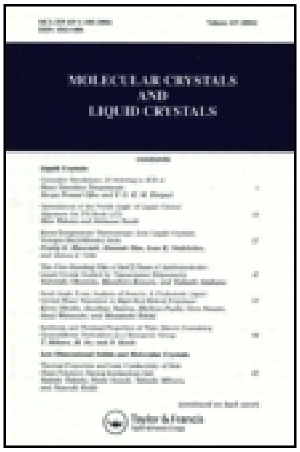

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NONLINEAR DIELECTRIC RELAXATION SPECTROSCOPY OF ANTIFERROELECTRIC LIQUID CRYSTALS

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Abstract The relaxation spectra of the linear and nonlinear dielectric constants of the antiferroelectric liquid crystals have been studied in their SmA, SmC* and SmC_A* phases. In the SmA phase near the boundary to the SmC* or SmC_A* phase, both the dielectric constants show a critical behavior due to the softening of the ferroelectric soft mode. In the SmC* phase, we obtain the third-order nonlinear spectrum of a higher-order Debye type with a negative increment, which corresponds to the ferroelectric Goldstone mode observed also in the linear spectrum. In the SmC_A* phase, the antiferroelectric Goldstone mode is observed not in the linear spectrum, but in the third-order spectrum as a Debye-type relaxation with a positive increment. All these spectra can be analyzed in terms of simple phenomenological models.

INTRODUCTION

Antiferroelectric liquid crystals (AFLC)[1] have attracted much attention of many researchers not only for their potential as a new type of display material but also for a fundamental interest in their structures and phase transitions since the discovery of the tristable switching in the chiral smectic C_A (SmC_A^*) phase of 4-(1-methyl-heptyloxycarbonyl-phenyl) 4′-octylbiphenyl-4-carboxylate (MHPOBC)[2] and the herring bone molecular alignment in the smectic O^* phase of 1-methyl-heptyl-terephthalidene-bis-aminocinnamate (MHTAC).[3] These smectic liquid crystals often show a variety of new electro-active smectic C phases such as the ferrielectric SmC_γ^* phase[4], the antiferroelectric SmC_A*[2,5], AF[6] phases and the mysterious SmC_α*[7] phase besides the conventional ferroelectric SmC* phase.

As the dielectric response is sensitive to the structures of these new smectic C phases and the phase transitions among them, the dielectric measurement has become one of the useful tools to investigate the phase sequences and the details of transitions in AFLCs. There are many experimental studies on the dielectric relaxation of AFLCs.[8-10]

Recently, the dielectric relaxation spectroscopy has been extended to the nonlinear regime and applied to a variety of materials including ferroelectric polymers[11] and ferroelectric liquid crystals.[12-14] In these materials, the nonlinear dielectric relaxation is regarded as a higher-order effect on the motional mode of molecular dipoles in the materials due to the applied electric field and has its counterpart in the linear relaxation spectrum. So, the nonlinear dielectric spectrum is expected to give more detailed information on the molecular motion and the microscopic environment of dipoles compared with the linear one.

In this paper, we report the results of the nonlinear dielectric relaxation spectroscopy for the AFLCs in their SmA, SmC* and $\mathrm{SmC_A}^*$ phases. The third-order nonlinear dielectric spectrum shows a peculiar shape in each smectic phase depending on the origin of their nonlinear response. The nonlinear spectra obtained are discussed by means of simple phenomenological equations of motion which take into consideration the main interaction between the liquid crystals and the applied electric field.

