Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: H. Murai, V. Bourny, A. Fajar & H. Orihara (2001): NONLINEAR DIELECTRIC MEASUREMENTS IN THE SMECTIC-A-SMECTIC-C_α* PHASE TRANSITION, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 645-651

To link to this article: http://dx.doi.org/10.1080/10587250108024005

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 645-651
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Nonlinear Dielectric Measurements in the Smectic-A-Smectic-C_α* Phase Transition

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We have performed precise measurements of the third-order dielectric constant in an antiferroelectric crystal MHPOCBC. In the vicinity of the SmA- SmC_α* phase transition point an anomalous increase of it was observed. We have developed a Landau theory taking into account the pretransitional fluctuations and shown that the fluctuation can contribute to the third-order response. The anomalous behavior near the transition point was discussed on the basis of the theoretical results.

Keywords: fluctuation; antiferroelectric liquid crystal; nonlinear dielectric constant; MHPOCBC

INTRODUCTION

Nonlinear dielectric spectroscopy has been made so far in ferroelectric and antiferroelectric liquid crystals and has been shown to be quite useful in studying the phase transitions [1-6]. In MHPOBC, we observed that the third-order dielectric constant drastically increases at the transition point from SmA to SmC_α*, while the linear dielectric constant is continuous with a small change of the slope in its temperature dependence [7]. The increase was explained by the Landau theory, which predicts a discontinuous jump in the third-order dielectric

permittivity at the transition point. Recently, on the other hand, unusually large pretransitional fluctuations have been reported in the SmA phase near the transition point by heat capacity [8], birefringence [9] and electrooptic effect [10]. This result suggests that the pretransitional effect may be observed also by the nonlinear dielectric measurement.

In this paper we calculated the third-order dielectric constant on the basis of a Landau theory, taking into account the strongly fluctuating modes. Experimentally, we made precise measurements of the linear and third-order dielectric constant near the transition point from SmA to SmC_α* with a distorsionmeter. The experimentally observed steep, but continuous increase in the third-order dielectric constant near the transition point was discussed on the basis of the theoretical results.

THEORY

Here, we present a Landau theory to describe the nonlinear dielectric response. According to the resonant X-ray scattering measurement results [11], the SmC_α* phase was found to be incommensurate, short-period ferroelectric-like structure. Therefore, the SmC_α* phase is considered to be formed by the soft mode condensation at a general point, $\boldsymbol{q}_c(0,0,q_c)$, of the smectic Brillouin zone. Therefore, the spatially dependent order parameter may be expressed as

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

where j is the layer number, d the layer spacing, (ξ_{fx},ξ_{fy}) the ferroelectric mode, $(\xi_{1\boldsymbol{q}},\xi_{2\boldsymbol{q}})$ the fluctuating mode, and the above summation is made over $\boldsymbol{q}$ around $\boldsymbol{q}_c$ since only large fluctuations there contribute to the third-order nonlinear response. In terms of these modes, the free energy density f may be expanded:

$$f=\frac{a_f}{2}\xi_{fx}^2+\frac{b_f}{4}\xi_{fx}^4+\chi_f\lambda_f\xi_{fx}E_x + \sum_{\boldsymbol{q}}\left\{\frac{a_{\boldsymbol{q}}}{2}\left(\left|\xi_{1\boldsymbol{q}}\right|^2+\left|\xi_{2\boldsymbol{q}}\right|^2\right)+b\left(\left|\xi_{1\boldsymbol{q}}\right|^2+\left|\xi_{2\boldsymbol{q}}\right|^2\right)\xi_{fx}^2-\frac{\varepsilon_a'}{4}\left(\left|\xi_{1\boldsymbol{q}}\right|^2+\left|\xi_{2\boldsymbol{q}}\right|^2\right)E_x^2\right\}, \quad (2)$$

with

$$a_q = a_0 + \kappa_\perp\left(q_x^2 + q_y^2\right) + \kappa_\parallel q_z^2, \tag{3}$$

where $\kappa_\perp$ and $\kappa_\parallel$ are the elastic constants and we have assumed that the electric field is applied along x-axis and a_0 is linearly dependent on temperature and becomes zero at the transition point, and ε_a' is the dielectric anisotropy at low frequencies, χ_f the dielectric susceptibility without the coupling between the polarization and ξ_{fx}, and λ_f the piezoelectric constant, by which the polarization due to the ferroelectric mode, $P_x^{(f)}$, is given as [6]

$$P_x^{(f)} = -\chi_f \lambda_f \xi_{fx} + \chi_f E_x. \tag{4}$$

From Eq. (2), we can calculate the free energy density only for ξ_{fx} within the Gaussian approximation:

