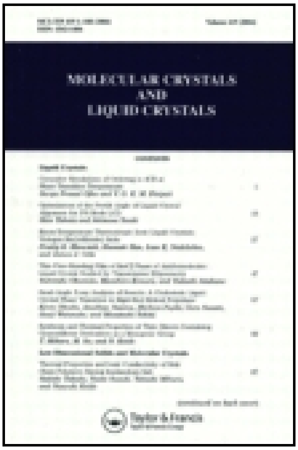


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# Nonlinear Dielectric Measurements of Antiferroelectric Liquid Crystals

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# Nonlinear Dielectric Measurements of Antiferroelectric Liquid Crystals

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We have measured the linear and the third-order dielectric constants of an antiferroelectric liquid crystal MHPOBC and mixtures of R and S-enantiomers. In the optically pure and nearly pure samples with the $SmC_\alpha{}^*$ phase, the third-order dielectric constant discontinuously increases at the transition point from SmA to $SmC_\alpha{}^*$, while the linear dielectric constant is continuous with a small change of the slope in its temperature dependence. These behaviors were well explained by the Landau theory. The optical purity dependence of the Curie constant was also investigated. The Curie constant slightly decreases as the optical purity is reduced, as predicted by the Landau theory.

*Keywords:* antiferroelectric liquid crystal; nonlinear dielectric constant

## INTRODUCTION

The nonlinear dielectric spectroscopy has been made so far in ferroelectric and antiferroelectric liquid crystals and has been shown to be quite useful in studying the phase transitions and the dielectric properties of them.[1-7] In the ferroelectric liquid crystal it has been shown that the nonlinear dielectric dispersion is well described in terms of the Landau-Khalatnikov equation of motion.[3,4] Also in the antiferroelectric liquid crystal, the equation of motion has been applied and the antiferroelectric modes have been theoretically shown to be observable by means of the nonlinear dielectric spectroscopy, though they do not produce polarizations and so they are not detectable by the linear one.[6,7] Actually in experiments the antiferroelectric Goldstone mode has been observed.[5,7]

In general, when a cosine electric field with an amplitude of $E_0$ and a frequency of $\omega$ is applied to the sample, the electric displacement can be expressed in terms of nonlinear dielectric constants as[8]

$$\begin{aligned} D(t) = &\left\{ \varepsilon_1(\omega)\left(\frac{E_0}{2}\right) + 3\varepsilon_3(\omega,\omega,-\omega)\left(\frac{E_0}{2}\right)^3 + \cdots \right\} e^{i\omega t} \\ &+ \left\{ \varepsilon_3(\omega,\omega,\omega)\left(\frac{E_0}{2}\right)^3 + 5\varepsilon_5(\omega,\omega,\omega,\omega,-\omega)\left(\frac{E_0}{2}\right)^5 + \cdots \right\} e^{i3\omega t} \\ &+ \cdots + \mathrm{c.c.}\,, \end{aligned} \tag{1}$$

where we have assumed that the sample is nonpolar, i.e., the eventh-order terms disappear. In the present experiments we have measured the linear and the third-order dielectric constants.

In this paper, we studied the phase transitions of MHPOBC by means of the nonlinear dielectric measurement with the use of an optically pure sample and mixtures of R- and S-enantiomers. In the pure sample and almost pure mixtures the phase sequence is SmA-SmC$_\alpha$*-SmC*-SmC$_\gamma$*-SmC$_A$*-SmI$_A$*-Cryst. In mixtures with low optical purity, on the other hand, the subphases SmC$_\alpha$* and SmC$_\gamma$* disappear.[10,11]

## EXPERIMENTAL AND RESULTS

We used mixtures of R- and S-MHPOBC with ratios of 1:0, 25:1, 19:1, 9:1, 6:1 and 5:1, where the first four samples had subphases. The samples were sandwiched between two glass plates with ITO electrodes, which were separated by PET films. The homogeneous alignment was obtained by coating the plates with polyimide and rubbing them. The thickness was about 2 μm and the area of the electrodes was 1 mm$^2$. In the nonlinear dielectric measurements we used a capacitance bridge (GR 1615A) to make precise measurements, though the measuring frequency range is restricted. The experimental details are described in Ref. [9].

We show the temperature dependences of the linear dielectric constant,

$\varepsilon_1(\omega)$, at 1 kHz for several ratios in Fig. 1. In the pure sample (Fig. 1 (a)) there is an anomaly in the real part, indicated by an arrow, corresponding to the phase transition from SmA to SmC$_\alpha$*, as has been reported by Fukui *et al.*[12] and Chandani *et al.*[11] This anomaly is continuous so that this transition should be of the second order. In the mixture of 19:1 (Fig. 1 (b)) a small anomaly is still seen. In the mixture of 6:1 (Fig. 1 (c)), on the other hand, the anomaly disappears, meaning that SmC$_\alpha$* disappears.

