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Nonlinear Electrooptical Relaxation Spectra of Ferroelectric and Antiferroelectric Liquid Crystals

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We have studied the nonlinear electrooptical relaxation spectra of the Goldstone mode in the ferroelectric SmC^* phase and antiferroelectric SmC_A^* phase of an antiferroelectric liquid crystal (AFLC). In the SmC^* phase, the experimentally obtained linear spectrum shows a single relaxation of Debye type and the second and third-order nonlinear spectra show extended forms of Debye type to nonlinear case. In the SmC_A^* phase, the linear spectrum shows no relaxation under 20kHz, but the second-order nonlinear spectrum shows a Debye type single relaxation corresponding to the antiferroelectric Goldstone mode. We have also studied the electrooptical response in these two phases by means of the torque balance equation describing the dynamics of the Goldstone mode. The calculated nonlinear spectra are found to be in a good agreement with experimentally obtained ones.

Keywords: electrooptical response; nonlinear spectrum; relaxation; ferroelectric liquid crystal; antiferroelectric liquid crystal; Goldstone mode

INTRODUCTION

There are two methods often used to investigate dynamical responses of ferroelectric liquid crystals (FLCs) and antiferroelectric liquid crystals (AFLCs) under a time-dependent electric field. One is the dielectric measurement and the other is the electrooptic measurement[1,2]. In both methods, we can obtain the frequency spectra by applying a sinusoidal electric field to the sample, but these methods have been restricted to a linear regime. As the fluctuation in the soft materials such as liquid crystals is large in general, their response to the external field is expected to become nonlinear easily even if the field is small. Recently, the dielectric relaxation spectroscopy has been extended to the nonlinear regime

and applied to FLCs[3-5] and AFLCs[6,7]. This new method enables us to obtain more detailed information on the dynamics of FLCs and AFLCs, which is not obtainable by the linear spectrum. On the other hand, the electooptical spectroscopy has not been so intensively used compared with the dielectric one, but is expected to be less influenced by the dc conductivity of samples and applicable to the measurement in more variety of cell configurations. This method has been also extended to the nonlinear regimes[8] and utilized to investigate the dynamics in the antiferroelectric SmC_A^* phase[9,10].

In this study, we developed the nonlinear electrooptic measurement in a similar manner to the nonlinear dielectric measurement and apply it to an AFLC in the SmC* and SmC_A^* phases. In these phases, there is the cooperative fluctuation of the directors around their helical axis called Goldstone mode and this mode dominates the dynamics of these phases. We also discuss the nonlinear electrooptic spectra of Goldstone mode theoretically by using the phenomenological equation for the azimuthal angle of directors and compare them with the experimental ones.

THEORY

The transmitted light intensity I through a homogeneously aligned cell (the smectic layers are perpendicular to the surfaces of cell) set between crossed polarizers can be calculated by averaging the local transmitted light intensity $I(z)$ over one helical pitch along the helical axis (z-axis) as is illustrated in Figure 1. The smectic liquid crystal in each layer can be modeled as an optically biaxial crystal. We define the principle refractive index parallel to the molecular long axis as n_3, that parallel to the two-hold symmetry axis as n_1 ($n_3>n_1$), and that perpendicular to those two axis as n_2, as are illustrated in Fig. 1. We also assume that the biaxiality of refractive indexes is very small and $\delta n=n_2-n_1$ is assumed to be very small. The intensity I at the angle $\psi=\pi/8$ for the small tilt angle ($\theta<<1$) is given as

$$\frac{I}{I_0}=\frac{1}{2}\sin^2\Theta-\frac{1}{2}\frac{\pi\delta nd}{\lambda}\sin(2\Theta)\langle\sin^2\varphi\rangle+2\theta\sin^2\Theta\langle\cos\varphi\rangle+\cdots, \qquad (1)$$

where I_0 is the intensity of incident light, d is the sample thickness, λ is the wavelength of the light, φ is the azimuthal angle of the director, Θ is defined as $\Theta \equiv \pi\Delta nd/\lambda$ in terms of the birefringence $\Delta n = n_3 - n_1$ and $\langle \cdots \rangle$ means the spatial average over one helical pitch.

