Observation of the soft-mode condensation in the Sm-A−Sm-C_α^* phase transition by nonlinear dielectric spectroscopy

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We have theoretically and experimentally studied the nonlinear dielectric response under large orientational fluctuations near the Sm-A−Sm-C_α^* phase transition point in a chiral smectic liquid crystal. The third-order nonlinear dielectric response due to the fluctuations was observed in the vicinity of the transition point. By using it, we have successfully observed the soft-mode condensation inducing the Sm-A−Sm-C_α^* phase transition.

Chiral smectic liquid crystals have various phases due to their XY-like nature [1]. In the Sm-A phase with the highest symmetry the molecules are perpendicular to smectic layers, while in lower temperature phases the molecules tilt but the tilting directions can be different in different layers to construct different phases. For example, in the Sm-C^* phase all the molecules tilt in the same direction and in the Sm-C_A^* phase the molecules in the neighboring layers tilt in the opposite directions, though these structures are slightly twisted along the layer normal by the chirality. The phase transitions from the Sm-A phase to these tilted smectic phases are considered to be brought about by the condensation of overdamped-collective-orientational soft modes. Actually, for the Sm-A−Sm-C^* phase transition the soft mode has been observed clearly in both Sm-A and Sm-C^* phases by means of dielectric spectroscopy [2] and photon correlation spectroscopy [3]. Among tilted phases, the Sm-C_α^* phase has been attracting much attention, which has an incommensurate, short-period ferroelectriclike structure [4]. For the Sm-A−Sm-C_α^* phase transition, we have observed the soft mode (the amplitude mode) only in the Sm-C_α^* phase by means of the second-order electro-optic measurement [5]. This result indicates that the soft mode must exist also in the Sm-A phase, though it could not be observed because the soft mode is a helically tilted mode with a short pitch, i.e., it exists at a general point of the smectic Brillouin zone in the Sm-A phase. Therefore, it was not observed in the Sm-A phase, but in the Sm-C_α^* phase because the soft mode becomes a zone-center mode by the symmetry breaking. In the Sm-C_α^* phase, when we apply an electric field parallel to smectic layers two modes can be excited; the ferroelectric mode (the tilting toward the direction perpendicular to the field) due to the electroclinic effect and the amplitude mode (the change of tilt angle), which bring about the rotation of indicatrix and the change of birefringence, respectively, to be observed by the electro-optic measurement.

In the Sm-A phase, on the other hand, unusually large pretransitional fluctuations have been observed near the transition point by heat capacity [6], birefringence [7], and layer compression modulus measurements [8]. These large fluctuations enable us to observe the soft mode in the Sm-A phase, as explained below. We have observed them also by electro-

optic [9] and third-order nonlinear dielectric measurements [10]. Their responses remarkably increased in intensity as the transition point was approached in the Sm-A phase. Theoretically, the second-order electro-optic and third-order nonlinear dielectric responses are both proportional to the susceptibility of the amplitude mode [11]. The anomalous increase of intensity originates in the development of fluctuating large Sm-C_α^* domains near the transition point. These facts indicates that even in the Sm-A phase we may observe the frequency dispersion in the third-order nonlinear dielectric response induced by the fluctuations to obtain the relaxation frequency of the soft-mode, the temperature dependence of which will give the direct evidence of the soft-mode condensation in the Sm-A−Sm-C_α^* phase transition. In this paper, we derive the formula describing the fluctuation-induced third-order nonlinear dielectric response under an ac field from the Langevin equation and then analyze experimental results.

