the nature of a second-order transition.

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