In order to study the dynamics of Goldstone mode in the smectic phases under electric field E and calculate the spatially averaged values $\langle \sin^2 \varphi \rangle$ and $\langle \cos\varphi \rangle$, we used a simple torque balance equation for the azimuthal angle $\varphi(z,t)$[11,11],

$$K\frac{\partial^2\varphi}{\partial z^2} - \gamma\frac{\partial\varphi}{\partial t} - \frac{1}{2}\Delta\varepsilon_a E^2 \sin 2\varphi = P_s E \sin\varphi, \tag{2}$$

where K is the torsional elastic constant, γ the rotational viscosity, P_s the spontaneous polarization, $\Delta\varepsilon_a$ the dielectric anisotropy and E is the applied electric field of sinusoidal form $E = E_0 \cos\omega t$ with the angular frequency ω and the amplitude E_0. When E_0 is small enough, the solution of Eq. (2) is given as a perturbed form to the homogenous solution φ for the helical structure with the wavenumber q_0 at E=0 and is expressed as a power series of E_0 with

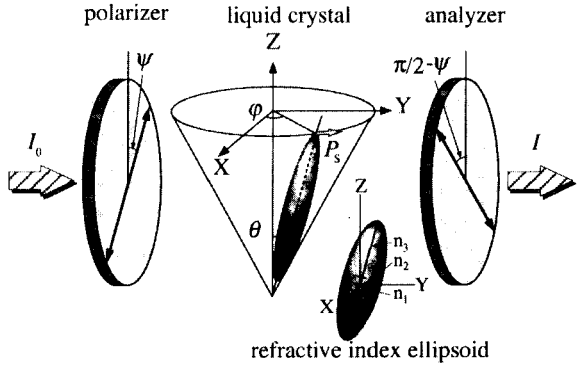

FIGURE 1 The arrangement of an AFLC cell for nonlinear electrooptical spectroscopy.

harmonic frequency of ω,

$$\varphi(z,t) = q_0 z + \sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{r=0}^{n} A_{nmr}\left(\frac{E_0}{2}\right)^n e^{i(n-2r)\omega t}\sin(mq_0 t). \tag{3}$$

The coefficients A_{mnr} are determined by putting Eq. (3) into Eq. (2) and setting to zero the sum of terms with the same power of E_0 and the same harmonic frequency. We can finally obtain from Eqs.(1) and (3) the transmitted intensity I as the sum of the dc, fundamental and harmonic components,

$$I = I_{dc} + \sum_{m=1}^{\infty}\sum_{n=m}^{\infty} a^*_{nm}\left(\frac{E_0}{2}\right)^n e^{im\omega t} + c.c. \tag{4}$$

When E_0 is small, the leading term in the m-th harmonic component is that proportional to $E_0^{\,m}$ with coefficient $a_{mm}^*(\equiv a'_{mm} - ia''_{mm})$ which is given as,

$$a_{11}^* = \frac{P_S\theta}{Kq_0^{\,2}}\sin^2\Theta\cdot\frac{1}{1+i\omega\tau}, \tag{5}$$

$$a_{22}^* = -\frac{\pi\delta nd}{2\lambda}\sin(2\Theta)\cdot\left\{\frac{P_S^{\,2}\theta^2}{8K^2q_0^{\,4}}\cdot\frac{3+i\omega\tau}{(1+i\omega\tau)^2(2+i\omega\tau)} + \frac{\Delta\varepsilon_a}{8Kq_0^{\,2}}\cdot\frac{1}{(2+i\omega\tau)}\right\}, \tag{6}$$

$$a_{33}^* = \frac{\theta}{4}\sin^2\Theta\cdot\left\{-\frac{P_S^{\,3}}{K^3q_0^{\,6}}\cdot\frac{3+5i\omega\tau-\omega^2\tau^2}{(1+i\omega\tau)^3(2+i\omega\tau)(1+3i\omega\tau)} + \frac{3P_S\Delta\varepsilon_a}{K^2q_0^{\,4}}\cdot\frac{1}{(1+i\omega\tau)(2+i\omega\tau)(1+3i\omega\tau)}\right\}, \tag{7}$$

where $\tau = \gamma/Kq_0^{\,2}$ is the relaxation time of the linear spectrum.

