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Critical behavior of nonlinear permittivity in the smectic-*A* phase of chiral liquid crystals

Yasuyuki Kimura, Hiroshi Isono, and Reinosuke Hayakawa
Department of Applied Physics, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
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We study the nonlinear permittivity of chiral liquid crystals in the smectic-*A* (Sm-*A*) phase near the ferroelectric smectic-C^* (Sm-C^*) phase and the smectic-C^*_α (Sm-C^*_α) phase theoretically and experimentally. The third-order nonlinear permittivity ε_3 shows the critical behavior with the exponent of four near the Sm-C^* phase and its sign depends on the order of the phase transition. In the case of the Sm-*A*–Sm-C^*_α phase transition, the sign inversion of ε_3, presumably due to the large fluctuation of order parameter, is observed near the transition temperature.

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The phase transition between the paraelectric smectic-*A* (Sm-*A*) phase and the ferroelectric smectic-C^* (Sm-C^*) phase has been intensively studied since the discovery of ferroelectricity in the Sm-C^* phase of chiral liquid crystals [1]. In those studies, the phenomenological theory of Landau-type (mean-field model) for the Sm-*A*–Sm-C^* phase transition [2–4] has been applied to describe the measured temperature dependence of spontaneous polarization, tilt angle, heat capacity, permittivity, etc. in the Sm-C^* phase. The comparison between theory and experimental data demonstrates that the mean-field model is a good approximation to describe the temperature dependence of these quantities. The critical behavior of susceptibility in the Sm-*A* phase also follows the mean-field model [2]. In addition, the critical region estimated from the Ginzburg-criterion argument is reported to be very narrow at this transition [5].

The critical behavior at the phase transition between smectic subphases also has been studied intensively for antiferroelectric liquid crystals (AFLC's) [1]. The recent precise measurement of heat capacity [6] and birefringence [7] at the phase transition between the Sm-*A* phase and the subphase referred to as the smectic-C^*_α (Sm-C^*_α) phase reveal unusually large pretransitional fluctuation of tilt order parameter. Their critical behavior deviates from that predicted by the mean-field model. The universality class of this transition is considered to be the three-dimensional (3D) *XY* critical or the Gaussian tricritical one [6].

Recently, the dielectric relaxation spectroscopy has been extended to the nonlinear regime and applied to soft condensed matters such as polymers [8] and liquid crystals [9,10]. In the case of ferroelectric liquid crystals (FLC's) [9] and AFLC's [10], it is reported the remarkable nonlinear dielectric response originated from the orientational saturation of molecular alignment due to the distortion of helical structure by an electric field. On the other hand, large nonlinear dielectric response is also expected in the Sm-*A* phase near the Sm-*A*–Sm-C^* and Sm-*A*–Sm-C^*_α phase transition due to the softening of tilt fluctuation (soft mode) and the vanishing of the harmonic term of tilt order parameter in the thermodynamic potential.

In this paper, we investigate the critical behavior of the nonlinear permittivity in the Sm-*A* phase of chiral liquid crystals experimentally and theoretically by using the phenomenological mean-field free energy. Since nonlinear permittivity reflects the higher-order terms of the order parameter in the Landau-type free energy, the comparison between experimental results and theoretical ones make it possible to obtain detailed information on the free energy. Moreover, in the case of the Sm-*A*–Sm-C^*_α phase transition, the deviation from the mean-field theory is expected to be observed more clearly in the critical behavior of nonlinear permittivity.

At first, we calculate the nonlinear permittivity in the Sm-*A* phase of FLC's by using the mean-field free energy near the Sm-*A*–Sm-C^* phase transition under the electric field *E* applied parallel to the smectic layers. The free-energy density *f* can be written with tilt angle θ and polarization *P* as order parameters [1,3,4],

$$f=f_0+\frac{1}{2}a(T-T_0)\theta^2+\frac{1}{4}b\theta^4+\frac{1}{6}c\theta^6+\frac{1}{2\chi}P^2+\frac{1}{4}\eta P^4 - CP\theta-\frac{1}{2}\Omega P^2\theta^2-PE, \tag{1}$$