We can express the spatially dependent order parameters $(\xi_x(x,y,jd),\xi_y(x,y,jd))$ [12], where j is the layer number and d the layer spacing, by the helicoidal coordinate [1] and the Fourier transformation

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

where (ξ_{fx},ξ_{fy}) and $(\xi_{1\mathbf{q}},\xi_{2\mathbf{q}})$ are, respectively, the ferroelectric mode (the tilting toward the direction perpendicular to the applied field) and the helically tilted mode in the soft-mode branch, and q_c is the wave number related to the Sm-A−Sm-C_α^* phase transition. It should be noted that the mode with $\mathbf{q}=0$, (ξ_{10},ξ_{20}), represents the soft mode (the helically tilted mode with q_c in the laboratory frame) inducing the Sm-A−Sm-C_α^* phase transition, but the modes with $\mathbf{q}\neq 0$ are also necessary for our purpose. In the fluctuation-induced nonlinear dielectric response, the nonlinear coupling between the ferroelectric mode (ξ_{fx},ξ_{fy}) and the modes $(\xi_{1\mathbf{q}},\xi_{2\mathbf{q}})$ with wave vectors around $\mathbf{q}=0$ plays an essential role as well as the dielectric anisotropy. Taking into account

these, we can write the free energy F divided by the sample volume V under an electric field along the x axis, E_x, in the Sm-A phase as

$$F/V = \sum_{\mathbf{q}} \left\{ \frac{a_{\mathbf{q}}}{2}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2) + \frac{\eta}{2}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2)\xi_{fx}^2 \right.$$
$$\left. - \frac{\epsilon_a}{4}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2)E_x^2 \right\} + \frac{a_f'}{2}\xi_{fx}^2 + \frac{b_f}{4}\xi_{fx}^4$$
$$- \lambda_f \xi_{fx} P_{fx} + \frac{1}{2\chi_f}P_{fx}^2 - P_{fx}E_x, \tag{2}$$

where P_{fx} is the macroscopic polarization along x axis, ϵ_a the dielectric anisotropy, and we assume that the dispersion is parabolic in the soft-mode branch, $a_{\mathbf{q}} = a_0 + \kappa_{\perp}(q_x^2 + q_y^2) + \kappa_{\parallel}q_z^2$, and a_0 is linearly dependent on the temperature and becomes zero at the Sm-A–Sm-C_{α}^* transition point. The equilibrium condition, $\partial F/\partial P_{fx} = 0$, yields

$$P_{fx} = \chi_f \lambda_f \xi_{fx} + \chi_f E_x, \tag{3}$$

and substituting this equation into Eq. (2) we get

$$F/V = \sum_{\mathbf{q}} \left\{ \frac{a_{\mathbf{q}}}{2}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2) + \frac{\eta}{2}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2)\xi_{fx}^2 \right.$$
$$\left. - \frac{\epsilon_a}{4}(|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2)E_x^2 \right\} + \frac{a_f}{2}\xi_{fx}^2 + \frac{b_f}{4}\xi_{fx}^4$$
$$- \chi_f \lambda_f \xi_{fx} E_x - \frac{1}{2}\chi_f E_x^2, \tag{4}$$

where $a_f = a_f' - 1/2\chi_f \lambda_f^2$. With the free energy and the dissipation function D,

$$D/V = \frac{\gamma_s}{2} \sum_{\mathbf{q}} (|\dot{\xi}_{1\mathbf{q}}|^2 + |\dot{\xi}_{2\mathbf{q}}|^2) + \frac{\gamma_f}{2}\dot{\xi}_{fx}^2, \tag{5}$$

the dynamics can be expressed as

$$\frac{\partial D}{\partial \dot{\xi}_{fx}} = -\frac{\partial F}{\partial \xi_{fx}}, \frac{\partial D}{\partial \dot{\xi}_{n\mathbf{q}}^*} = -\frac{\partial F}{\partial \xi_{n\mathbf{q}}^*} + R_{n\mathbf{q}}(t) \quad (n = 1,2), \tag{6}$$

where $R_{n\mathbf{q}}(t)$ is the random force satisfying the following relation:

$$\langle R_{n\mathbf{q}}(t)^* R_{n'\mathbf{q}'}(t') \rangle = 2V\gamma_s k_B T \delta_{nn'} \delta_{\mathbf{qq}'} \delta(t-t'). \tag{7}$$

