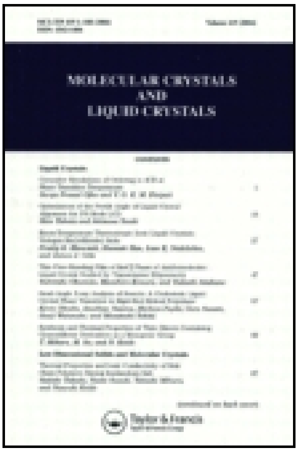

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Critical Behaviour of Nonlinear Dielectric Constants of Ferroelectric Liquid Crystals in the Smectic A Phase

Yasuyuki Kimura [a] & Reinosuke Hayakawa [a]
[a] Department of Applied Physics, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113, Japan
Version of record first published: 23 Sep 2006.

Mol. Cryst. Liq. Cryst. 1995, Vol. 261, pp. 225–232
Reprints available directly from the publisher
Photocopying permitted by license only

THE CRITICAL BEHAVIOR OF NONLINEAR DIELECTRIC CONSTANTS OF FERROELECTRIC LIQUID CRYSTALS IN THE SMECTIC A PHASE

YASUYUKI KIMURA and REINOSUKE HAYAKAWA
Department of Applied Physics, Faculty of Engineering, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract The critical behaviors of the linear and higher-order nonlinear dielectric constants of ferroelectric liquid crystals (FLCs) are studied in the SmA phase near the SmA-SmC* phase transition. The critical exponents of the linear, third-order and fifth-order dielectric constants experimentally obtained are 1, 4 and 7, respectively. These exponents and the signs of nonlinear dielectric constants are in good agreement with those calculated theoretically from the phenomenological theory of Landau type. The influence of the order of phase transition (first or second) on the critical behavior of FLCs is also studied.

INTRODUCTION

The phase transition between the paraelectric smectic A (SmA) phase and the ferroelectric smectic C* (SmC*) phase has been intensively studied[1,2] since the discovery of ferroelectricity in DOBAMBC.[3] In these studies, the phenomenological theory of Landau type (mean-field model) for the phase transition has been applied to interpret the measured temperature dependences of spontaneous polarization, tilt angle, heat capacity, dielectric constant etc. in the SmC* phase. The comparison between the theory and the experimental data has shown that the mean-field model accounts systematically for the critical behaviors of these quantities[1,4,5] and that the critical region estimated from the Ginzburg criterion is very narrow in the SmA-SmC* transition compared with the other cases.[4] The critical behaviors of Curie-Weiss type observed in the SmA phase for the permittivities[4,6,7] such as dielectric and electroclinic constants are also explainable by the mean-field model.

Recently, the dielectric relaxation spectroscopy in the linear regime has been extended to the nonlinear regime and applied to soft materials including liquid crystals[8] and polymers[9]. We have applied the nonlinear dielectric relaxation spectroscopy to the ferroelectric liquid crystals (FLCs) in the SmC* phase and found a large dielectric nonlinearity due to the orientational saturation of dipoles related to the unwinding of helical structure by the electric field.[8] We have also found large nonlinear dielectric constants even in the SmA phase near the SmA-SmC* transition temperature due to the fluctuation of the tilt angle (the soft mode).

In the present study, we investigate the critical behaviors of the nonlinear dielectric constants in the SmA phase of FLCs. The observed behaviors are compared with those predicted by the phenomenological theory of Landau type for the phase transition. The nonlinear dielectric constants reflect the higher-power terms of the order parameter θ (or P) in the Landau-type theory and the comparison makes it possible to check the applicability of the mean-field model for the SmA phase. The influence of the order of the phase transition on the critical behaviors are also studied for two different types (first- and second-order) of FLCs.