EXPERIMENTAL

Under the weak applied electric field E, the electric displacement D can be expanded as the power series of E in terms of the nonlinear response functions ε.[11,12] When the applied field is a sinusoidal one with the amplitude E_0 and the angular frequency ω, D is expressed as a sum of the dc, fundamental and higher-order complex harmonic components D_n^* (n=0,1,2,$\cdots$) as

$$D(t) = \mathrm{Re}\, D_0^* + \sum_{n=1}^{\infty} \mathrm{Re}\left[D_n^* \exp(in\omega t)\right]. \tag{1}$$

The amplitude D_n^* is given as a sum of the power series of E_0 as

$$D_n^* = \sum_{r=0}^{\infty} 2\cdot\left(\frac{E_0}{2}\right)^{n+2r} \cdot {}_{n+2r}C_r \cdot \varepsilon_{n+2r}^*(\underbrace{\omega,\cdots,\omega,}_{n+r}\underbrace{-\omega,\cdots,-\omega}_{r}) \qquad (n \geq 1), \tag{2}$$

where $\varepsilon^*(\omega)$ is the complex dielectric spectrum defined as the Fourier transform of $\varepsilon(t)$. We can obtain the nth-order nonlinear dielectric constant $\varepsilon_n^*(\omega)$ defined by

$$\varepsilon_n^*(\omega) \equiv \varepsilon_n^*(\omega,\omega,\cdots,\omega) \equiv \varepsilon_n' - i\varepsilon_n'' \tag{3}$$

from the applied field dependence of D_n^* as[11,12]

$$\varepsilon_n^*(\omega) = \lim_{E_0 \to 0} \frac{D_n^*}{E_0^{\,n}} \cdot 2^{n-1}. \tag{4}$$

The applied sinusoidal electric field was generated from the synthesizer in the frequency range from 20Hz to 300kHz. The electric displacement D detected by the charge amplifier was digitized and averaged on the storage oscilloscope. The fundamental and harmonic components of D were obtained by the Fourier transform of the time-domain data on a personal computer.

The AFLC used in this study is 4-(1-trifluoromethyl-heptyloxy-carbonyl) phenyl 4′-octyloxy-biphenyl-4-carboxylate (TFMHPOBC)[15] whose chemical structure is similar to MHPOBC, but which has a simpler phase sequence (Iso.-SmA-SmC$_A$*) compared with other AFLCs. We studied its pure (R)-enantiomer and its slightly racemised (R:S=8:2) mixture[15] which has a phase sequence, Iso.-SmA-SmC*-SmC$_A$*. The AFLC samples were sandwiched between two glass plates with ITO electrodes. The surfaces of both plates were spin-coated with polyimide and rubbed unidirectionally to attain a homogeneous alignment of liquid crystals. The cell gaps were about 20 μm, which were determined by measuring the capacitance of empty cells.

NONLINEAR DIELECTRIC SPECTRA IN THE SmA PHASE

The temperature dependences of the linear and the third-order nonlinear dielectric constants ε_1 and ε_3, respectively at the frequency lower than the relaxation in the SmA phase are shown in Fig. 1. The linear constant ε_1 shows a critical behavior of Curie-Weiss type near both SmA-SmC* and SmA-SmC$_A$* phase transitions due to the softening of the ferroelectric soft mode, which was the same result reported before.[15,16] The third-order constant ε_3 also shows the critical behavior whose critical exponent is four and takes the positive value near both the transitions. In the case of SmA-SmC* phase transition, it has been found theoretically and experimentally in our previous study[13] that the sign of ε_3 depends on the order of transition (first or second) and ε_3 is positive for 3M2CPHpOB(C$_7$), which is indicative of the first-order transition. In the present study, the positive sign of ε_3 in the mixture sample is in agreement with the fact that it is reported to show the first-order SmA-SmC* phase transition.[17] The positive sign of ε_3 in the pure sample is due to the fact that the critical behavior in the SmA phase is, even in the antiferroelectric case, governed by the coupling between the ferroelectric order parameter (tilt angle) and the polarization.

