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Fluctuation-Induced Kerr Effect Near the Smectic-A–Smectic-C_α* Phase Transition

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The anomalous increase of Kerr effect due to pretransitional fluctuations has been investigated in the SmA phase close to the SmA-SmC_α* transition point in antiferroelectric liquid crystals MHPOBC and MHPOCBC. We have developed a Landau theory taking into account the fluctuations and shown that there are two contributions to the Kerr effect. On the basis of theoretical results, the experimental results obtained in MHPOBC and MHPOCBC were discussed and a clear evidence of the fluctuation-induced Kerr effect was presented.

Keywords: fluctuation; Kerr effect; antiferroelectric liquid crystals; MHPOBC; MHPOCBC

INTRODUCTION

Unusually large pretransitional behavior due to orientational fluctuations has been observed in the SmA phase near the SmA-SmC_α* phase transition of chiral smectics by high-resolution heat capacity [1] and birefringence measurements [2]. Quite recently, on the other hand, we have shown that an anomalous increase in the Kerr effect due to the pretransitional fluctuations is also observable by means of electrooptic measurements near the SmA-SmC_α* phase transition point in

MHPOBC [3]. We designated this anomaly as the fluctuation-induced Kerr effect. In the previous experiments, however, the transition temperature was not clearly determined because the peak temperatures of the first- and second-order electrooptic responses are different. Furthermore, we gave a brief explanation for the fluctuation-induced Kerr effect, but it was not enough as will be described later.

In this paper we developed a Landau theory taking into account the effect caused by strongly fluctuating modes related to the SmA-SmC$_\alpha$* phase transition. Experimentally, we performed both the measurements of electrooptic response and birefringence simultaneously to determine the transition temperature. The pretransitional phenomena observed in Kerr effect are discussed on the bases of the theory.

THEORY

The transmitted light intensity I due to the application of an AC electric field to a homogeneous cell between crossed polarizers, where the z-axis is set to be along the layer normal and the x-axis along the electric field direction, can be expressed as the sum of the DC component, I_{DC}, and modulated components due to the electrooptic effect, ΔI, which are given as follows [4]:

$$I_{DC}/I_0 = \sin^2(2\alpha_0)\sin^2(\beta n_{a0}), \tag{1}$$

$$\Delta I/I_0 = 2\sin 4\alpha_0 \sin^2(\beta n_{a0})\Delta\alpha + 4\cos 4\alpha_0 \sin^2(\beta n_{a0})\Delta\alpha^2 + \beta \sin^2 2\alpha_0 \sin(2\beta n_{a0})\Delta n_a, \tag{2}$$

where $\beta = \pi d/\lambda$, I_0 is the incident light intensity, d the sample thickness, λ the light wavelength, α_0 and n_{a0} are, respectively, the angle between the optical axis and one of the polarizer directions and the anisotropy of refractive index in the absence of field, and $\Delta\alpha$ and Δn_a are electrically induced parts. Since $\Delta\alpha$ and Δn_a are proportional to the field and the square of it, respectively, as will be shown later, the first term in Eq. (2) can be detected in the first-order electrooptic response while the others in the second-order one. $\Delta\alpha$, Δn_a and n_{a0} are calculated from the dielectric tensor, whose components are [4],

$$\varepsilon_{zz} = \varepsilon_{\parallel} - \varepsilon_a\left(\left\langle \xi_x^2 \right\rangle + \left\langle \xi_y^2 \right\rangle\right),\ \varepsilon_{yy} = \varepsilon_{\perp} + \varepsilon_a\left\langle \xi_x^2 \right\rangle,\ \varepsilon_{yz} = \varepsilon_a\left\langle \xi_x \right\rangle \tag{3}$$

where $\varepsilon_\perp$ and $\varepsilon_{||}$ are the dielectric constants perpendicular and parallel to the director, respectively, and $\varepsilon_a = \varepsilon_{||} - \varepsilon_\perp$ is the dielectric anisotropy for the visible light. ξ_x and ξ_y are order parameters and <...> means the spatial or statistical average. The above averages are calculated as follows.