Solving the above set of equations under an ac electric field, $E_x = E_0 \cos \omega t$, by the pertubation method with respect to E_0, we get

$$\xi_{fx} = \text{Re}[\chi_f \lambda_f \chi_f(\omega)e^{i\omega t}]E_0 - \frac{1}{4}\text{Re}\left[\left\{\frac{a_0^{-1/2}\eta k_B T}{4\pi\sqrt{\kappa_{\parallel}}\kappa_{\perp}} \right.\right.$$
$$\times \chi_f \lambda_f \chi_f(\omega)\chi_f(3\omega)c(\omega)g(i\omega\tau_s)$$
$$\left.\left. + b_f \chi_f^3 \lambda_f^3 \chi_f(3\omega)\chi_f^3(\omega) \right\} e^{i3\omega t}\right]E_0^3 + \cdots \tag{8}$$

with

$$g(Z) = 2(\sqrt{1+Z}-1)/Z,$$
$$\chi_f(\omega) = \left(a_f + \eta \sum_{\mathbf{q}} \langle |\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2 \rangle_{E_x=0} + i\omega\gamma_f \right)^{-1},$$
$$c(\omega) = \frac{1}{2}\epsilon_a - \eta\chi_f^2 \lambda_f^2 \chi_f^2(\omega), \tag{9}$$

where $\tau_s(=\gamma_s/a_0)$ is the relaxation time of the soft mode at $\mathbf{q}=0$ and the thermal average $\sum_{\mathbf{q}}\langle|\xi_{1\mathbf{q}}|^2 + |\xi_{2\mathbf{q}}|^2\rangle_{E_x=0}$ in the absence of field is calculated as $2k_B T/V\sum_{\mathbf{q}}a_{\mathbf{q}}^{-1} \simeq k_B TA(1-Ba_0^{1/2})$ (A and B are constants). Note that $\chi_f(\omega)$ is the susceptibility of the ferroelectric mode and $g(i\omega\tau_s)$ with a broad frequency dispersion comes from the modes in the soft-mode branch. The macroscopic polarization P_{fx} due to ξ_{fx} is easily obtained from Eq. (3). In addition to P_{fx}, we have to calculate the field-induced polarization due to the dielectric anisotropy. The corresponding dielectric displacement $D_x^{(diel)}$ is expressed as $\epsilon_{xx}E_x \simeq (\epsilon_{\perp} + \epsilon_a \langle \xi_y(x,y,jd)^2 \rangle)E_x$ [11]. The thermal average can be calculated from the equations of motion and we get

$$D_x^{(diel)} = \text{Re}[\{\epsilon_{\perp} + \epsilon_a k_B TA(1-Ba_0^{1/2})\}e^{i\omega t}]E_0$$
$$+ \frac{1}{4}\text{Re}\left[\frac{a_0^{-1/2}\eta k_B T}{8\pi\sqrt{\kappa_{\parallel}}\kappa_{\perp}}\epsilon_a c(\omega)g(i\omega\tau_s)e^{i3\omega t}\right]E_0^3 + \cdots. \tag{10}$$

The total dielectric displacement, $D_x = P_{fx} + D_x^{(diel)}$, should be expressed as

$$D_x = \text{Re}[\epsilon_1(\omega)e^{i\omega t}E_0] + \text{Re}[\epsilon_3(\omega)e^{i3\omega t}E_0^3] + \cdots, \tag{11}$$

where $\epsilon_1(\omega)$ and $\epsilon_3(\omega)$ are, respectively, the linear and third-order dielectric constants. Thus, we finally have

$$\epsilon_1(\omega) = \epsilon_{\perp} + \chi_f + \epsilon_a k_B TA(1-Ba_0^{1/2}) + \chi_f^2 \chi_f^2 \chi_f(\omega), \tag{12}$$

$$\epsilon_3(\omega) = \frac{a_0^{-1/2}k_B T}{4\pi\sqrt{\kappa_{\parallel}}\kappa_{\perp}}[\frac{1}{2}\epsilon_a - \eta\chi_f^2 \lambda_f^2 \chi_f^2(\omega)]$$
$$\times [\frac{1}{2}\epsilon_a - \eta\chi_f^2 \lambda_f^2 \chi_f(\omega)\chi_f(3\omega)]g(i\omega\tau_s)$$
$$- b_f \chi_f^4 \lambda_f^4 \chi_f(3\omega)\chi_f^3(\omega). \tag{13}$$