The spectra of ε_1^* and ε_3^* can be discussed by the phenomenological equation of motion for the tilt angle θ derived from the thermodynamic potential of Landau type[18] as

$$-\gamma\frac{\partial\theta}{\partial t} = a(T-T_0)\theta + b\theta^3 - \chi_0\varepsilon_0 CE \tag{5}$$

where γ is the viscosity, a and b are the phenomenological coefficients, C the coupling constant between P and θ, $\chi_0\varepsilon_0$ the susceptibility, ε_0 the vacuum permittivity and T_0 the transition temperature of racemic mixture. We can obtain the linear and nonlinear spectra from the solution θ of eq. (5) and the relation $D = \varepsilon_0(1+\chi_0)E + \chi_0\varepsilon_0 C\theta$ as

$$\varepsilon_1^* = (\chi_0+1)\varepsilon_0 + \frac{\chi_0^2\varepsilon_0^2C^2}{a(T-T_C)}\frac{1}{1+i\omega\tau} \tag{6}$$

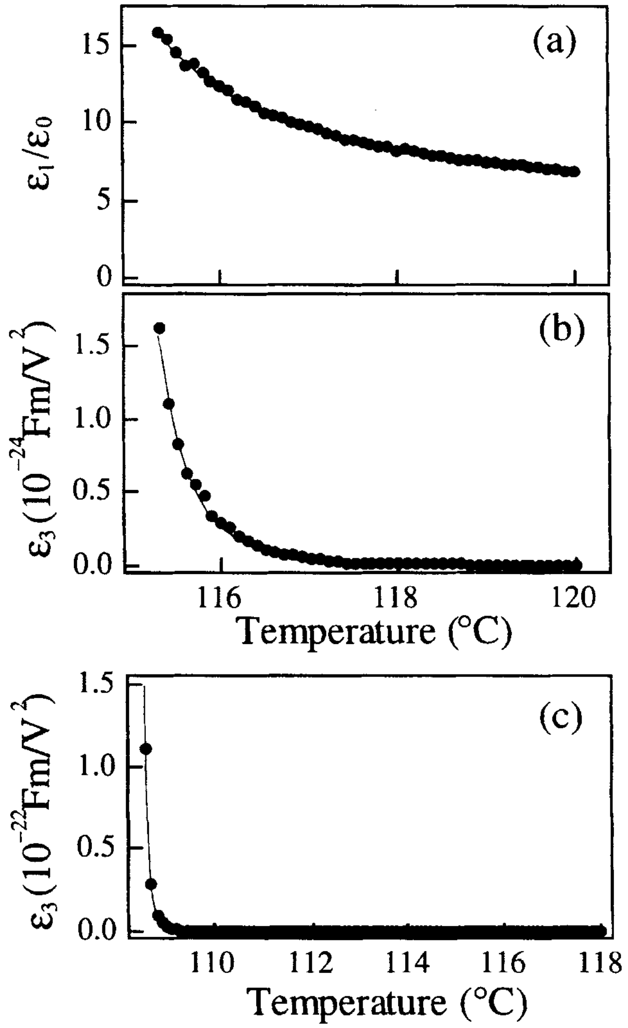

FIGURE 1 The linear spectrum ε_1 (a) and the third-order nonlinear spectrum ε_3 (b) in the SmA phase of (R)-TFMHPOBC and ε_3 of (R) &(S) mixture of TFMHPOBC (c).

$$\varepsilon_3^* = -\frac{b\chi_0^4\varepsilon_0^4C^4}{a^4(T-T_C)^4}\frac{1}{(1+i\omega\tau)^3(1+3i\omega\tau)} \tag{7}$$

$$\tau = \frac{\gamma}{a(T-T_C)} \tag{8}$$

where $T_C(=T_0+\chi_0\varepsilon_0C^2/a)$ is the transition temperature of chiral sample and τ is the relaxation time of soft mode. The linear spectrum ε_1^* shows a single Debye type relaxation whose increment and relaxation time both increase on approaching to the transition temperature (softening). The third-order spectrum ε_3^* has a more complicated form consisting of the product of four Debye type functions. The sign of the increment of ε_3^* is determined by the sign of b, which is positive for the second-order transition and negative for the first-order transition. The even-order nonlinear constants disappear due to the symmetry. The observed spectra ε_1^* and ε_3^* are shown in Fig. 2. The solid lines in the figure are the best-fitted one using eqs. (6) and (7) in which the term $i\omega\tau$ is replaced by $(i\omega\tau)^\beta$ in order to take into account the distribution of relaxation times and to