The temperature dependences of the third-order dielectric constant, $\varepsilon_3(\omega, \omega,\omega)$, at 1 kHz for several ratios are shown in Fig. 2. In the pure sample (Fig.

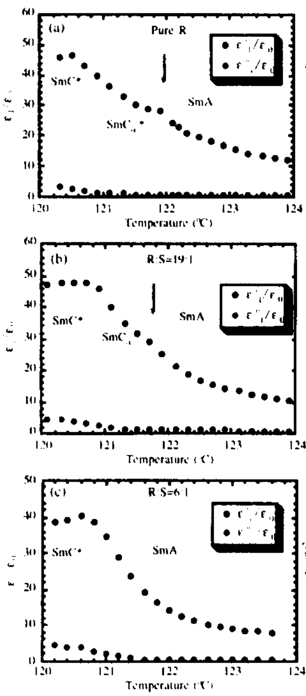


FIGURE 1 Temperature dependences of the linear dielectric constant.

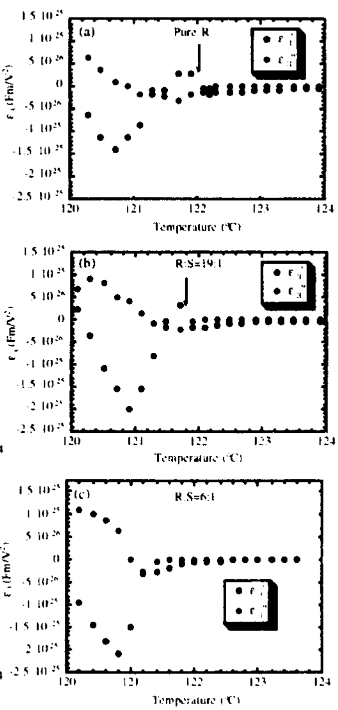


FIGURE 2 Temperature dependences of the third-order dielectric constant.

2 (a)) there is a jump in the real part at the SmA to SmC$_\alpha$* phase transition. Also in the mixture of 19:1 (Fig. 2 (b)) a clear jump is seen. In the mixture of 6:1 (Fig. 1 (c)), on the other hand, the jump disappears since there is no SmC$_\alpha$*. Also for other samples with SmC$_\alpha$*, the jump was observed, in which the real part of the third-order dielectric constant in SmC$_\alpha$* is always larger than that in SmA.



## LANDAU THEORY

In this section we will consider the experimental results on the basis of the Landau theory. The symmetry of SmC$_\alpha$* is not yet clarified, though it is a tilted phase[13]. Therefore, we cannot explicitly define the order parameter by relating it with the structural change. However, there should exist an order parameter and we may apply the Landau theory to this phase transition since it is of the second order. Let us expand the free energy in terms of the order parameter, $\eta$, characterizing the transition:

$$f=\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4+\frac{a}{2}\theta^2+\frac{b}{2}\theta^4+\frac{\delta}{2}\eta^2\theta^2+\frac{1}{2\chi}P^2+\lambda\theta P-PE\ , \qquad (2)$$

where $\theta$ and $P$ are, respectively, the tilt angle and the polarization. In the above free energy, it is natural that there is no $\eta^3$ term because the transition would become the first order if there was the third-order term (the Landau condition [14]) and it is readily understood that all the terms are invariants. We assume that the coefficients $\alpha$ and $a$ depend linearly on the temperature, and in particular $\alpha$ becomes zero at the transition point from SmA to SmC$_\alpha$*. It should be noted that the biquadratic coupling term $\eta^2\theta^2$ is responsible for the jump in the real part of the third-order nonlinear dielectric constant, as will be shown later, though it always exists. In addition, the coefficient $\lambda$ should depend on the optical purity because it has to vanish for the racemic mixture, in which no spontaneous polarization appears. The minimization of the free energy with respect to the polarization, $\partial f/\partial P=0$, yields

$$P=-\lambda\chi\theta+\chi E\ . \tag{3}$$

Substituting this into eq. (2), we get

$$f=\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4+\frac{a'}{2}\theta^2+\frac{b}{4}\theta^4+\frac{\delta}{2}\eta^2\theta^2+\chi\lambda\theta E-\frac{\chi}{2}E^2, \tag{4}$$

where $a'=a-\chi\lambda^2$. From the equilibrium conditions a set of simultaneous equations is obtained as

$$\alpha\eta+\beta\eta^3+\delta\eta\theta^2=0\ , \tag{5.a}$$

$$a'\theta+b\theta^3+\delta\eta^2\theta+\chi\lambda E=0\ . \tag{5.b}$$

Under no field ($E$=0), the equilibrium values are given as

$$\eta_0=0 \text{ and } \theta_0=0 \text{ in SmA}, \tag{6.a}$$

$$\eta_0=\sqrt{-\alpha/\beta} \text{ and } \theta_0=0 \text{ in SmC}_\alpha^*. \tag{6.b}$$