$$\begin{aligned}\bar{f}(\xi_{fx}) &= -k_B T \log \int \mathrm{e}^{-Vf/k_B T} \prod_q d\xi_{1q}' \, d\xi_{1q}'' \, d\xi_{2q}' \, d\xi_{2q}'' \\ &= \bar{f}_0 + \frac{1}{2}\left(a_f + k_B T b I_1\right)\xi_{fx}^2 + \frac{1}{4}\left(b_f - k_B T b^2 I_2\right)\xi_{fx}^4 \\ &\quad + \frac{1}{8} k_B T b \varepsilon_a' I_2 \xi_{fx}^2 E_x^2 + \chi_f \lambda_f \xi_{fx} E_x,\end{aligned} \tag{5}$$

where V is the sample volume and it can be shown that $I_1 \propto 1 - ca^{1/2}$ (c is a positive constant) and $I_2 \propto a^{-1/2}$. From the equilibrium condition, $\partial \bar{f} / \partial \xi_{fx} = 0$, we get

$$\begin{aligned}P_x^{(f)} &= \left((\chi_f \lambda_f)^2 \chi_{fs}^{(1)} + \chi_f\right) E_x - b_f (\chi_f \lambda_f)^4 \chi_{fs}^{(1)4} E_x^3 \\ &\quad + k_B T b I_2 (\chi_f \lambda_f)^2 \chi_{fs}^{(1)2}\left(b(\chi_f \lambda_f)^2 \chi_{fs}^{(1)2} - \frac{\varepsilon_a'}{4}\right) E_x^3.\end{aligned} \tag{6}$$

where $\chi_{fs}^{(1)}$ is the susceptibility of the ferroelectric mode, given as $\left(a_f + k_B T b I_1\right)^{-1}$.

In addition to the above polarization due to the ferroelectric mode, we have to take into account the field-induced dipoles of molecules [6].

The dielectric constant along the x-axis is $\varepsilon_{xx}' = \varepsilon_{\perp}' + \varepsilon_a' \langle \xi_y(x,y,jd)^2 \rangle$, where $\varepsilon_{\perp}'$ is the dielectric constant perpendicular to molecules. $\langle \xi_y(x,y,jd)^2 \rangle$ is easily obtaind from Eqs. (1) and (2), and $\varepsilon_{xx}' E_x$ yields the polarization due to the dielectric anisotropy

$$P_x^{(m)} = \left(\varepsilon_{\perp}' + \frac{k_B T}{4} I_1 \varepsilon_a' \right) E_x - k_B T I_2 \frac{\varepsilon_a'}{4} \left(b(\chi_f \lambda_f)^2 \chi_{fs}^{(1)2} - \frac{\varepsilon_a'}{4} \right) E_x^3. \quad (7)$$

Thus, we have the total polarization, $P_x = P_x^{(f)} + P_x^{(m)}$, up to the third order:

$$\begin{aligned} P_x = & \left(\chi_f + \varepsilon_{\perp}' + \chi_{fs}^{(1)} (\chi_f \lambda_f)^2 + \frac{k_B T}{4} \varepsilon_a' I_1 \right) E_x \\ & + k_B T I_2 \left(b(\chi_f \lambda_f)^2 \chi_{fs}^{(1)2} - \frac{1}{4} \varepsilon_a' \right)^2 E_x^3 - b_f (\chi_f \lambda_f)^4 \chi_{fs}^{(1)4} E_x^3. \end{aligned} \quad (8)$$

The last term in r.h.s. comes from the fourth-order term with respect to ξ_{fx} in the free energy (2), which is well known in the nonlinear dielectric response [1]. On the other hand, the second term has been derived for the first time, which originates in the fluctuations of the soft mode. It should be noted that this term is always positive and proportional to I_2, i.e., $a_0^{-1/2}$. Namely, the third-order response should diverge as $a_0^{-1/2}$ at the transition point in the Gaussian approximation.

EXPERIMENTAL

The sample used was MHPOCBC. The phase sequence is SmA-SmC$_\alpha$*-SmC$_A$. The sample was introduced into a cell with ITO electrodes and polyimide layers (EHC) in the isotropic phase and cooled down slowly to the SmA phase. The thickness was about 25 μm and the area of electrodes was 4×4 mm^2.

We used a distortion meter (HDM-1, Nippon Audio), composed of an oscillator and a high-pass filter, to make precise measurements. The output signal was analysed with a vector signal analizer (HP89410). In general, when a cosine electric field with an amplitude of E_0 and a frequency of ω is applied to the sample, the electric displacement can be expressed in terms of nonlinear dielectric constants [12]:

$$D(t) = 2\left\{\varepsilon_1(\omega)\left(\frac{E_0}{2}\right) + 3\varepsilon_3(\omega,\omega,-\omega)\left(\frac{E_0}{2}\right)^3 + \cdots\right\}e^{i\omega t}$$
$$+ 2\left\{\varepsilon_3(\omega,\omega,\omega)\left(\frac{E_0}{2}\right)^3 + 5\varepsilon_5(\omega,\omega,\omega,\omega,-\omega)\left(\frac{E_0}{2}\right)^5 + \cdots\right\}e^{i3\omega t} \quad (9)$$
$$+ \cdots + c.c.,$$

where we have assumed that the sample is nonpolar, i.e., the eventh-order terms disappear. In the present experiments we measured the linear dielectric constant $\varepsilon_1(\omega)$ and the third-order dielectric constant $\varepsilon_3(\omega,\omega,\omega)$.