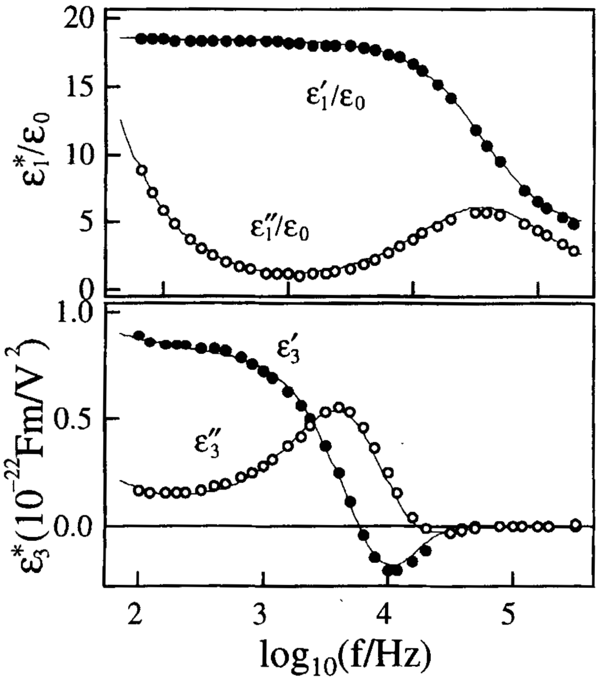

FIGURE 2 The linear and third-order nonlinear spectra, ε_1^* and ε_3^*, in the SmA phase (108.6℃) of (R)&(S) mixture of TFMHPOBC.

which the effect of conductivity is added. The agreement between the observed spectra and the best-fitted curves are found to be good.

NONLINEAR DIELECTRIC SPECTRA IN THE SmC* PHASE

The main dielectric relaxation mode in the SmC* phase except in the vicinity of the SmA-SmC* transition is the Goldstone mode, which is the fluctuation of directors in the azimuthal angle direction. The linear and third-order spectra, ε_1^* and ε_3^*, in the SmC* phase of mixture sample are shown in Fig. 3. The spectrum of ε_3^* shows a Debye type relaxation extended to the nonlinear case with the negative increment. This has a counterpart in ε_1^*, which is a single Debye relaxation with a relaxation frequency of several hundred Hz. This situation is the same as in other ferroelectric liquid crystals reported so far.[13,14]

The shapes of ε_1^* and ε_3^* can be discussed by the phenomenological torque balance equation for the azimuthal angle ϕ including the ferroelectric coupling between the spontaneous polarization P_S and the electric field E in the direction vertical to the

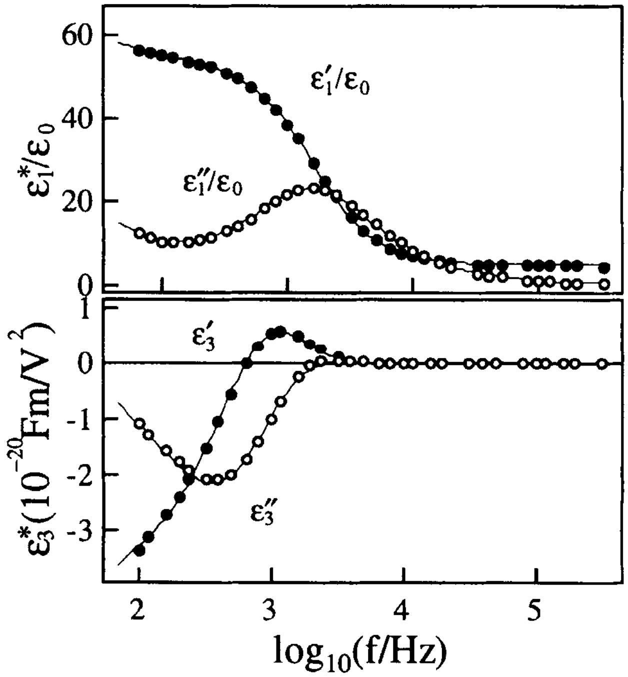

FIGURE 3 The linear and third-order nonlinear spectra, ε_1^* and ε_3^*, in the SmC* phase (106.8℃) of (R)&(S) mixture of TFMHPOBC.