where f_0 is the nonsingular part of *f*, χ is the dielectric susceptibility, *C* and Ω are the coupling constants, and T_0 is the "unrenormalized" transition temperature. In Eq. (1), we ignore the terms involving the wave vector of the helix. The constant *b* is positive for the second-order Sm-*A*–Sm-C^* phase transition and is negative for the first-order one, while *a*, *c*, η, and Ω are the positive constants. By minimizing *f* with respect to θ and *P*, one obtains

$$a(T-T_0)\theta+b\theta^3+c\theta^5-CP-\Omega P^2\theta=0, \tag{2}$$

$$P-\chi(C\theta+E+\Omega P\theta^2-\eta P^3)=0. \tag{3}$$

Both θ and *P* are zero without the electric field in the Sm-*A* phase. But, *P* is induced parallel to *E* by the alignment of the dipole moments transverse to the molecular axis under electric field. At the same time, θ is also induced by the coupling between θ and *P* originated from the chirality of molecules (electroclinic effect) [1]. When a small electric field $E=E_0$ is applied, the field-induced tilt θ and polarization *P* can be expanded into the power series of E_0 as $\theta=\sum_{n=1}^{\infty}a_nE_0^n$ and $P=\sum_{n=1}^{\infty}b_nE_0^n$. By replacing θ and *P* in Eqs. (2) and (3) by these power series, all the coefficients a_n

and b_n are obtained one by one in numerical order of n. Since the nth order nonlinear permittivity ε_n is generally defined as the nth derivative of the electric displacement D with E_0:

$$\varepsilon_n = \lim_{E_0 \to 0} \frac{1}{n!} \frac{\partial^n D}{\partial E_0^n}, \tag{4}$$

the third-order ε_3 and fifth-order nonlinear permittivity ε_5 are, respectively, obtained as

$$\varepsilon_3 = -\frac{bC^4\chi^4}{a^4(T-T_c)^4} + \frac{2\Omega C^2\chi^4(T-T_0)^2}{a^2(T-T_c)^4} - \frac{\eta\chi^4(T-T_0)^4}{(T-T_c)^4}, \tag{5}$$

$$\varepsilon_5 = \frac{3\chi^7(T-T_0)^7}{(T-T_c)^7}\left\{\eta - \frac{2\Omega C^2}{a^2(T-T_0)^2} + \frac{bC^4}{a^4(T-T_0)^4}\right\}^2 + \frac{3C^2\chi^6(T-T_0)^3}{a^3(T-T_c)^6}\left\{\Omega - \frac{bC^2}{a^2(T-T_0)^2}\right\}^2 - \frac{cC^6\chi^6}{a^6(T-T_c)^6}, \tag{6}$$

where T_c is the transition temperature defined as $T_c \equiv T_0 + C^2\chi/a$. The even-order nonlinear permittivity $(\varepsilon_2, \varepsilon_4, \ldots)$ disappears by the symmetry of polarization to the electric field.

The third-order nonlinear permittivity ε_3 consists of three terms. At the vicinity of T_c, the most significant term in Eq. (5) is the first one. This term shows the critical behavior with the exponent of four and its sign depends on the sign of b; $\varepsilon_3 < 0$ for the second-order transition $(b > 0)$ and $\varepsilon_3 > 0$ for the first-order transition $(b < 0)$. The most significant term in ε_5 near T_c is $3b^2C^6\chi^6/a^7(T-T_c)^7$. This term shows the critical behavior with the exponent of seven and its sign is positive, which is independent of the type of the phase transition.

We measured the temperature dependence of nonlinear permittivity in the Sm-*A* phase for two FLC's to verify the calculated critical behavior. The sinusoidal electric field E whose frequency is much lower than the relaxation frequency of the soft mode is applied to a FLC sample parallel to the smectic layers. The electric displacement D detected by a charge amplifier is measured by a storage oscilloscope. The nth order nonlinear permittivity ε_n is obtained from the applied electric-field dependence of the nth harmonic component of the applied frequency in D. The experimental details of nonlinear dielectric measurement are described elsewhere [9]. The FLC's used in this study are a mixture FLC, 764E (Merck) and 4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxybiphenyl (abbreviated to C7). It is reported that the former FLC shows the second-order Sm-*A*–Sm-*C** phase transition [11] and the latter shows the first-order one [12].