In the SmC* phase, the response to a small electric field is mainly governed by the ferroelectric coupling to the spontaneous polarization and we can set $\Delta\varepsilon_a$=0 in Eq. (2) approximately. The linear spectrum, a^*_{11}, the second-order and third-order nonlinear spectra, a^*_{22}, a^*_{33} for $\Delta\varepsilon_a$=0 are shown in Figure 2. The linear spectrum a^*_{11} shows a single relaxation of Debye type. The second-order spectrum a^*_{22} and the third-order one a^*_{33} are of an extended form of

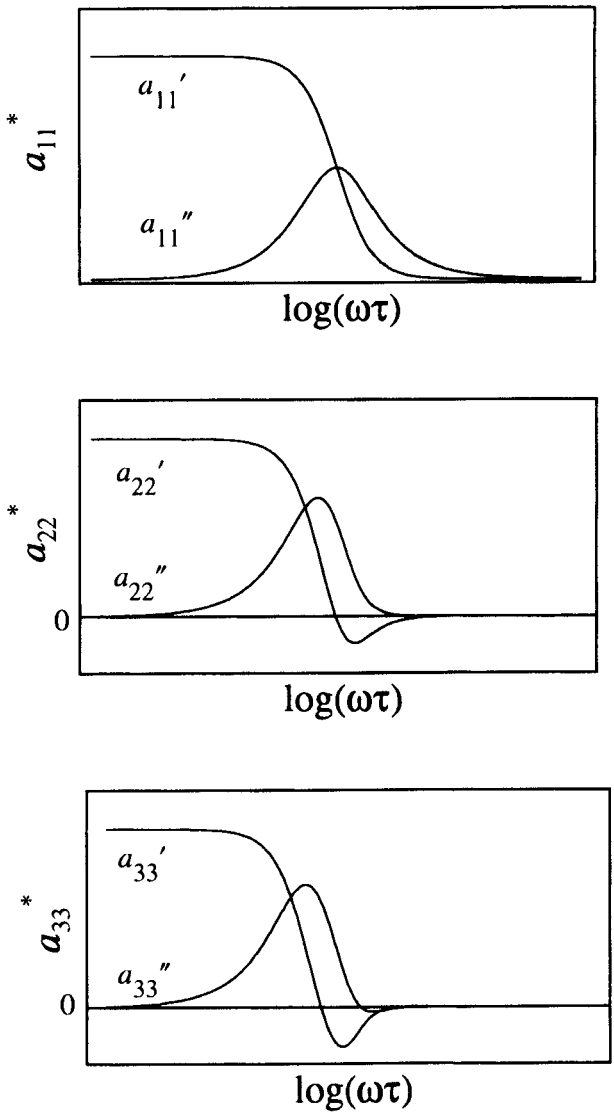

FIGURE 2 The linear a^*_{11}, the second- a^*_{22} and the third-order a^*_{33} nonlinear electrooptic relaxation spectra calculated for Goldstone mode.

Debye relaxation to the nonlinear case and they show spirals over two and three quadrants around the origin in the Cole-Cole representation (real part vs. imaginary part). The sign of the increment of each spectrum depends on the signs of P_s, θ and δn, but the increments of a^*_{11} and a^*_{33} are always opposite in sign.

In the SmC_A^* phase, the spontaneous polarization P_s is locally canceled by the anti-parallel alignment of P_s in neighboring layers. The main response to a small electric field is originated from the coupling to the dielectric anisotropy $\Delta\varepsilon_a$ and we can assume P_s=0 in the limited case. The linear spectrum, a^*_{11}, shows no relaxation behavior and the leading term of the second-order nonlinear spectra, a^*_{22} are calculated as

$$a_{22}^{*} = -\frac{\pi\delta n d}{32\lambda}\sin(2\Theta)\cdot\frac{\Delta\varepsilon_a}{Kq_0^{\,2}}\frac{1}{1+i\omega\tau'}, \tag{8}$$

where $\tau' = \gamma/2Kq_0^{\,2}$ is the relaxation time of the Goldstone mode in this phase. The spectrum of a^*_{22} is a single relaxation of Debye type corresponding to the Goldstone mode in the antiferroelectric phase.