EXPERIMENTAL

We apply to the FLC sample the sinusoidal electric field E with the angular frequency ω much lower than the relaxation frequency of the sample. The electric displacement D detected by a charge amplifier is digitized and averaged by a storage oscilloscope (Yokogawa DL3120), and is fed to a personal computer, in which the fundamental and harmonic components of D are obtained by the Fourier transform of the time-domain data.[8] The electric displacement D induced by the sinusoidal electric field E with the amplitude E_0 is given as

$$D=\sum_{n=1}^{\infty}\mathrm{Re}\left[D_{2n-1}\exp\{i(2n-1)\omega t\}\right], \tag{1}$$

where D_m is the amplitude of the m-th order harmonic component of D and is given as

$$D_m=2\sum_{r=0}^{\infty}{}_{m+2r}C_r\cdot\varepsilon_{m+2r}\left(\frac{E_0}{2}\right)^{m+2r}. \tag{2}$$

Here, ε_{m+2r} is the $(m+2r)$-th order dielectric constant. The even-order harmonic components of D do not appear owing to the symmetry in the SmA phase. We use the terms up to r=1 in eq.(2) for the data analysis in this study. The advantage of the frequency-domain measurement of nonlinear dielectric constants is that we can easily obtain the higher-order nonlinear responses separately from each other by their frequencies, which results in a high resolution measurement of the nonlinear responses.

The FLCs used in this study are a FLC mixture, 764E (Merck) and a single component FLC, 3M2CPHpOB[10] (C_7). The former shows a second-order SmA-SmC* transition[11,12] and the latter shows a first-order one[13,14]. The FLC sample is sandwiched between two glass plates with ITO electrodes. The surfaces of both plates are spin-coated with polyimide and rubbed unidirectionally for attaining the homogeneous alignment of FLC.

RESULTS AND DISCUSSION

The applied electric field dependences of the fundamental, third-order and fifth-order harmonic components (real parts) of the electric displacement D_1, D_3 and D_5 for 764E (12Hz) at various temperatures are shown in Fig. 1, in which the solid lines are the best fitting curves using the two terms with r=0 and 1 in eq. (2). The temperature dependences of the linear, third-order and fifth-order nonlinear dielectric constants ε_1, ε_3 and ε_5 obtained from the best fitting procedure are shown in Fig. 2. Both the linear constant and the nonlinear constants increase their magnitudes as we approach to the transition temperature due to the increase of the tilt angle fluctuation (softening). The even-order harmonic components are much smaller compared with odd ones.

To interpret theoretically these data, we calculate the nonlinear dielectric constants by using the free energy density of Landau type[1,2,11,12,14] as

$$g = g_0 + \frac{1}{2}a(T-T_0)\theta^2 + \frac{1}{4}b\theta^4 + \frac{P^2}{2\chi_0\varepsilon_0} - CP\theta - PE - \frac{1}{2}\varepsilon_0 E^2, \tag{3}$$

where g_0 is the energy density of the SmA phase without the electric field E, θ the tilt angle of the FLC molecules, P the polarization parallel to E, $\chi_0\varepsilon_0$ the susceptibility, ε_0 the vacuum permittivity, C the coupling constant between θ and P, and T_0 the transition temperature of racemic mixture. The constant b is positive for the second-order transition and negative for the first-order one, while the constants a, χ_0, and C are always positive. By minimizing g in eq. (3) with respect to θ and P, the stability conditions for θ and P are obtained as

$$a(T-T_0)\theta + b\theta^3 - CP = 0 \tag{4}$$

$$P - \chi_0\varepsilon_0 (C\theta + E) = 0 \tag{5}$$

The stable state in the SmA phase without the electric field (E=0) is θ=P=0, while in the case of $E\neq0$, the dipole moments transverse to the molecular axis align parallel to E and the macroscopic polarization P is induced. At the same time, the tilt angle θ is also induced by the coupling between θ and P (the electroclinic effect[6,7,11,12,14]). By use of the relation $D = \varepsilon_0 E + P$, we can calculate the n-th order nonlinear dielectric constant ε_n defined as