According to the resonant X-ray scattering measurements [5], the SmC$_\alpha$* phase was found to be incommensurate, short-period ferroelectric-like structure. Therefore, the SmC$_\alpha$* phase is considered to be formed by the soft mode condensation at a general point, $\boldsymbol{q}_c$, of the smectic Brillouin zone. Here, we express the spatially dependent order parameters $\xi_x(x,y,jd)$ and $\xi_y(x,y,jd)$, where j is the layer number and d the layer spacing, by the helicoidal coordinate [6] and the the Fourier transformation:

$$\begin{pmatrix}\xi_x(x,y,jd)\\ \xi_y(x,y,jd)\end{pmatrix}=\begin{pmatrix}\xi_{fx}\\ \xi_{fy}\end{pmatrix}+\begin{pmatrix}\cos q_c jd & -\sin q_c jd\\ \sin q_c jd & \cos q_c jd\end{pmatrix}\sum_q\begin{pmatrix}\xi_{1q}\\ \xi_{2q}\end{pmatrix}e^{i(q_x x+q_y y+q_z jd)}, \quad (4)$$

where q_c is the wave number related to the SmA-SmC$_\alpha$* phase transition and (ξ_{fx},ξ_{fy}) is the ferroelectric mode, (ξ_{1q},ξ_{2q}) the fluctuating mode around q_c. In the fluctuation-induced Kerr effect the nonlinear couplings between the modes with wave vectors around $\boldsymbol{q}_c=(0,0,q_c)$ and the ferroelectric mode at the Brillouin zone center play an essential role as well as the dielectric anisotropy. In the previous paper, we considered only the modes just at q_c, i.e., ξ_{10} and ξ_{20}, where it should be noted that the mode at q_c in the Cartesian coordinate corresponds to the one at q=0 in the present helicoidal coordinate. We can write the free energy density f under an electric field along the x-axis, E_x, in the SmA phase as

$$\begin{aligned} f =& \frac{a_f}{2}\xi_{fx}^2 + c\xi_{fx}E_x \\ &+ \sum_q\left\{\frac{a_q}{2}\left(|\xi_{1q}|^2+|\xi_{2q}|^2\right)+b\left(|\xi_{1q}|^2+|\xi_{2q}|^2\right)\xi_{fx}^2-\frac{\varepsilon_a'}{4}\left(|\xi_{1q}|^2+|\xi_{2q}|^2\right)E_x^2\right\}, \end{aligned} \quad (5)$$

with

$$a_q = a_0 + \kappa_\perp(q_x^2+q_y^2)+\kappa_{||}q_z^2 , \quad (6)$$

where ξ_{fx} is spatially homogeneous ferroelectric mode, ε_a' the dielectric anisotropy at low frequencies, a_0 is assumed to be linearly dependent on the temperature and become zero at the SmA-SmC$_\alpha$* transition point, and the above summation is made over $\boldsymbol{q}$ around $\boldsymbol{q}_c$ since only large fluctuations there contribute to the fluctuation-induced Kerr effect.

From Eq. (4) and (5), by adopting the Gaussian approximation, we can calculate $\langle\xi_y^2\rangle$ in Eq. (3) [7] :

$$\left\langle \xi_y^2 \right\rangle = \left\langle \xi_y^2 \right\rangle_0 + \left\langle \xi_y^2 \right\rangle_E \tag{7}$$

with

$$\begin{aligned} \left\langle \xi_y^2 \right\rangle_0 &\approx \frac{k_B T}{4} I_1 , \\ \left\langle \xi_y^2 \right\rangle_E &\approx -\frac{k_B T}{4} I_2 \left(bc^2 \chi_{fs}^{(1)2} - \frac{\varepsilon_a'}{4} \right) E_x^2 , \end{aligned} \tag{8}$$