It is easily seen that the first term in the right hand side of $\epsilon_3(\omega)$ comes from the fluctuations through the coupling and the dielectric anisotropy because it has $k_B T$, η, and ϵ_a, and
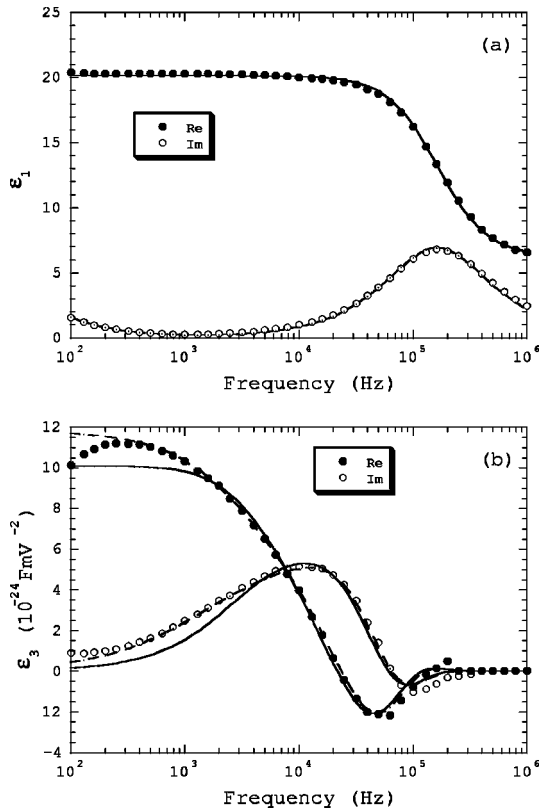
FIG. 1. Frequency dispersions of (a) the linear dielectric response and (b) the third-order nonlinear dielectric response at 102.7 °C in Sm-A.

FIG. 2. Temperature dependence of the frequency dispersion in $\epsilon_3''(\omega)$. The transition point is about 102.64 °C.

it diverges at the transition point as $a_0^{-1/2}$ within the Gaussian approximation. It should be noted that this contribution is always positive at $\omega=0$, the physical meaning of which has been discussed in detail [11]. On the other hand, the second term is due to the fourth-order term with respect to ξ_{fx} in the free energy (4), which always exists irrespective of the fluctuation and the sign of which depends on b_f.

The sample used in the present experiment was MHPOCBC, the phase sequence of which is Sm-C_A^*–Sm-C_α^*–Sm-A [13]. The sample was sandwiched between two glass plates with indium tin oxide electrodes and polyimid alignment layers. The thickness was about 12 μm and the area of electrodes was 16 mm^2. The cell was mounted in a hot stage (Instec HS1). A sinusoidal electric field was applied to the cell and the output signal proportional to the electric displacement was analyzed with a vector signal analyzer (HP89410).

Figure 1 shows the frequency dispersions of the linear dielectric constant, ϵ_1, and the third-order dielectric constant, ϵ_3, at 102.7 °C near the transition point in Sm-A. The ferroelectric mode is clearly observed in the linear dielectric response. The solid lines in the figure represent the best fit with ϵ_1 of Eq. (12), where we added a dispersion due to conduction such as $\sigma/i\omega$ at low frequencies. In the third-order dielectric response, on the other hand, a complex dispersion is seen, which is expressed by Eq. (13). The complexity comes from $\chi_f(\omega)$ and $\chi_f(3\omega)$ included in Eq. (13). The solid lines in the figure represent the best fit with Eq. (13). At low
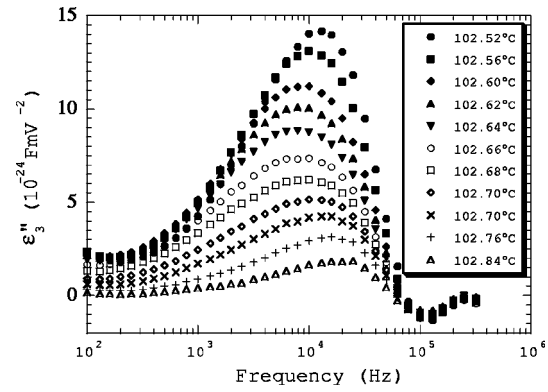
frequencies the agreement between the theory and the experiment is not good. This is improved by introducing β in Eq. (13); by replacing $i\omega\tau_s$ by $(i\omega\tau_s)^\beta$. The parameter β brings the distribution of relaxation frequency as in the Cole-Cole function, $1/[1+(i\omega\tau_s)^\beta]$. The fitting result is shown by the broken lines in Fig. 1(b). The agreement becomes much better. This result indicates that we need another distribution, though the function $g(i\omega\tau_s)$ itself has a distribution as described above. It may originate from the temperature distribution in the sample. However, we have to mention another possibility that, in principle, $g(i\omega\tau_s)$ should have a more broad distribution since we have used some assumptions such as the Gaussian approximation and the parabolic dispersion in deriving Eq. (13). The origin is not yet clear. Therefore, we used $g(i\omega\tau_s)$ without β when we analyzed the data to obtain the relaxation frequency of the soft mode.