The linear and the third-order nonlinear components are originated from the change in the averaged (apparent) optical axis by the electric field and the second-order nonlinear components comes from the change of the birefringence of liquid crystals. In general, the advantage of the nonlinear electrooptic spectroscopy lies in that we can distinguish the type of electrical interaction (verctorial or tensorial value) by the order of nonlinear component which appears in the response.

EXPERIMENT

The transmitted light intensity I thorough an AFLC cell was detected and converted into voltage signal by a high-speed PIN photodiode module (Hamamatsu S3387) attached to a polarizing microscope (Olympus BHSP). This optical response was amplified and decomposed into frequency components by an FFT analyzer (Advantest R9211) as

$$I = I_{dc} + \mathrm{Re}\left[\sum_{m=1}^{\infty} I_m^* e^{im\omega t}\right], \tag{9}$$

where I_m* is the Fourier-decomposed complex amplitude of the m-th harmonic component. We measured the dependences of complex amplitude I_m* on the amplitude of electric field E_0 and obtained the nonlinear spectra a^*_{11}, a^*_{22} and a^*_{33} by means of Eq. (3). The homogeneously aligned AFLC cell was placed between crossed polarizers, one of which was set to make an angle of $\psi=\pi/8$ with the layer normal direction. We define the position of $\psi=0$ as the direction where the transmitted light intensity would take the minimum value around the rubbing direction in the SmA phase.

The AFLC sample used in this study was (R)-MHPOBC, which was the first smectic liquid crystal reported to show antiferroelectricity. The sample was sandwiched between two glass plate with ITO electrodes. The surface of the plates were spin-coated with polyimide and rubbed unidirectionally to attain a homogenous alignment of molecules. The cell thickness was about 25μm, which was determined by the capacitance of an empty cell. The cell was set up in a holder whose temperature was controlled with in $\pm$0.05C by a temperature controller (CHINO DJ-11).

RESULTS AND DISCUSSION

In the SmC* phase at 117℃, we studied the applied field dependence of the complex amplitude I_1*, I_2* and I_3* from E_0=12kV/m to 28kV/m. It is found that I_1*, I_2* and I_3* are almost proportional to E_0, E_0^2 and E_0^3, respectively. The obtained linear, second and third-order nonlinear spectra a^*_{11}, a^*_{22} and a^*_{33} are respectively shown in Figure 3. The linear spectrum shows a single relaxation profile of Debye type and the best-fit curve of Eq. (5) with τ=0.102ms is drawn as a solid line in Fig. 3. As the contribution of soft mode to the electrooptical response seems to be negligibly small at this temperature, a'_{11} approaches to zero at high frequencies. Similarly, we can analyze a^*_{22} and a^*_{33} by using Eqs. (6) and (7) in which the dielectric anisotropy $\Delta\varepsilon_a$ sets to

