Ferroelectric properties of smectic liquid crystals

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Direct measurements were made of the temperature dependences of the spontaneous polarization (P_s) and of the molecule inclination angle (θ) in the chiral smectic "C" phase of a ferroelectric liquid crystal. The critical exponents of the temperature dependences of these parameters are estimated.

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Recently advanced[1,2] symmetry arguments and experimental facts offer evidence of dipole ordering of the ferroelectric type in the optically active isomer of the liquid crystal *p*-decyloxybenzylidene *p'*-amino 2-methyl butyl cinnamate (DOBAMBC) in the smectic "C" and "H" phases.

In contrast to solid ferroelectric crystals, where the principal role is played by the long-range dipole-dipole interactions, in liquid crystals the contribution of the constant dipoles of the molecules to the total interaction energy is small in comparison with the short-range dispersion forces. Therefore ferroelectricity in the chiral smectic "C" phase of a liquid crystal is possible as a consequence of the matched inclination of the molecules and the hindering of their rotation about their long axes.[1]

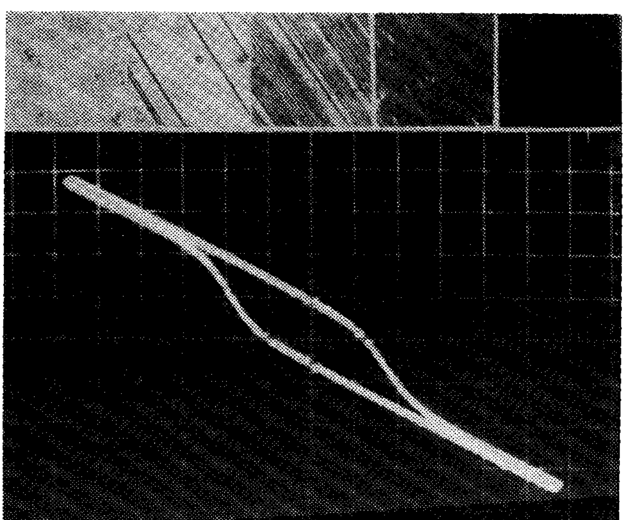

FIG. 1. Oscillogram of polarization reversal of DOBAMBC and microphotographs of the sample corresponding to one polarization-reversal cycle. The dimensions of the microphotographs are 150×150 μ.

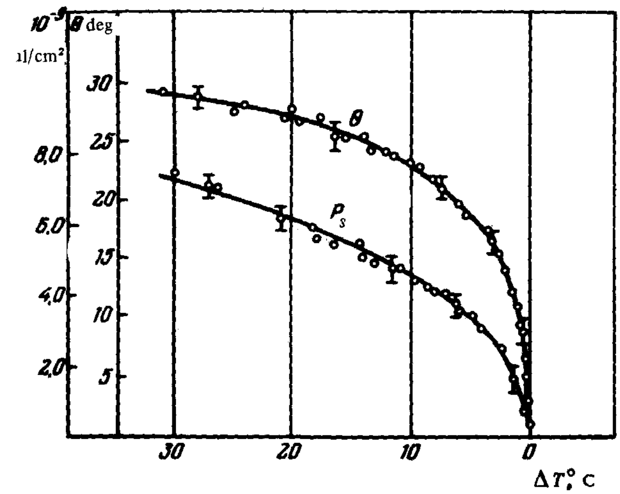

FIG. 2. Temperature dependences of P_c and θ in DOBAMBC.

To ascertain the singularities of the ferroelectric properties of smectic liquid crystals, we performed direct measurements, in the smectic "C" phase of DOBAMBC, of the spontaneous polarization (P_s) and of the inclination angle (θ) of the long axes of the molecules to the normal of the smectic layers, the angle being a parameter of the smectic "A"—smectic "C" transition.

The measurements were performed on smectic single-domain compounds of homogeneous orientation obtained by cooling the samples placed between glasses with conducting coatings from the isotropic phase to the smectic "C" phase in a magnetic field of intensity 17 kOe. According to heat-capacity measurements, the temperature of the transition from the smectic "C" to the smectic "A" phase was 93.1 °C.

The values of P_s were measured with the aid of polarization-reversal oscillograms[3] at frequencies 0.1—8 Hz. The polarization-reversal was monitored by observing of the samples through a microscope in polarized light. Figure 1 shows a typical oscillogram of the polarization reversal of DOBAMBC. The microphotographs illustrate one cycle of the polarization reversal, which is accompanied by simultaneous untwisting of the helical structure. As seen from Fig. 1, the helical ordering of the chiral smectic phase "C" can be likened to the breakup of a solid ferroelectric single crystal into domains.[1] Figure 2 shows the temperature dependence of P_s, calculated from the polarization-reversal oscillograms. We note that in the smectic "A" phase the oscillogram degenerates into a straight line and the polarization vanishes accordingly. The value obtained by us for the spontaneous polarization of DOBAMBC, $P_s \cong 7 \times 10^{-9}$ C/cm^2 at $T_c - T = 25°$, agrees with the indirect estimates of this quantity obtained in[1,2] by comparing the interaction energy of the electric field with the constant molecule dipole moments and the elastic-deformation energy.

The temperature dependence of P_s, measured on different samples, is approximated by the expression $P_s \sim (T - T_c)^{0.37\pm0.10}$.

The dipole ordering in the smectic "C" phase of a liquid crystal of the considered type provides a unique possibility of measuring by a simple optical method with a polarization microscope. The slope angle θ of the molecules is determined by a new method, based on measurement, in crossed polaroids, of the extinction angles of a smectic single-domain compound having a homogeneous orientation at different values of the constant electric field that reorients the slope of the molecules. When an untwisting electric field is applied, the interaction of the latter with the constant dipole moments of the molecules causes then to rotate together in the plane of the sample, so that the optical axis in a homogeneously oriented compound makes an angle $\pm\theta$ with the initial direction of the helix axis.

Figure 2 shows the temperature dependence of the angle θ, which can be approximated by the expression $\theta \sim (T - T_c)^{0.31\pm0.05}$.

As seen from the plots of $\theta(T)$ and $P_s(T)$, the smectic "A"—smectic "C" phase transition is indeed a continuous phase transition, and the temperature T_c is the true Curie point.

The obtained values of the critical exponents attest to the short-range character of the forces that lead to the appearance of the inclination of the molecules and the polarization in the smectic "C" phase of a chiral liquid crystal. The molecule slope angle θ has the same transformation properties as P_s, so that they are linearly connected.[1] The experimentally observed systematic excess of the critical exponent of $P_s(T)$ over that of $\theta(T)$ may indicate the presence of a weak singularity of the corresponding coefficients of the expansion of the free energy, which are constant in the ordinary Landau theory.

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