Substituting $\eta=\eta_0+\Delta\eta$ and $\theta=\theta_0+\Delta\theta$ into eq. (5), where $\Delta\eta$ and $\Delta\theta$ are the induced parts by the field, we get for SmA,

$$\Delta\eta=0, \tag{7.a}$$

$$\Delta\theta=-a'^{-1}\chi\lambda E+ba'^{-4}(\chi\lambda E)^3, \tag{7.b}$$

and for SmC$_\alpha$*,

$$\Delta\eta=-\delta\eta_0(a'+\delta\eta_0^2)^{-2}(\alpha+3\beta\eta_0^2)^{-1}(\chi\lambda E)^2, \tag{8.a}$$

$$\begin{aligned}\Delta\theta=&-(a'+\delta\eta_0^2)^{-1}\chi\lambda E\\&+\left\{b-2(\delta\eta_0)^2(\alpha+3\beta\eta_0^2)^{-1}\right\}(a'+\delta\eta_0^2)^{-4}(\chi\lambda E)^3.\end{aligned} \tag{8.b}$$

It should be noted that in SmA the electric field does not induce the order parameter of SmC$_\alpha$*, while in SmC$_\alpha$* it does and the induced order parameter $\eta$ is proportional to the square of the field. The appearance of the coupling between the order parameter and the square of the field is explained as follows. From eq. (4) it is easily seen that in SmC$_\alpha$* such a linear-quadratic coupling term as $\delta\eta_0\Delta\eta(\Delta\theta)^2$ appears. Therefore, taking into account that $(\Delta\theta)^2$ is proportional to $E^2$ in the lowest order, we can understand the above results. With the use of eq. (3) we obtain the static linear and third-order dielectric constants for SmA

$$\varepsilon_1 = \varepsilon_0 + a'^{-1}(\chi\lambda)^2 + \chi \ , \tag{9.a}$$

$$\varepsilon_3 = -b(\chi\lambda)^{-4}(\varepsilon_1 - \chi - \varepsilon_0)^4 \ , \tag{9.b}$$

and for $SmC_\alpha$*

$$\varepsilon_1 = \varepsilon_0 + (a' + \delta\eta_0^2)^{-1}(\chi\lambda)^2 + \chi \ , \tag{10.a}$$

$$\varepsilon_3 = -\left\{b - 2(\delta\eta_0)^2(\alpha + 3\beta\eta_0^2)^{-1}\right\}(\chi\lambda)^{-4}(\varepsilon_1 - \chi - \varepsilon_0)^4 \ , \tag{10.b}$$

where $\varepsilon_0$ is the dielectric constant of vacuum. Equations (9.a) and (9.b) have been already obtained by Sako *et al.*[15]

On the basis of eqs. (9) and (10), we will discuss the experimental results. As for the linear dielectric constant we easily see that it is continuous at the transition point from SmA to $SmC_\alpha$* because $\eta_0=0$ there. We can determine the sign of $\delta$ from the fact that in Figs. 1 (a) and (b) the slope decreases at the transition point from SmA to $SmC_\alpha$*, indicating that $\delta$ should be positive. On the other hand, the third-order dielectric constant jumps at the transition point because the second term in the curly bracket in eq. (10.b) becomes $-\delta^2/\beta$. The magnitude of the jump, $\Delta\varepsilon_3=\varepsilon_3(SmC_\alpha^*)-\varepsilon_3(SmA)$, is

$$\Delta\varepsilon_3 = \delta^2\beta(\chi\lambda)^{-4}(\varepsilon_1 - \chi - \varepsilon_0)^4 \tag{11}$$

This is positive because $\beta>0$ for the second order transition. Therefore, the third-order dielectric constant increases discontinuously at the transition point from SmA to $SmC_\alpha$*, as has been shown in the experiments. Here, we would like to emphasize that such a positive jump in the third-order dielectric constant may take place for any nonferroelectric phase transitions, and so the third-order dielectric constant is sensitive even to nonferroelectric second-order phase transitions.

