Pretransitional anomalies in the rotation of the plane of polarization of light in ferroelectric liquid crystals

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It is observed that the sign of the fluctuation contribution to the rotation in the smectic *A* phase differs from the sign of the rotation in the smectic C^* phase and isotropic phase. A theoretical explanation of the observed anomaly is given.

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Short-range orientational order in the isotropic phase of liquid crystals leads to a number of experimentally observed pretransitional phenomena. One such effect, which reveals the nature of the fluctuation regions of correlated positioning of molecules in the isotropic phase of a cholesteric liquid crystal, is the pretransitional rotation of the plane of polarization of light (PR) observed experimentally in Ref. 1. The theory of the effect was developed in a number of papers[2,6] and it agrees quantitatively with the experiment in Ref. 6. In the present work, pretransitional effects in the chiral smectic C^* liquid crystal, which differs qualitatively from the cholesteric liquid crystal, are observed and explained.

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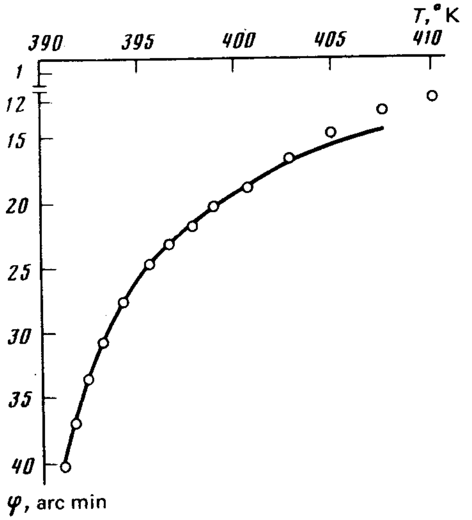

FIG. 1. Pretransitional rotation in the isotropic phase of the liquid crystal DOBAMBC ($\lambda = 633$ nm); the thickness of the specimen is $d = 1$ mm.

The measurements of PR are performed in the isotropic and smectic A phases of the liquid crystals n-decyloxybenzylidene-n'-amino-2-methylbutyl cinnamate (DOBAMBC) and 4/2-methylbutoxyphenyl ester of 4-decyloxybenzoic acid (MBOPEDOBA) at wavelengths $\lambda = 633$ nm and $\lambda = 422$ nm. In the A phase, the measurements were performed in the homeotropic orientation to eliminate birefringence. The temperature dependence of PR in the isotropic phase of DOBAMBC is shown in Fig. 1. The intrinsic molecular rotation, which is measured in a benzene solution, is equal to 0.75 arc minutes and has the same sign as PR in the isotropic phase.

In the cholesteric liquid crystal, the pretransitional effect is related to the appearance of regions with correlated positioning of molecules with chiral orientational ordering in the isotropic phase, reflecting the helical structure of the ordered cholesteric phase. In our case, the molecules are chiral, but the transition from the isotropic phase proceeds the A phase, where there is no helical twisting. Nevertheless, the fluctuation contribution to the rotation of the plane of polarization is determined, as before, by the orientational ordering of the anisotropic molecules over the correlation length ξ_I, which can be described (in first order with respect to the fluctuations) using expressions analogous to those in the Landau theory for the isotropic liquid—cholesteric phase transition. In this approximation, we ignore the effect of smectic fluctuations as a secondary effect with respect to fluctuations of the order parameters. Then PR is (ϕ_0 is the characteristic molecular rotation)

$$\phi = \phi_0 + B T \xi_I, \quad \xi_I = \xi_0 (T^* / T - T^*)^{\alpha}, \tag{1}$$

T^* is the temperature of absolute instability of the isotropic phase with respect to the transition to the cholesteric phase.

The values $T^* = 388.4$ °K, $B\xi_0(T^*)^\alpha = 2.3 \times 10^{-5} K^{\alpha-1}$·rad, and $\alpha = 0.54 \pm 0.06$

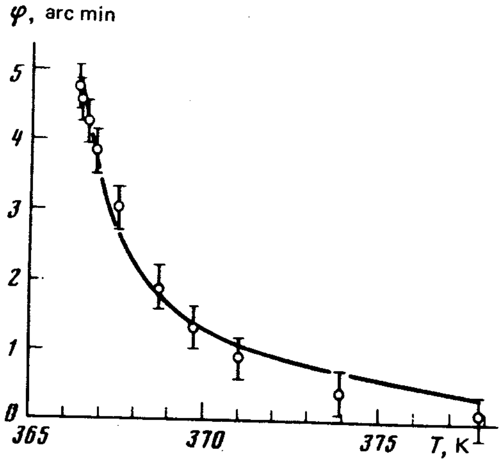

FIG. 2. Pretransitional rotation in the smectic phase of the liquid crystal DOBAMBC ($\lambda = 442$ nm). The curve corresponds to the critical exponent $\alpha = 0.56$; $d = 0.1$ mm.

were determined using the method of least squares applied to the experimental data in the interval $T - T_{IA} = 10°$ as a function of the transition temperature (the corresponding curve is shown in Fig. 1). The critical index is nearly equal to $\alpha = 0.5$, corresponding to the self-consistent-field theory,[7] which agrees with the approximation adopted above.