The temperature dependence of ε_3 of 764E and C7 in the Sm-*A* phase are, respectively, shown in Figs. 1(a) and 1(b). As is expected by the theoretical discussion, the sign of ε_3 is negative for the second-order Sm-*A*–Sm-*C** phase transition and positive for the first-order transition. The solid curves in Fig. 1 are the best-fitted ones with $\varepsilon_3 = A(T-T_c)^{-4}$ and the critical exponent of ε_3 is found to be about four in both samples. The obtained best-fitted values are $A = -1.58 \times 10^{-21}$ Fm/V^2 and $T_c = 28.4\,°\mathrm{C}$ for 764 E, and $A = 2.20 \times 10^{-25}$ Fm/V^2 and $T_c = 53.9\,°\mathrm{C}$ for C7. The best-fitted value A for 764E agrees with the calculated value $A = -bC^4\chi^4/a^4 = -2.2\times 10^{-21}$ Fm/V^2 by using the literature values [11] of $a = 2\times 10^4$ J/m^{2}K, $b = 1.7\times 10^6$ J/m^2, and $C\chi = 3.8\times 10^{-3}$ FV/m^2.

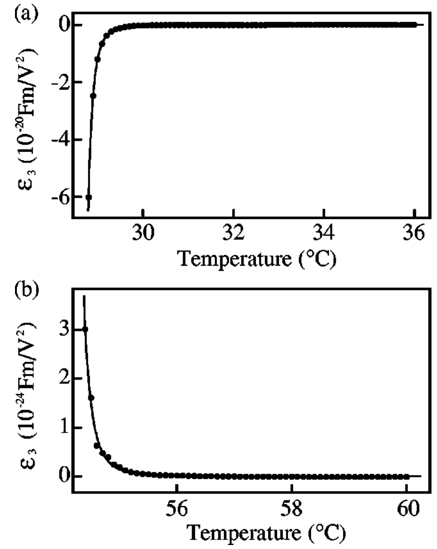

FIG. 1. Temperature dependence of the third-order nonlinear permittivity ε_3 of (a) 764E and (b) C7 in the Sm-*A* phase. The solid line is the best-fitted one with the critical exponent of four.

To observe the critical behavior more in detail, we redraw Fig. 1 in the logarithmic scales as Fig. 2. The apparent deviation from the simple critical behavior drawn as a solid line is observed in both FLC's at high temperature. The value of ε_3 seems to approach a certain negative value far above T_c. Although these deviations might be due to the inadequate accuracy in the measurement of small nonlinear response, such behavior agrees with the calculated temperature dependence of Eq. (5); ε_3 approaches the negative constant value of $-\eta\chi^4$ far above T_c. Therefore, in the case of C7, ε_3 changes its sign from positive to negative at a certain temperature above T_c as shown in Fig. 2.

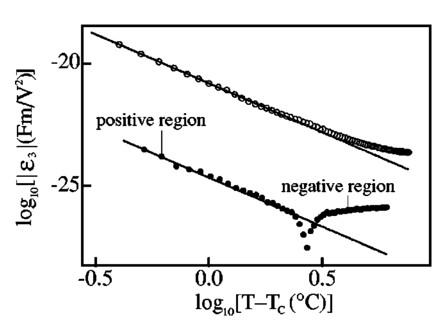

FIG. 2. Temperature dependence of the third-order nonlinear permittivity ε_3 of 764E (○) and C7 (●) redrawn in logarithmic scales. For C7, the sign of ε_3 inverts from positive to negative with increasing temperature. The solid lines are the best-fitted curves in Fig. 1.

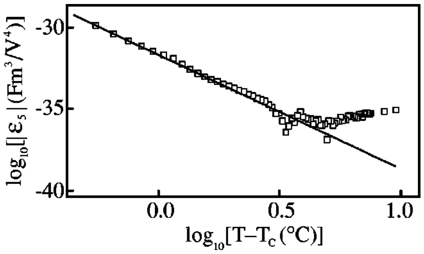

FIG. 3. Temperature dependence of the fifth-order nonlinear permittivity ε_5 of 764E in logarithmic scales. The solid line is the best-fitted one with the critical exponent of seven.