where $\langle\xi_y^2\rangle$ has been devided into the field-independent part $\langle\xi_y^2\rangle_0$ and the field-dependent part $\langle\xi_y^2\rangle_E$,and $I_1 \propto 1 - A a_0^{1/2}$ (A is a positive constant), $I_2 \propto a_0^{-1/2}$ and $\chi_{fs}^{(1)}$ is the linear susceptibility of the ferroelectric mode, given as $\left(a_f + k_B T b I_1\right)^{-1}$. In addition, Eq. (4) yields $\langle\xi_x^2\rangle = \langle\xi_y^2\rangle + \xi_{fx}^2$ and $\langle\xi_x\rangle = \xi_{fx} = \chi_{fs}^{(1)} c E_x$. In terms of these quantities, $\Delta\alpha$ and Δn_a in Eq. (1) are given as

$$\Delta\alpha \approx \xi_{fx} , \tag{9}$$

$$\Delta n_a \approx -\frac{\varepsilon_a}{2}\left(\frac{2}{\sqrt{\varepsilon_\parallel}} + \frac{1}{\sqrt{\varepsilon_\perp}} \right) \left\langle \xi_y^2 \right\rangle_E - \frac{3\varepsilon_a}{2}\left(\frac{1}{\sqrt{\varepsilon_\parallel}} - \frac{1}{\sqrt{\varepsilon_\perp}} \right) \left\langle \xi_y^2 \right\rangle_0 \xi_{fx}^2 . \tag{10}$$

By using the above equations we can analyze the results obtained in the electrooptic measurements. At the end of this section, we would like to emphasize that the above two contributions to Δn_a originate in the fluctuations because they vanish at T=0.

EXPERIMENTAL

The samples used were MHPOBC and MHPOCBC compounds. The phase sequences are SmA-SmC_α*-SmC*-SmC_γ*-SmC_A* and SmA-SmC_α*-SmC_A*, respectively. We used homogeneous cell with thickness 25 μm for MHPOBC and 12 μm for MHPOCBC. The cell was mounted in a hot stage, then set on the stage of a polarizing microscope and illuminated by an Ar-ion laser at 488 nm. A sinusoidal electric field was applied to the cell. In electrooptic measurement, the transmitted light was detected and converted into a voltage signal by a photodiode (Hamamatsu Photonics, C6386) attached to the microscope. The amplified signal decomposed into the DC and AC components. The DC component was measured using a digital multimeter, and the AC component was measured simultaneously with a vector signal analyzer (HP89410) to obtain the amplitudes and the phases of the first-order and the second-order responses. The transition point from SmA to SmC_α* phase was determined from the DC signal, which reflects the change of birefringence through Eq. (1).

RESULTS AND DISCUSSIONS

We show in Figure 1 the temperature dependencies of the amplitudes of the first-order electrooptic response $|\Delta I_{1f}|$, and that of the second-order one $|\Delta I_{2f}|$ measured at 1 kHz in MHPOBC and MHPOCBC. We observed at α_0=22.5°, therefore the first-order response originates in the optical axis change $\Delta\alpha$ and the second-order one only in the birefringence change Δn_a, as is seen from Eq. (2). In both compounds the DC component decreases gradually with decreasing temperature in the SmA phase and at the transition point the slope changes and then it decreases more steeply in the SmC_α* phase. This behavior comes from the change of Δn_{a0} in Eq. (1) and has been already observed by means of precise birefringence measurements in the transitions from SmA to tilted phases [2]. In Figure 1 the dotted line indicates the transition point from SmA to SmC_α* phase determined from the DC component.

In the first-order response, we observed the gradual increase in intensity with decreasing temperature in the SmA phase. From Eqs. (2) and (9), the first-order response is proportional to the ferroelectric mode, therefore this increase indicate the softening of ferroelectric mode. Actually, the partial softening of the ferroelectric mode in the

temperature dependence of the relaxation frequency has been experimentally found [8]. In the SmC_α^*, on the other hand, the intensity becomes to decrease. It should be noted that the linear response takes a maximum at the transition temperature determined by the DC component.

