Temperature-induced inversion of rotation of the polarization plane of light in liquid crystals

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The temperature-induced inversion of rotation of the polarization plane of light in the isotropic phase of cholesteric and smectic *A* phase of ferroelectric liquid crystals is studied. The presence of inversion in the isotropic phase indicates that the mean-field approximation cannot be used to describe the intermediate blue phases.

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Rotation of the polarization plane of light (RPPL) in liquid crystals (LC) consists of structural, fluctuation, and intrinsic (molecular) contributions. In cholesteric and smectic C^* phases, which have a chiral structure, the structural contribution is always dominant. However, the same LC can have phases without chiral long-range order (for example, isotropic and smectic *A*), where the interest in RPPL is related to studying the contribution of chiral short-range order: fluctuation orientational modes.[1–5,7]

A new effect is described in this paper: temperature-induced inversion of the

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fluctuation part of RPPL in LC phases without chiral long-range order. The effect is due to transitions into the structural regime of fluctuations, which arises near the point of absolute phase instability. The presence of an inversion of the sign of RPPL in the isotropic phase indicates that the mean-field approximation cannot be used to describe the intermediate blue phases.

Let us examine the isotropic phase of a cholesteric LC. The fluctuation part of RPPL is determined by the eigenvalues of the dielectric-constant tensor of the medium $\epsilon_{\alpha\beta}(\mathbf{k}_0) = \epsilon_0\delta_{\alpha\beta} + \Delta\epsilon_{\alpha\beta}(\mathbf{k}_0)$ in the form[4]

$$\Delta\epsilon_{\alpha\gamma}(\mathbf{k}_0) = \frac{k_0^2}{8\pi\epsilon_0}\int\frac{d\mathbf{q}}{(2\pi)^3}D_{\beta\delta}(\mathbf{k}_0+\mathbf{q})[G^{\gamma\delta}_{\alpha\beta}(\mathbf{q}) - G^{\gamma\delta}_{\alpha\beta}(-\mathbf{q})], \tag{1}$$

where $D_{\beta\delta}(\mathbf{q})$ and $G^{\gamma\delta}_{\alpha\beta}(\mathbf{q})$ are the Green's function of the photon ($\Phi = 0$ gauge) and by the anisotropy of the local dielectric-constant tensor of the medium $Q_{\alpha\beta}(\mathbf{q}) = \epsilon_{\alpha\beta}(\mathbf{q}) - (1/3)\delta_{\alpha\beta}\epsilon_{\gamma\gamma}$. The tensor $Q_{\alpha\beta}(\mathbf{q})$ is the order parameter of the isotropic liquid-cholesteric phase transition, and its correlation function is determined from the Landau–de Gennes free-energy functional:

$$(F-F_0)/T = \sum_{s=0}^{4}\int\frac{d\mathbf{q}}{2(2\pi)^3}\tau_s(q)|\phi^s(\mathbf{q})|^2 + \int dV\,\{\mu Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \lambda Q^2_{\alpha\beta}Q^2_{\gamma\delta}\},$$

$$Q_{\alpha\beta}(\mathbf{q}) = \sum_{s=0}^{4}\phi^s(\mathbf{q})\,\sigma^s_{\alpha\beta}(\mathbf{q}),\quad \tau_0(q) = a + (b+2c/3)q^2, \tag{2}$$

$$\tau_{1,2}(q) = a + bq^2 \mp 2bq_0q,\quad \tau_{3,4}(q) = a + (b + c/2)q^2 \mp bq_0q;\quad a = a_0(T-T^*).$$

Far from the phase transition point, the correlation lengths of the five fluctuation modes (2) $\xi_s \sim (b/a)^{1/2} \ll k_0^{-1}$ and the fluctuation part of RPPL are determined by the contribution of the conical spiral modes ($s = 3, 4$): $\phi(T) - \phi_0 = \Delta\phi_3(T)$

$$\Delta\phi_3(T) = \frac{k_0^2 b^{1/2} q_0 \xi_3}{48\pi\epsilon_0^2(b + c/2)^{3/2}}, \tag{3}$$

where $b\xi_3^{-2} = a - b^2q_0^2/(4b+2c)$ and ϕ_0 is the intrinsic rotation. However, near the point of absolute phase instability, the large dip in the plane spiral mode ($s = 1$) at $\tau = (a - bq_0^2)/bq_0^2 \ll 1$ leads to a large $\xi_1 = q_0^{-1}\tau^{-1/2}$ and a considerable contribution of structural fluctuations of the $s = 1$ mode to the RPPL

$$\phi(T) = \phi_0 + \Delta\phi_3(T) - \frac{k_0^2 f(x,\tau)}{48\pi\epsilon_0^2 b\sqrt{\tau}},\quad x = q_0/2k_0 = \lambda_0/p_0, \tag{4}$$

where $f(x,0) = -(3/2)(x^2 + 4/3) + (3/4)(x + x^3)\ln|(1+x)/(1-x)|$. The contribution of the conical spiral mode, $\Delta\phi_3(T)$ in expression (4), retains the form (3) quite precisely up to $\tau = 0$, where $\xi_{3,4} \approx q_0^{-1}$. The form of the function $f(x,\tau)$ is shown in Fig. 1. Inversion of the sign of RPPL at the wavelength in the fluctuation mode $s = 1$ leads to a temperature-induced inversion of the sign $\phi - \phi_0$ with $\tau \approx f^2(x,\tau)$ and $\lambda_0/p_0 > x_i(\tau)$. This situation is possible only for short-pitch cholesteric LC ($p_0 = 4\pi/q_0 = (2\text{–}4)\times 10^3$ Å), where at the point of the first-order phase transition $\tau_c \ll 1$,[3,6,8] and the experimen-