From eqs. (9.b) and (10.b) it is seen that $\varepsilon_3$ divided by $(\varepsilon_1-\chi-\varepsilon_0)^4$ is an important quantity, which represents the nonlinearity and the coupling between order parameter and the tilt (the polarization). In our experimental results, however, the imaginary part is considerably large because the relaxation frequency is low. Therefore, in calculating the quantity we have to take into account the frequency dispersion. To do so, we used a general formula[16]

$$\varepsilon_3(\omega,\omega,\omega)(\varepsilon_1(3\omega)-\chi-\varepsilon_0)^{-1}(\varepsilon_1(\omega)-\chi-\varepsilon_0)^{-3}, \tag{12}$$

where we measured the linear dielectric constant at 3 kHz, $\varepsilon_1(3\omega)$, in addition to $\varepsilon_1(\omega)$, and replaced $\chi+\varepsilon_0$ by the background in the experimental data, i.e., we used

$$B(\omega)=\varepsilon_3(\omega,\omega,\omega)(\varepsilon_1(3\omega)-\varepsilon_B)^{-1}(\varepsilon_1(\omega)-\varepsilon_B)^{-3} \tag{13}$$

in the actual analyses. Figure 3 shows the temperature dependences of the

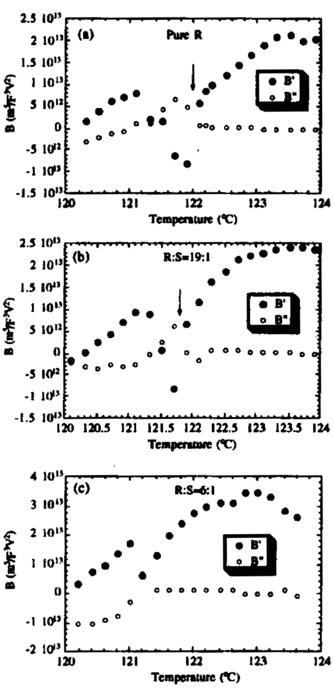


FIGURE 3 Temperature dependences of B.

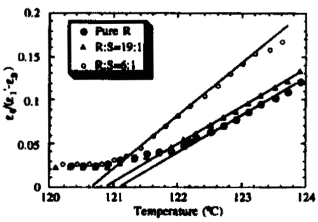


FIGURE 4 Temperature dependences of the reciprocal dielectric constant.

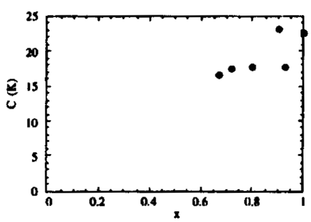


FIGURE 5 Optical purity dependence of the Curie constant.

above quantity. In all the samples, irrespective of whether it has $SmC_\alpha$* or not, the real part of $B(\omega)$ gradually decreases in SmA as the temperature is decreased, as has been reported by Sako *et al*.[14] This decrease indicates that the coefficients should depend on the temperature. Among the three samples, on the other hand, the two samples with SmC$_\alpha$* have a discontinuous decrease in the real part at the transition point from SmA to SmC$_\alpha$*, which is given as $\delta^2\beta(\chi\lambda)^{-4}$ from eq. (11). It should be noted that $B(\omega)$ depends on the temperature in SmC$_\alpha$* and the imaginary part of it becomes to be not zero, though it is theoretically expected to be a real constant, implying that the coefficients depend on temperature and frequency, as described above, or the higher-order terms are involved. Also in SmC$_A$*, $B(\omega)$ depends on the temperature. This temperature dependence may come from the fact that in SmC$_A$* such a simple relation between $\varepsilon_1$ and $\varepsilon_3$ as eqs. (9.b) and (10.b) does not hold.[2]

Lastly, we investigate the optical purity dependence of the linear dielectric constant. From eq. (9.a) it is expected that the Curie constant $C$ may decrease as the optical purity is reduced, since the coefficient $\lambda$ should decrease. We show the temperature dependences of the inverse dielectric constant for the three samples in Fig. 4. The data fall on a straight line in each sample. In Fig. 5 the optical purity dependence of the Curie constant is shown, where the optical purity $x$ is define as $x=(R-S)/(R+S)$. The Curie constant slightly decreases, as predicted by the Landau theory. The measurement in the low optical purity region is now in progress and the result will be reported soon.

## CONCLUSIONS

We have measured the linear and the third-order dielectric constants of an antiferroelectric liquid crystal MHPOBC and mixtures of R- and S- enantiomers . The third-order dielectric constant discontinuously increases at the transition point from SmA to SmC$_\alpha$*, while the linear dielectric constant is continuous with a small change of the slope in its temperature dependence. These behaviors were well explained by the Landau theory, in which we assumed that

$SmC_\alpha$* is nonpolar and there is a bi-quadratic coupling between the tilt angle and the order parameter related to the SmA to $SmC_\alpha$* transition. As for the optical purity dependence it has been found that the Curie constant slightly decreases, as predicted by the Landau theory.

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