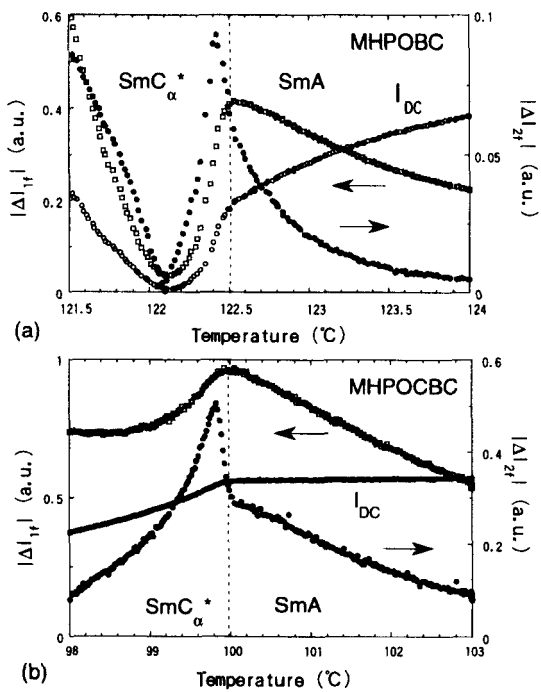

FIGURE 1 Temperature dependencies of the amplitude of the first-order response, $|\Delta I_{1f}|$, and that of the second-order one, $|\Delta I_{2f}|$, obtained at α_0=22.5° on cooling process in **a)** MHPOBC, and **b)** MHPOCBC.

In the second-order electrooptic response, the temperature dependence of the intensity is more complicated. In both compounds, the intensity increases in SmA, but it still increases in SmC_α^* and takes a maximum inside. The steep increase in SmC_α^* may be due to the appearance of spontaneous value in the order parameter, as was shown in our previous paper [3]. The slope change at the transition point is remarkable in MHPOCBC, but a slight change can be seen also in

MHPOBC. Furthermore, there is a difference in the intensity increase between MHPOBC and MHPOCBC. According to Eq. (10), there are two different origins in the increase of the second-order intensity, and the singularities of the first and the second terms with respect to the temperature are, respectively, $a_0^{1/2}$ and $a_0^{-1/2}$, where the former changes more slowly than the latter. The above experimental results and this theoretical result may indicate that in our experiment the latter is dominant in MHPOBC, while in MHPOCBC the former.

Lastly, we show another experimental result, which were obtained at $\alpha_0 = 18.3°$ in a 2 μm cell. As shown in Figure 2, a large difference is seen in the results between 22.5° and 18.3°. Especially, at 18.3° the intensity vanishes near the transition point. Such a behavior was not observed in 25 μm cell. This difference is brought about by the $\Delta\alpha^2$ term in Eq. (2); at 18.3° it contributes to Δn_a. The difference is a clear evidence that the fluctuation-induced Kerr effect, i.e., Δn_a should exist because if $\Delta n_a = 0$ the temperature dependence of the second-order response is independent of α_0, resulting in no difference.

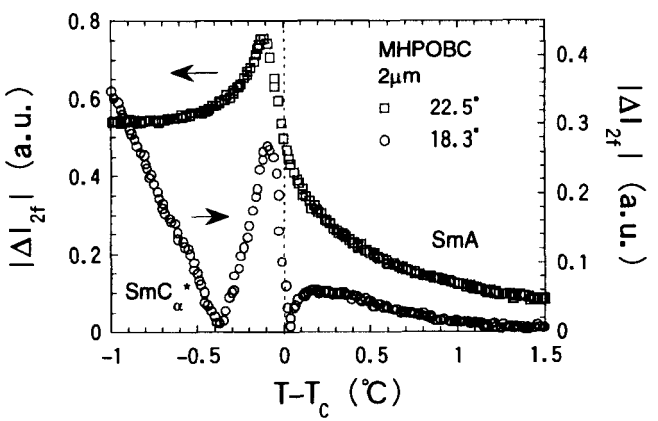

FIGURE 2 Temperature dependencies of the second-order response of MHPOBC in 2 μm measured at α_0=22.5° and 18.3° on cooling process.

In conclusion, we have theoretically shown that there are two different origins in the fluctuation-induced Kerr effect, which have different temperature dependencies. It was experimentally found that

MHPOBC and MHPOCBC are different in the temperature dependence of the second-order response, which is ascribable to the difference in the contribution of the above two origins. Furthermore, it was clearly shown that the field-induced Kerr effect should exist by measuring at different α_0 .

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