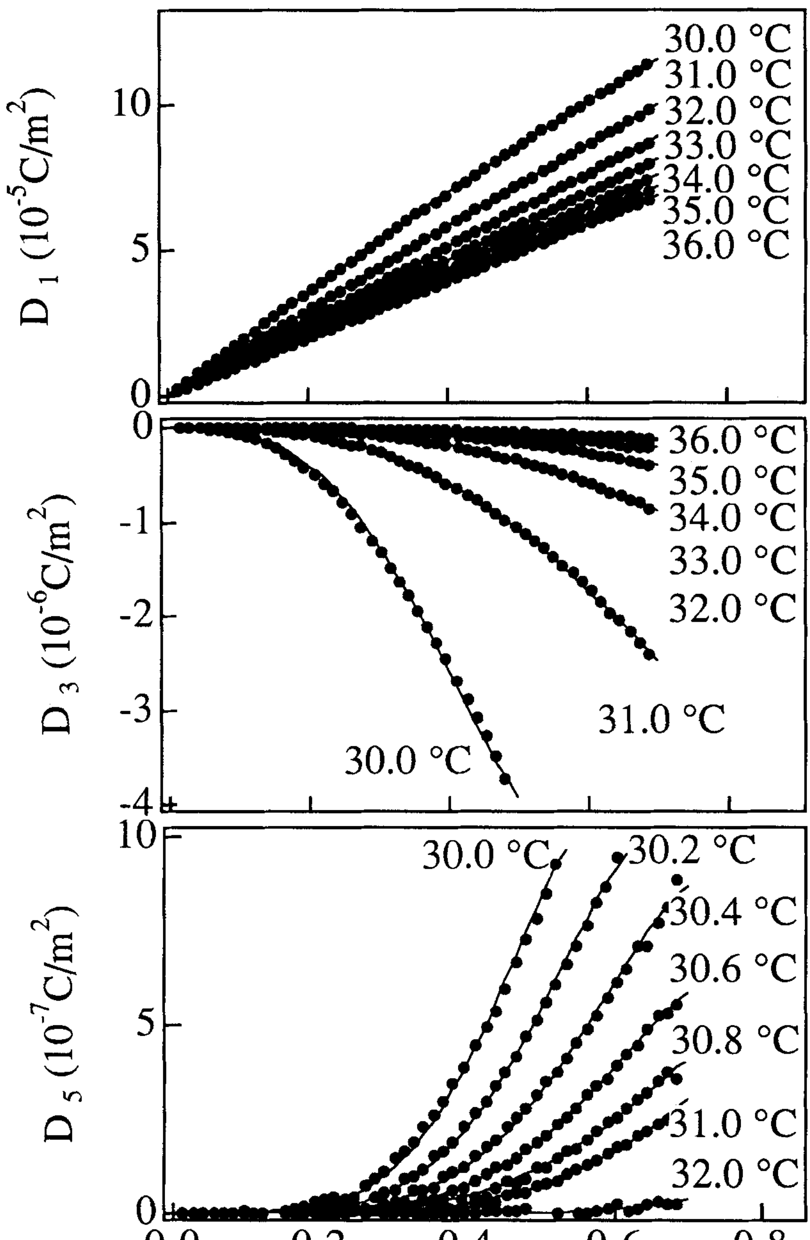

FIGURE 1 The applied electric field dependence of the fundamental, third-order and fifth-order nonlinear components of electric displacement D_1, D_3 and D_5 at various temperatures (764E).