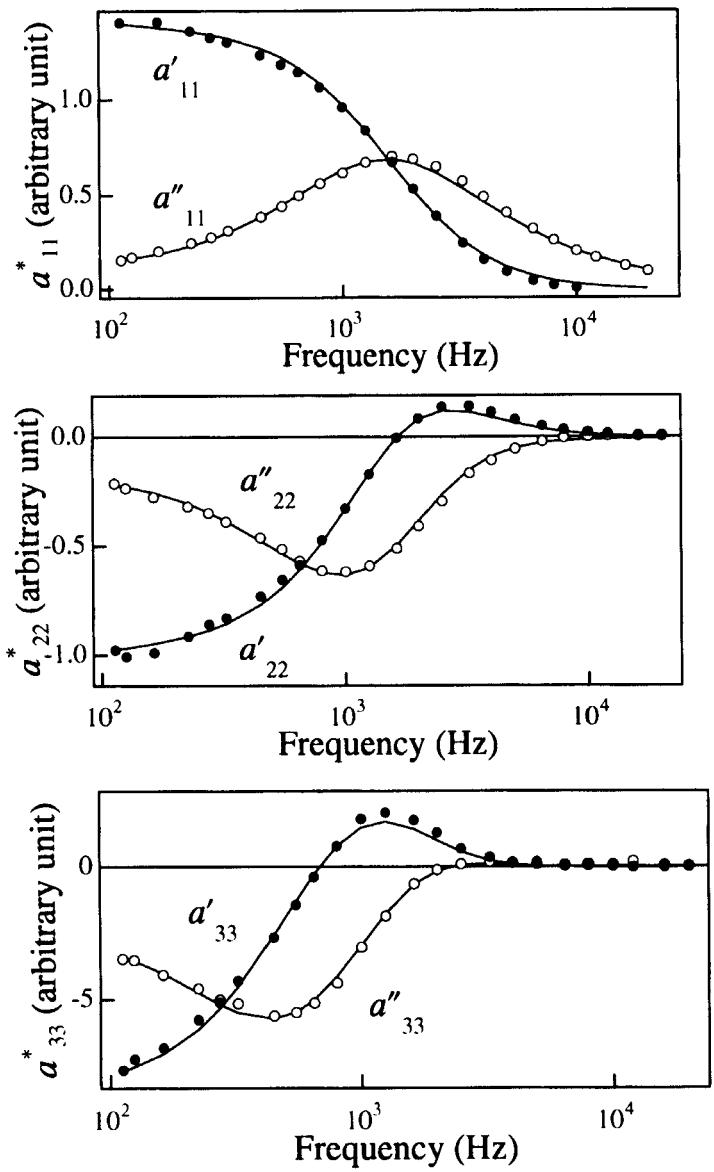

FIGURE 3 The linear a^*_{11}, the second-order a^*_{22} and the third-order a^*_{33} nonlinear electrooptic relaxation spectra in the SmC* phase.

zero. The best-fitted curve of Eq. (6) with τ=0.089ms and that of Eq. (7) with τ=0.092ms are also shown as solid lines in Fig. 3. The best-fitted values of τ_i (i=1,2,3) do not strongly depend on i, which confirms the theoretical prediction that the shape of the nonlinear spectra is determined by the relaxation time of the linear spectrum τ.

In the SmC_A* phase at 100℃, we studied the applied field dependence of the complex amplitude I_1* and I_2* from E_0=200kV/m to 560kV/m. It is found that I_1* and I_2* are almost proportional to E_0 and E_0^2. The obtained linear spectrum a^*_{11} shows no relaxation behavior under 20kHz, but the second-order nonlinear spectrum a^*_{22} shows a single relaxation profile of Debye type as is shown in Figure 4, which corresponds to the antiferroelectric Goldstone mode. The best-fit line of Eq. (8) with τ'=0.042ms is shown as a solid line in Fig. 4. The detected fluctuation of directors concerning to the acoustic-like Goldstone mode where the directors in neighboring layers fluctuate in the same direction and this mode couples to the dielectric anisotropy which can be observed in the second-order nonlinear spectrum.

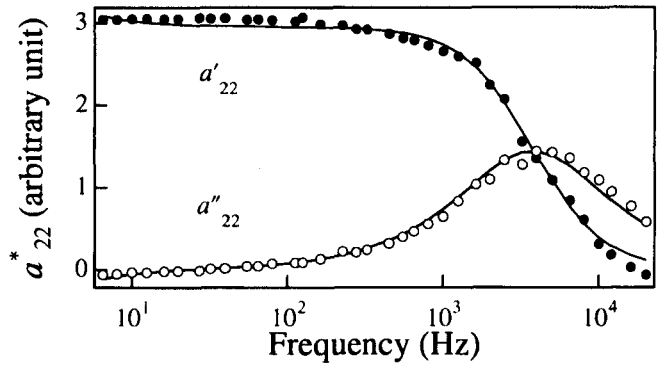

FIGURE 4 The second-order a^*_{22} nonlinear electrooptic relaxation spectra in the SmC_A* phase.

CONCLUSIONS

We have applied the nonlinear electrooptical spectroscopy in the frequency domain to the Goldstone mode in the SmC* and SmC_A* phases of MHPOBC. It is found that the nonlinear spectra obtained experimentally are in good agreement with theoretically calculated ones. We have shown that the method is useful for various types of electrical interactions in the liquid crystals and various phases.

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