Next, we show the temperature dependence of the frequency dispersion in $\epsilon_3''(\omega)$. As shown in Fig. 2, we can clearly see the softening of the soft mode both in the Sm-A and Sm-C_α^* phases, where the transition temperature is about 102.64 °C.

Last, we show the temperature dependencies of the relaxation frequencies of the soft mode and the ferroelectric mode, $f_{r,s}=1/2\pi\tau_s$ and $f_{r,f}=1/2\pi\tau_f$, obtained by fitting in Fig. 3. This exhibits the direct evidence of the soft-mode condensation in the Sm-A phase. The behavior of the soft
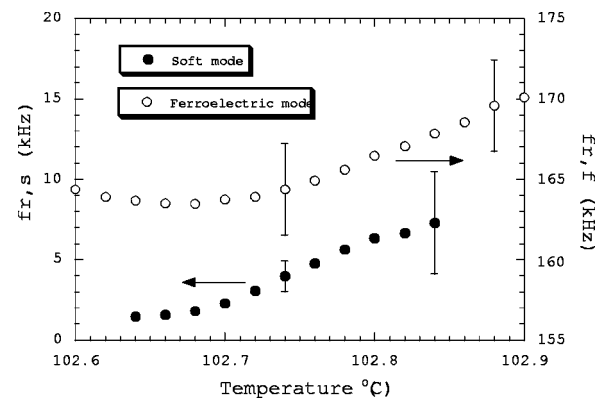

FIG. 3. Temperature dependencies of the relaxation frequency of the ferroelectric mode $f_{r,f}$ and that of the soft mode $f_{r,s}$.

mode (the amplitude mode) in the Sm-C_α^* phase will be reported elsewhere because we need different formula to analyze the data there [14]. Note that the ferroelectric mode becomes soft and the slopes of the soft and ferroelectric modes are nearly the same. This fact supports a discrete model to describe the phase transitions in antiferroelectric liquid crystals, where it is assumed that the transitions to tilted phases from the Sm-A phase take place in each layer even without interactions between neighboring layers, leading to the result that the doubly degenerate dispersion branch in the Sm-A phase goes down without changing the shape as the temperature is decreased, i.e., the slope of the relaxation frequency vs the temperature measured at any point in the smectic Brillouin zone should be the same [12].

In conclusion, by using the fluctuation-induced third-order nonlinear dielectric spectroscopy, we have observed the soft-mode condensation taking place at a general point of the Brillouin zone in the Sm-A–Sm-C_α^* phase transition,

which could not be observed by conventional methods. This soft mode is a simple helix with a short pitch in the Sm-A phase. Therefore, it is natural that the Sm-C_α^* phase induced by its condensation should have a simple helix and be similar to Sm-C^*, but only different in pitch, at least near the transition point. We have also clearly demonstrated that the third-order nonlinear dielectric spectroscopy has an outstanding merit that we can measure the frequency dispersion, compared with the other methods such as the heat capacity, birefringence, and layer compression modulus measurements by which the fluctuations were observed.

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