helical axis (z-axis) as

$$K\frac{\partial^2\phi}{\partial z^2}-\gamma\frac{\partial\phi}{\partial t}=P_SE\sin\phi \tag{9}$$

where K is the elastic constant and γ is the rotational viscosity. The spatial distribution of ϕ along the z-axis is calculated from eq. (9). The spectra $\varepsilon_1{}^*$ and $\varepsilon_3{}^*$ are obtained from the average value of the induced polarization over one helical pitch as

$$\varepsilon_1{}^*=\frac{P_S{}^2}{2Kq_0{}^2}\frac{1}{1+i\omega\tau} \tag{10}$$

$$\varepsilon_3{}^*=-\frac{P_S{}^4}{16\left(Kq_0{}^2\right)^3}\frac{3+5i\omega\tau+(i\omega\tau)^2}{(1+i\omega\tau)^3(1+3i\omega\tau)(1+i\omega\tau/2)} \tag{11}$$

$$\tau=\frac{\gamma}{Kq_0{}^2} \tag{12}$$

where q_0 is the wavenumber of the helical structure and τ is the relaxation time of $\varepsilon_1{}^*$.

The linear spectrum $\varepsilon_1{}^*$ shows a single Debye type relaxation and the third spectrum $\varepsilon_3{}^*$ has a more complicated form consisting of the sum of product of three Debye type functions. The negative sign of $\varepsilon_3{}^*$ indicates that the origin of the nonlinearity in the SmC* phase is the saturation in the alignment of the spontaneous polarization by the applied electric field. Its increment strongly depends on the value of the spontaneous polarization and is much larger than those observed in the polymer systems.[11] The best-fitted curves using eqs. (10) and (11), in which the term $i\omega\tau$ is replaced by $(i\omega\tau)^\beta$ and the effective conductivity is taken into account, are shown as solid lines in Fig. 3. We obtain the relaxation time τ=97.7μs with β=0.92 from $\varepsilon_1{}^*$ and τ=98.4μs with β=0.94 from $\varepsilon_3{}^*$, which are in a good agreement with each other. This implies that the nonlinear spectrum is also governed by the relaxation time τ of the linear spectrum.

NONLINEAR DIELECTRIC SPECTRA IN THE SmC$_A$* PHASE

In the SmC$_A$* phase, the relaxation spectra of the ferroelectric soft mode and the rotational motion of a molecule around its short axis were observed by using the linear dielectric relaxation spectroscopy with no bias field.[15-17,19] The main relaxational mode in the SmC$_A$* phase is the fluctuation of the azimuthal angle (antiferroelectric Goldstone mode), but this mode is unfortunately dielectric inactive due to a local cancellation of the spontaneous polarization P_S by the anti-parallel alignment of P_S. Then, no relaxational mode is observed in the lower frequency range in the linear dielectric spectrum $\varepsilon_1{}^*$ as shown in Fig. 4. Instead, the third-order spectrum ε_3^* is found to show a Debye type single relaxation spectrum with a positive increment and a relaxation frequency of about 1kHz as seen in Fig. 4.[20,21]