The temperature dependence of ε_5 for 764E is shown in Fig. 3. It was found that the critical behavior of ε_5 near T_c is well ascribed by $\varepsilon_5 = B(T-T_c)^{-7}$ shown as a solid line with $B = 2.10\times 10^{-32}$ $\mathrm{Fm^3/V^4}$ and $T_c = 28.4\,^\circ\mathrm{C}$. The best-fitted value of B agrees with the calculated one by using the literature values [11], $B = 3b^2C^6\chi^6/a^7 = 2.0\times 10^{-32}$ $\mathrm{Fm^3/V^4}$. According to Eq. (6), ε_5 approaches the positive value of $3\eta^2\chi^7$ far above T_c. This is certainly observed in Fig. 3 after ε_5 inverts its sign twice. In the case of C7, the value of ε_5 is so small ($\varepsilon_5 \approx 10^{-38}$ $\mathrm{Fm^3/V^4}$ at $T-T_c = 1\,^\circ\mathrm{C}$) that the experimental accuracy for ε_5 is rather poor and the deviation from the simple critical behavior is clearly observed at $T-T_c = 1.3\,^\circ\mathrm{C}$.

We have also studied the critical behavior of ε_3 for AFLC's near the Sm-A–Sm-C_α^* phase transition. The detailed layer structure of Sm-C_α^* has not been well understood until recently, but the excellent studies of resonant x-ray scattering [13] and optical measurement [14] reveal that the tilted directors form a short-pitched helical structure whose pitch is about several layers. Since this transition is reported to be the second order [15], the critical behavior of ε_3 in the Sm-A phase is expected to be the same one for 764E. The temperature dependence of ε_3 in the Sm-A phase for 4-(1-methylheptyloxycarbonyl) phenyl 4'-octylbiphenyl-4-carboxylate (MHPBC) [16] is shown in Fig. 4 as an example. At the temperature much higher than the Sm-A–Sm-C_α^* phase-transition temperature T_c, ε_3 is negative as expected. But, ε_3 inverts its sign from negative to positive at a certain temperature T_{inv} near T_c. Such critical behavior of ε_3 is also observed in the Sm-A phase of other AFLC's which exhibit the Sm-A–Sm-C_α^* phase transition.

Recently, Bourny and Orihara [17] discussed the spectrum of the linear permittivity of an AFLC near the Sm-A–Sm-C_α^*

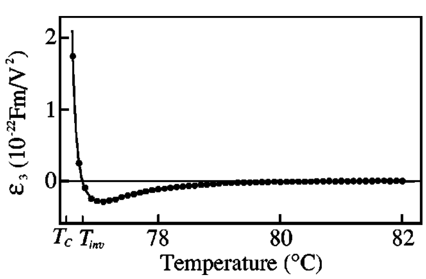

FIG. 4. Temperature dependence of the third-order nonlinear permittivity ε_3 of MHPBC. The solid line is the best-fitted one of Eq. (10) with $T_f = 76.17\,^\circ\mathrm{C}$, $T_c = 76.47\,^\circ\mathrm{C}$, and $\delta = -0.0066$.

phase transition under a dc bias field by the phenomenological free energy that includes the ferroelectric order parameter ξ_f and the order parameter of the Sm-C_α^* phase ξ_q. It is possible to discuss the nonlinear dielectric response near the Sm-A–Sm-C_α^* phase transition by using this simple free energy. By minimizing the free-energy with respect to the ferroelectric polarization P, one obtains the relation $P = \chi(C\xi_f + E)$. After replacing P with this relation, the free-energy density f is written as a function of the tilt angle θ_q and θ_f instead of ξ_q and ξ_f as

$$f = f_0 + \frac{1}{2}\alpha_q\theta_q^2 + \frac{1}{4}\beta_q\theta_q^4 + \frac{1}{2}\alpha_f\theta_f^2 + \frac{1}{4}\beta_f\theta_f^4 + \frac{1}{2}\gamma\theta_q^2\theta_f^2 - C\chi\theta_f E - \frac{1}{4}\varepsilon_a\theta_q^2E^2, \tag{7}$$

where γ is the coupling constant between two order parameters and ε_a is the dielectric anisotropy. By minimizing f with respect to θ_q and θ_f, one obtains

$$\alpha_q\theta_q + \beta_q\theta_q^3 + \gamma\theta_q\theta_f^2 - \frac{1}{2}\varepsilon_a\theta_qE^2 = 0, \tag{8}$$

$$\alpha_f\theta_f + \beta_f\theta_f^3 + \gamma\theta_f\theta_q^2 - C\chi E = 0. \tag{9}$$