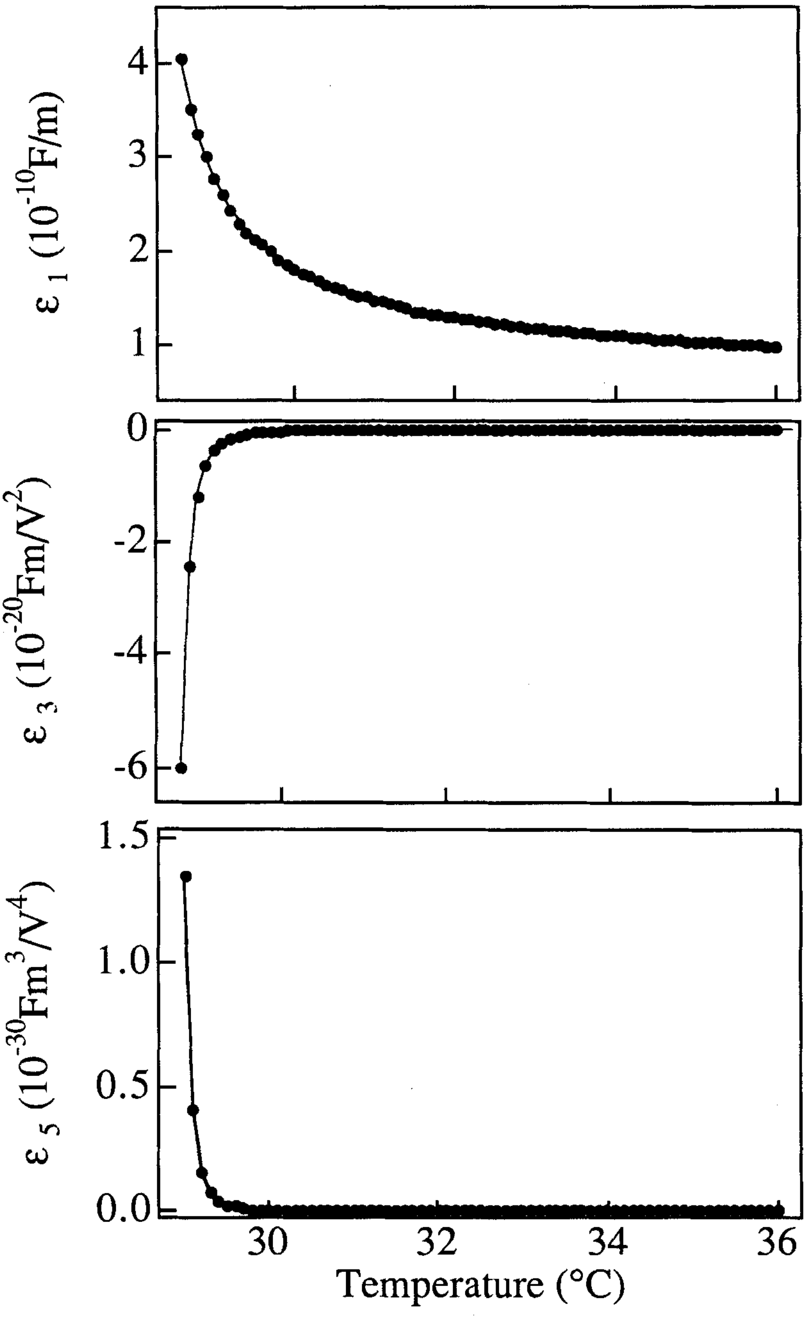

FIGURE 2 The temperature dependence of the linear, third-order and fifth-order nonlinear dielectric constants ε_1, ε_3 and ε_5 (764E).

$$\varepsilon_n = \lim_{E\to 0}\frac{1}{n!}\left(\frac{\partial^n P}{\partial E^n}\right), \tag{6}$$

by differentiating eqs. (4) and (5) with respect to E. The results are

$$\varepsilon_1 = (\chi_0 + 1)\varepsilon_0 + \frac{C^2\chi_0{}^2\varepsilon_0{}^2}{a(T - T_C)}, \tag{7}$$

$$\varepsilon_2 = 0, \tag{8}$$

$$\varepsilon_3 = -\frac{bC^4\chi_0{}^4\varepsilon_0{}^4}{a^4(T - T_C)^4}, \tag{9}$$

$$\varepsilon_4 = 0, \tag{10}$$

$$\varepsilon_5 = \frac{3b^2C^6\chi_0{}^6\varepsilon_0{}^6}{a^7(T - T_C)^7}, \tag{11}$$

where T_C is the transition temperature of chiral sample defined as

$$T_C = T_0 + \frac{C^2\chi_0\varepsilon_0}{a}. \tag{12}$$

The best-fitting curves of eqs. (7), (9), (11) for the measured nonlinear constants are shown as solid lines in Fig. 2. The fitting is satisfactory near the transition temperature. The linear dielectric constant ε_1 consists of two terms: one is a non-chiral term and the other is due to the coupling between θ and P resulting from the chirality of molecules. The latter term shows a critical behavior with an exponent of unity (Curie-Weiss type behavior). The third-order nonlinear constant also shows a critical behavior with an exponent of four and a negative sign. The fifth-order nonlinear constant shows a critical behavior with an exponent of seven and a positive sign. The sign of ε_3 is opposite to the sign of b as seen in eq. (9). For the second-order transition, $b>0$ and thus $\varepsilon_3<0$ which applies to the case of 764E, while for the first-order transition, $b<0$ and hence $\varepsilon_3>0$. The signs of ε_1 and ε_5 are always positive independent of the order of the transition as seen from eqs. (7) and (11). To confirm the dependence of the sign of ε_3 on the order of the transition, we have measured ε_3 for 3M2CPHpOB (or C_7) which is reported by Ratna *et. al.*[13] and Ch. Bahr *et. al.*[14] to exhibit the first-order SmA-SmC* transition. The temperature dependence of ε_3 for C_7 in the SmA phase measured at 100 Hz is shown in Fig. 3. The solid line represents the best-fitting curve of eq. (9) for the measured data, which indicates that ε_3 is positive and the critical exponent is 4. The magnitude of ε_3 for C_7 is much smaller than that for 764E and hence a much larger