The origin of this nonlinear relaxation is mainly due to the helix deformation induced by the coupling between the dielectric anisotropy and the electric field without destroying the antiparallel ordering.[21] The destruction of the antiparallel ordering induces the linear dielectric relaxation and this is not the case with our experimental results mentioned above. By neglecting the tilt angle change, which is a proper assumption in the SmC$_A$* phase far from the transition, we can calculate ε_1^* and ε_3^* from the torque balance equation taking into account the coupling between the electric field and the dielectric anisotropy $\Delta\varepsilon = (\varepsilon_1 - \varepsilon_2) + (\varepsilon_3 - \varepsilon_1)\sin^2\theta$ ($\varepsilon_1, \varepsilon_2, \varepsilon_3$: the principle values of dielectric tensor) as

$$K\frac{\partial^2\phi}{\partial z^2} - \gamma\frac{\partial\phi}{\partial t} + \frac{1}{2}\Delta\varepsilon E\sin 2\phi = 0. \qquad (13)$$

The results are

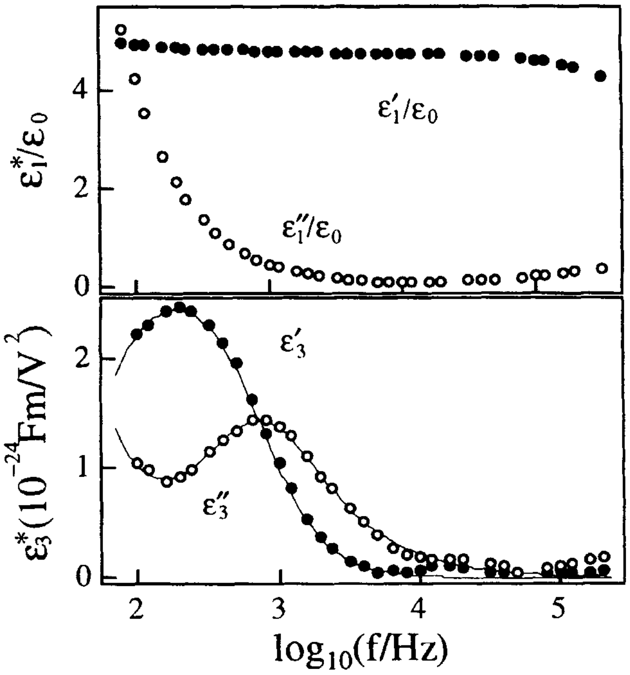

FIGURE 4 The linear and third-order nonlinear spectra, ε_1^* and ε_3^*, in the SmC$_A$* phase (104.0℃) of (R)&(S) mixture of TFMHPOBC.

$$\varepsilon_1^* = \frac{1}{2}\left\{(\varepsilon_1 + \varepsilon_2) + (\varepsilon_3 - \varepsilon_1)\sin^2\theta\right\} \tag{14}$$

$$\varepsilon_3^* = \frac{\Delta\varepsilon^2}{48Kq_0^2}\frac{1}{1+i\omega\tau} \tag{15}$$

$$\tau = \frac{\gamma}{2Kq_0^2} \tag{16}$$

where τ is the relaxation time of ε_3^*. The third-order spectrum ε_3^* has a positive increment and a relaxation frequency which reflects the antiferroelectric Goldstone mode. We can detect the fluctuation of helix from the third-order spectrum through the helix deformation due to the electric field. This kind of field-induced biaxiality can be the origin of the nonlinear spectrum also in the SmA phase, but the intensity is much smaller than that originated from the unharmonic terms in the thermodynamic potential mentioned before. The best-fitted curve using eq. (15), which is drawn as a solid line in Fig. 4, is in a good agreement with the observed spectrum. In the SmA and SmC* phases, the nonlinear spectrum is only the higher-order effect to the linear spectrum, but in the SmC$_A$* phase, it gives a more essential information on the dynamics of AFLCs.

CONCLUSIONS

We have studied the nonlinear dielectric relaxation spectra in the SmA, SmC*, and SmC$_A$* phases. In each of these smectic phases, the nonlinear relaxation spectrum shows a characteristic form which depends on the main interaction between the liquid crystal and the electric field. The experimental results can be analyzed by the phenomenological equation of motion. The present study shows the applicability and the usefulness of the nonlinear dielectric relaxation spectroscopy in studying the dynamics of the antiferroelectric liquid crystals.

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