When a small electric field $E = E_0$ is applied, there appears the field-induced parts $\delta\theta_q$ and $\delta\theta_f$ in the order parameters as $\theta_q = \theta_{q0} + \delta\theta_q$ and $\theta_f = \delta\theta_f$. Although both order parameters are zero without electric field in the Sm-A phase, we dare to leave θ_{q0} to take into account the fluctuation of θ_q in the Sm-A phase. The field-induced parts can be expanded into the power series of E_0, respectively, as $\delta\theta_q = \Sigma_{n=1}^{\infty} a_nE_0^n$ and $\delta\theta_f = \Sigma_{n=1}^{\infty} b_nE_0^n$. By replacing θ_q and θ_f in Eqs. (8) and (9) by these power series, all the coefficients a_n and b_n are obtained one by one in numerical order of n.

In addition to the ferroelectric polarization P, we take into account the induced polarization due to the change of dielectric tensor by electric field $\delta\varepsilon = \varepsilon_a\theta_q^2/2$ [10,17]. The third-order nonlinear permittivity ε_3 in the Sm-A phase is calculated as

$$\varepsilon_3 = -\frac{\beta_fC^4\chi^4}{\alpha_f^4} + \frac{\varepsilon_a^2\theta_{q0}^2}{6\alpha_q}\left(\frac{2\gamma C^2\chi^2}{\alpha_f^2\varepsilon_a} - 1\right)\left(\frac{6\gamma C^2\chi^2}{\alpha_f^2\varepsilon_a} - 1\right). \tag{10}$$

The first term in Eq. (10) is the contribution of the ferroelectric soft mode already discussed for FLC's and the second term is the contribution of the soft mode for the Sm-C_α^* phase. Although the latter term is not induced by the electric field in the Sm-A phase, we can introduce it by replacing θ_{q0}^2 with its thermal averaged value $\langle\theta_{q0}^2\rangle$. When the second term is positive near $T = T_c$, its contribution will overcome the first term at $T = T_c$ and the inversion of sign in ε_3 can be observed just above T_c.

The critical behavior of $\langle\theta_{q0}^2\rangle$ is written in general as $\langle\theta_{q0}^2\rangle \approx (T-T_c)^{1-\alpha}$, where α is the critical exponent of heat capacity [7]. If we assume that α_f and α_q

are the linear function of temperature T as $\alpha_f \propto (T-T_f)$ and $\alpha_q \propto (T-T_c)$, Eq. (10) can be rewritten as $\varepsilon_3 = -A'/(T-T_f)^4 + B'\{C'/(T-T_f)^2-1\}\{3C'/(T-T_f)^2-1\}/(T-T_c)^{\delta}$, where the exponent δ is identical to α. Since there are so many fitting parameters in this fitting function, we made the fitting procedure by holding the parameter δ to -0.0066 that is the theoretical exponent of α for 3D-XY critical behavior [6]. The best-fitted curve of Eq. (10) drawn as a solid line in Fig. 4, seems to agree well with the data. The obtained value of T_c is 76.47 °C and that corresponds to the temperature where ε_1 shows a maximum value. Therefore, the temperature dependence of ε_3 in the Sm-A phase near the Sm-C_α^* phase is explainable by the phenomenological theory which takes into account the large fluctuation of tilt.

In conclusion, we have studied the critical behavior of nonlinear permittivity in the Sm-A phase of chiral liquid crystals. In the case of FLC's, their critical behaviors are found to be describable by the phenomenological mean-field model and all the coefficients that appeared in the Landau expansion of Eq. (1) would be determined by the measurement of the critical behavior of nonlinear permittivity in the Sm-A phase. In the case of AFLC's near the Sm-C_α^* phase, anomalous temperature dependence of nonlinear permittivity is observed and this is found to reflect the large fluctuation of tilt order parameter in the Sm-A phase.

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