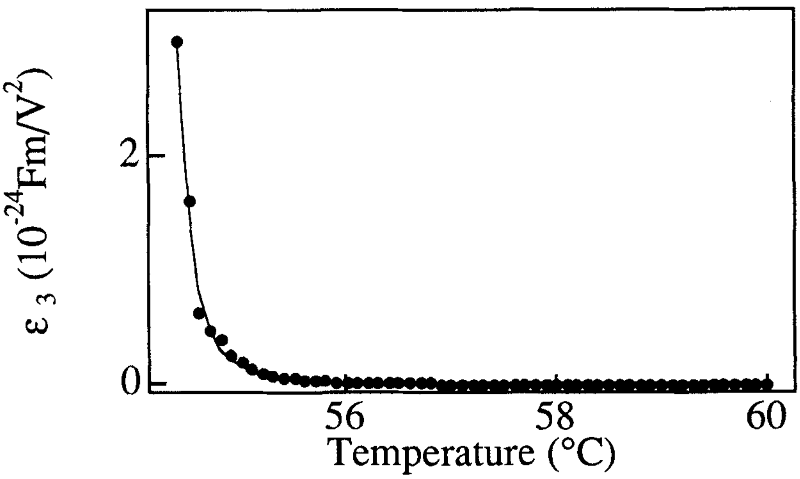

FIGURE 3 The temperature dependence of the third-order nonlinear dielectric constant ε_3 (C_7).

electric field has been used to keep the accuracy of measurement in this case. As mentioned above, the simple phenomenological model given by eq. (3) describes at least qualitatively the critical behaviors of the linear and nonlinear dielectric constants ε_1, ε_3 and ε_5 for both the first and second orders of phase transitions. The nonlinear dielectric constants ε_3 and ε_5 show a deviation from those predicted by eqs. (9) and (11) far above the transition temperature and approach to finite values. In order to explain the critical behaviors in a wider temperature range, it is necessary to add higher-order terms of θ and P to the free energy density in eq. (3). The detailed discussion will appear in a forth-coming paper.

ACKNOWLEDGMENT

The authors thank to Drs. M. Takahashi and T. Sakurai at Ajinomoto Co. Inc. for supplying the 3M2CPHpOB sample. This work is partly supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1. See for example, R. Blinc, in Phase Transitions in Liquid Crystals, edited by S. Martellucci and A. N. Chester (Plenum, New York, 1992) Chap. 22.
2. S. A. Pikin and V. L. Indenbom, Sov. Phys. Usp., 21, 487 (1978).
3. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris), 36 L69 (1975).
4. R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. Goodby, Phys. Rev. A, 27, 1251

(1983).
5. S. Dumrongrattana, C. C. Huang, G. Nounesis, S. C. Lien, and J. M. Viner, Phys. Rev. A, 34, 5010 (1986).
6. S. Garoff and R. B. Meyer, Phys. Rev. Lett., 38, 848 (1977), Phys. Rev. A, 19, 338 (1979).
7. Ch Bahr and G. Heppke, Liq. Cryst., 2, 825 (1987).
8. Y.Kimura and R.Hayakawa, Jpn. J. Appl. Phys., 32, 4571 (1993).
9. T.Furukawa, M.Tada, K.Nakajima, and I.Seo, Jpn. J. Appl. Phys., 26, 1039 (1987).
10. M.Ozaki, K.Yoshino, T.Sakurai, N.Mikami, R.Higuchi, J. Chem. Phys., 86 3648 (1987).
11. Sin-Doo Lee and J. S. Patel, Appl. Phys. Lett., 54, 1653 (1989), 55 122 (1989).
12. Y. B. Yang, A. Mochizuki, N. Nakamura and S. Kobayashi, Jpn. J. Appl. Phys., 30 L612 (1991).
13. B. R. Ratna, R. Shashidhar, G. G. Nair, and S. Krishna Prasad, Phys. Rev. A, 37 1824 (1988).
14. Ch. Bahr and G. Heppke, Phys. Rev. A, 39 5459 (1989), 41 4335 (1990).