RESULTS AND DISCUSSION

In the measurement of nonlinear dielectric constants it is necessary to check that the nth-order response should be proportional to E_0^n. If not so, the higher-order contributions are included and the correct value cannot be obtained. In Figure 1 we show the dependence of $|D_3|$ on E_0^3 at 102.6°C just below the SmA-SmC$_\alpha$* phase transition point, where D_3 is the third-order harmonics of D, i.e., the coefficient of $e^{i3\omega t}$. We applied 0.215 V/μm in the measurement of temperature dependence.

In Figure 2 are shown the temperature dependencies of the real parts of the linear and third-order dielectric constants measured at 1 kHz. The linear dielectric constant increases gradually in the SmA phase as the transition point is approached and takes a maximum, and then it decreases in the SmC$_\alpha$* phase. In this experiment we thought that the peak temperature of the linear dielectric constant corresponds to the transition temperature, which was confirmed by the simultaneous measurements of the dielectric constant and the birefringence. The increase in the linear dielectric constant in SmA is due to the partial softning of the ferroelectric mode.

In the third-order dielectric response, the temperature dependence is more complicated. At high temperatures far from the transition point in the SmA phase the real part is negative and increases with decreasing temperature and then it becomes zero above the transition point to change the sign positive. In the vicinity of the transition point it increases most steeply and takes a sharp peak below the transition

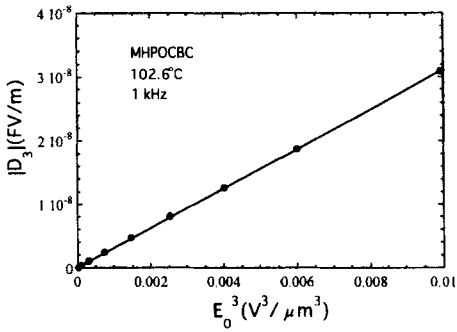

Figure 1. Plot of $|D_3|$ vs. E_0^3.

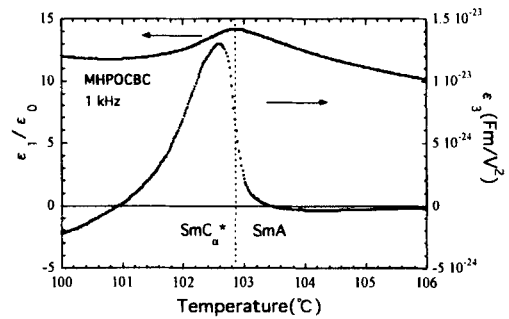

Figure 2. Temperature dependencies of $\varepsilon_1'(\omega)$ and $\varepsilon_3'(\omega,\omega,\omega)$.

temperature in SmC$_\alpha$* phase. The above temperature dependence of the third-order dielectric response in SmA may be explained by our theory. In Eq. (8) there are two contributions to the third-order dielectric constant; one comes from the pretransitional fluctuations and the other from the fourth-order term with respect to ξ_{fx} in Eq. (2). The former is positive and proportional to $a_0^{-1/2}$ and so it takes positive large values near the transition point, while the latter is negative because the transition is of second order, i.e., $b_f > 0$. Therefore, at temperatures far from the transition point the latter is dominant and so ε_3' is negative, while near the transition temperature the former becomes dominant and ε_3' becomes positive and increases steeply. In the SmC$_\alpha$* phase, on the other hand, the third-order dielectric constant still increases and takes a

maximum to decrease. The further increase in SmC_α^* may be due to the appearance of spontaneous value in the order parameter, as was shown in our previous paper [7].

In conclusion, we have theoretically shown that there are two different origins in the third-order dielectric response; the pretransitional fluctuations and the fourth-order term in the free energy. In the experiment, we have successfully observed the fluctuation-induced third-order response and the competition between these origins in the temperature dependence of ε_3'.

ACKNOWLEDGEMENTS

We would like to thank Showa Shell Sekiyu Co. Ltd. for supplying MHPOCBC. One of the authors (V. B.) thanks the Japan Society of Promotion of Science. This study was partly supported by a Grant-in Aid from the Ministry of Education, Science, Sports and Culture (No. 11099724 and 12650882).

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