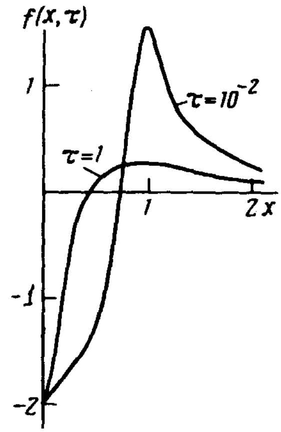

FIG. 1.

tally observed change in sign of the total $\phi(T)$ near the phase transition[7] can be interpreted as the appearance of structural fluctuations according to (4) (in Ref. 7, $p_0 \approx 2\times 10^3$ Å, $x \approx 2$). The interest that has recently appeared in short-pitch cholesteric LC is due to the presence of so-called "blue" phases in a narrow temperature range between the isotropic and short-pitch cholesteric phases. However, the Landau-De Gennes theory without fluctuations, which gives a phase diagram with a region of intermediate phases, disagrees appreciably with the experimental data.[8] This disagreement could be related to the inapplicability of the mean-field approximation. At the same time, the change in sign of $\phi(T)-\phi_0$ in the isotropic phase with decreasing temperature indicates that the mean-field approximation is no longer applicable. Indeed, from expression (4), $\phi(T)-\phi_0$ changes sign for $\tau \lesssim 0.1$, i.e., in the region of strongly developed structural fluctuations of the $s=1$ mode, leading to a replacement of the quantity τ in (4) by its renormalized value $V(\tau)$ in the form[6]

$$V(\tau) = \tau + Q r^{-1/2} - R r^{-1}, \tag{5}$$

where $R \ll Q \sim 0.1$ is the relative contribution of the interaction of fluctuations for $q_0 = 0$ [anharmonicity of third and fourth orders in (2)]. Renormalization of the expression coefficients in the free energy of intermediate "blue" phases in powers of the order parameter $Q_{\alpha\beta}(\mathbf{q}_0)$ analogously to (5), leads to an appreciable difference between the thermodynamic characteristics of intermediate phases and their mean field values.

$\phi(T)-\phi_0$ should also change sign in the smectic A phase if, by analogy with the preceding situation, the sign of $\phi(T)-\phi_0$ far from the transition ($\xi_A^{-2} \gg 2k_0^2$) is opposite to the sign of RPPL in the smectic C^* phase following a decrease in temperature. This condition is satisfied for $\lambda_0 < p_c$.[5] Equation (1) can be used to calculate RPPL in the smectic A phase if the anisotropy of the dielectric constant of the A phase of the ferroelectric LC $\Delta\epsilon$ is small and if the relation between $Q_{\alpha\beta}(\mathbf{q})$ and the order parameter $\beta_\alpha(\mathbf{q})$ of the phase transition $A \to C^*$: $Q_{\alpha\gamma} = \Delta\epsilon(\beta_\alpha n_\gamma + \beta_\gamma n_\alpha)$, is used where $\mathbf{n}$ is the normal to the smectic layers ($\vec{\beta} \perp \mathbf{n}$). The correlation function $\langle \beta_\alpha(\mathbf{q})\beta_\gamma(-\mathbf{q})\rangle$ is deter-

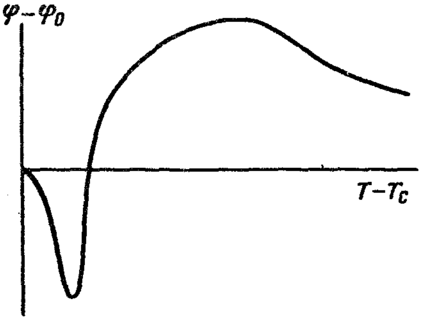

FIG. 2.

mined by a Landau expansion of the form

$$(F-F_0)/T=(1/2)\int dV\{a\beta_\alpha^2+b(\partial_\alpha\beta_\gamma)^2+2bq_c e_{\alpha\gamma\mu}\beta_\gamma\partial_\mu\beta_\alpha+\lambda\beta_\alpha^2\beta_\gamma^2\}. \qquad (6)$$

The dependence of $\phi(T)-\phi_0$ on $\xi_A^{-2}=a/b\propto T-T_c$ is shown in Fig. 2 for $q_c/k_0\simeq 0.3$ ($\mathbf{k}_0\|\mathbf{n}$).[5] As assumed, for $\lambda_0<p_c$, there is a temperature-induced inversion in the region $\xi_A^{-2}\sim 2q_c k_0$, and, in addition, the extrema of the function $\phi-\phi_0$ are of the same order of magnitude. The suppression of the quantity $\phi-\phi_0$ in the critical region $T\to T_c$ is related to the vanishing of RPPL on the conical spiral which accompanies the propagation of light along the spiral axis: RPPL in the C^* phase is determined by the structure of the plane spiral, which fluctuates weakly and which is not singular for $T\to T_c$. For standard values of the phenomenological constants in the free-energy functional (6) and $\lambda_0=3\cdot 10^3$ Å, we have the following estimate of the temperature interval with nonmonotonic behavior of $\phi(T)-\phi_0$: for $\xi_A^{-2}=2k_0^2$ we have $T-T_c\sim 1°$. The estimate gives only the order of magnitude, since in (6) we ignored the anisotropy of the gradient terms.

In a cholesteric with a spiral untwisted by the field, the fluctuations of the director $\mathbf{n}=\mathbf{n}_0+\vec{\beta}$ lead to an analogous behavior for $\phi(H)-\phi_0$, ($\mathbf{k}_0\|\mathbf{n}_0$) and, in addition, $\xi_H^{-2}=\chi H^2/K$, ($K=K_{ii}$).

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