Figure 2 shows the temperature dependence of PR in the A phase of DOBAMBC. The sharp change in ϕ as the temperature of the transition to the C^* phases is approached ($T_{AC} = 365.8$ °K) indicates the pretransitional nature of the effect. The critical index $\alpha = 0.56 \pm 0.08$. The qualitative difference between the observed pretransitional effect and fluctuation rotation in isotropic phases of cholesteric and ferroelectric liquid crystals lies in the fact that the sign of PR in the A phase differs from the sign of PR in the isotropic phase. The anomalous sign of the pretransitional effect in the A phase is also observed in the liquid crystal MBOPEDOBA, in which the twisting of the helix in the C^* phase is oriented oppositely to the twisting of the helix in DOBAMBC.

To explain this behavior of PR in smectic A, we shall use the Landau expansion of the free-energy functional for the smectic A—smectic C^* transition:

$$(F - F_0)/T = (1/2) \int d\mathbf{r} \{ a\beta_a^2 + b_c(\partial_a \beta_\gamma)^2 + 2b_c q_c e_{\alpha\gamma\mu}\beta_\gamma \partial_\mu \beta_a + \lambda\beta_a^2\beta_\gamma^2 \}, \quad (2)$$

where $\vec{\beta} = (\beta_1, \beta_2, 0)$ is the order parameter of the phase transition, determining the position of the axis of orientational order of molecules relative to the normal $\mathbf{n} = (0,0,1)$ to the smectic planes.

As in the case of the isotropic phase, PR is determined by fluctuations of the anisotropy of the dielectric constant tensor of the medium and is related to the appearance, after averaging over fluctuations, of a term in the dielectric constant tensor $\epsilon_{\alpha\gamma}(\mathbf{k})$ that is invariant with respect to the substitution $\mathbf{k} \to -\mathbf{k}$[4,5]:

$$\epsilon_{\alpha\gamma}(\mathbf{k}) - \epsilon_{\alpha\gamma}(-\mathbf{k}) = \frac{k_0^2}{4\pi\epsilon_0} \int \frac{d\mathbf{q}}{(2\pi)^3} D_{\beta\delta}(\mathbf{q}+\mathbf{k})[G_{\alpha\beta}^{\gamma\delta}(\mathbf{q}) - G_{\alpha\beta}^{\gamma\delta}(-\mathbf{q})]. \quad (3)$$

In the A phase we have the fluctuations:

$$Q_{\alpha\gamma}(\mathbf{q}) = \Delta\epsilon[\beta_\alpha(\mathbf{q})n_\gamma + n_\alpha\beta_\gamma(\mathbf{q})], \quad (\beta_\alpha^2 \ll 1), \quad (4)$$

where $\Delta\epsilon$ is the anisotropy of the dielectric constant.

To simplify the calculations we shall ignore in the leading order with respect to $\Delta\epsilon$ the dielectric anisotropy of smectic A without fluctuations ($\epsilon_{\alpha\beta} = \epsilon_0\delta_{\alpha\beta}$). Then the contribution of fluctuations (3) differs in the isotropic and A phases only by the structure of the orientational fluctuations $Q_{\alpha\gamma}(\mathbf{q})$. We shall calculate expression (3) for smectic A, using (2) and (4) for propagation of light in the direction $\mathbf{k}\|\mathbf{n}$:

$$\epsilon_{\alpha\gamma}(\mathbf{k}) - \epsilon_{\alpha\gamma}(-\mathbf{k}) = -\frac{2(\Delta\epsilon)^2 k_0 q_c \xi_A}{15\pi\epsilon_0 b_c} L_{\alpha\gamma}, \quad (5)$$

where $\xi_A = (b_c/a)^{1/2}$ is the correlation length of orientational fluctuations in smectic A, and $L_{\alpha\gamma} = ie_{\alpha\gamma\mu}k_\mu/k$, $|\mathbf{k}| = k_0$.

In the isotropic phase, as noted above, analogously to the case of the isotropic liquid—cholesteric phase transition, we have[5]

$$\epsilon_{\alpha\gamma}(\mathbf{k}) - \epsilon_{\alpha\gamma}(-\mathbf{k}) = \frac{k_0 q_0 \xi_I}{6\pi\epsilon_0 b} L_{\alpha\gamma}, \quad (q_0/q_c > 0), \quad (6)$$

where ξ_I is the correlation length of orientational fluctuations in the isotropic phase, b, and q_0 are coefficients multiplying the gradient terms in the Landau–de Gennes expansion, and $|\mathbf{k}| = k_0$.

In this case, orientational fluctuations $Q_{\alpha\gamma}(\mathbf{q})$ have the following orientational structure[4]:

$$Q_{\alpha\gamma}(\mathbf{q}) = l_\alpha(\mathbf{q})\, q_\gamma + q_\alpha l_\gamma(\mathbf{q}), \quad (\mathbf{l} \perp \mathbf{q}). \quad (7)$$

In deriving expressions (5) and (6), we used the condition $\xi_{I,A} \ll \lambda, p_c$, where p_c is the pitch of the helix in smectic C^*, which is satisfied in our case ($p_c \approx 5\times10^4$ Å) for $T - T_{AC} > 0.5°$. In the leading, with respect to $\Delta\epsilon$, approximation, the coefficients multiplying $L_{\alpha\gamma}$ in (5) and (6) represent the difference between the squares of the refractive indices for right- and left-polarized waves. The rotation of the plane of polarization in smectic C^* with $\lambda < p_c$ (analogously to the case of the cholesteric with $\lambda < 2\pi/q_0$) has the same sign as in the isotropic phase. At the same time, the sign of the fluctuation contribution to smectic A differs from that of (5), consistent with the experimental results. Thus the anomaly observed by us is a result of the qualitatively different structure of the orientational fluctuations (7) and (4) in the isotropic and A phases of ferroelectric liquid crystals.

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