The Investigation of the Relaxation Process in Antiferroelectric Liquid Crystals by Electro-Optic Spectroscopy

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The investigation of the relaxation processes in antiferroelectric liquid crystals by electro-optic spectroscopy

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Electrooptic spectroscopy of an antiferroelectric liquid crystal is carried out over a range of frequencies from 1 Hz to 100 kHz. In the antiferroelectric SmC\textsubscript{A} phase two relaxation processes are found, one at the fundamental frequency of a mode and the second at twice the frequency of a different mode. A comparison of the results of the electro-optic spectroscopy with a theoretical study of the motion of the director of an antiferroelectric helix subject to a weak alternating field enables a determination of the origin of the relaxation processes in antiferroelectric phases.

Antiferroelectric liquid crystals (AFLC) are prospective materials for the flat panel displays\textsuperscript{1} for the reason that at least one additional stable state can be added to the bistable switching discovered by Clark and Lagerwall\textsuperscript{2} in FLCs. A determination of the origin of the collective modes will allow for a further improvement in these materials to occur with regard to their switching speeds and hence increase their usefulness for displays and electro-optic devices. A study of the relaxation processes has been made using dielectric spectroscopy,\textsuperscript{3–6} electro-optics,\textsuperscript{4} and photon correlation spectroscopy.\textsuperscript{5} Nevertheless, the problem of finding the mechanisms governing the various relaxation processes in the antiferroelectric phase has not yet been solved and the aim of this letter is to unambiguously establish these mechanisms using electrooptic spectroscopy of an AFLC. Though the nature of the relaxation process in SmC\textsubscript{A} phase has somewhat been speculated in earlier experimental publications,\textsuperscript{3–5} and theoretical works,\textsuperscript{8,9} nevertheless no clear evidence is given and theoretical investigations are divorced from the experiments. In this letter, the mechanism of the collective processes is found on comparing the results of the dielectric and electro-optic spectroscopy with those from the theoretical investigations.

We investigated the dynamics of an AFLC in the 20 \textmu m. The sample used in experiments was AS-573 (Hull, UK) with the phase transition sequence being as follows:\textsuperscript{6}

\begin{align*}
\text{SmC}_A &\quad 78 \degree C \quad \text{SmC}_\text{γ} \quad 81 \degree C \quad \text{AF} \quad 83 \degree C \quad \text{FiLC} \quad 90 \degree C \\
\text{SmC*} &\quad 93 \degree C \quad \text{SmA} \quad 106 \degree C \quad \text{Is.}
\end{align*}

The cell is placed between the crossed polarizers. For the electro-optic spectroscopy, the signal from the photo diode is fed to a lock-in amplifier with a facility of the latter being locked to both the fundamental and the second-harmonic frequency of the signal applied across the sample.

The relaxation processes observed in the SmC\textsubscript{A} phase have been found in the previous papers,\textsuperscript{3–6} The dielectric spectra in the frequency range from 10 Hz to 1 GHz show the existence of two collective relaxation processes and two molecular relaxation processes in the SmC\textsubscript{A} phase and these are denoted as Processes 0,1,2,3 with increasing of the relaxation frequency.\textsuperscript{6} The lower frequency processes (Process 0 and Process 1) are found to exist\textsuperscript{6} only in the two antiferroelectric phases SmC\textsubscript{A} and AF phases. The frequency of Process 0 is \(\sim 2.5\) kHz, whereas that of Process 1 lies between 10 and 70 kHz depending on the temperature.\textsuperscript{5} Hence it can only be concluded that these processes are specifically related to the common characteristics of antiferroelectric phases; however the origin of these processes is still to be explained. Four possible physical mechanisms, some of these already suggested\textsuperscript{3–5} for the collective molecular reorientations in the antiferroelectric phase, are schematically presented in Fig. 1:

(i) A deviation from the antiferroelectric order by the azimuthal angle \(\varphi\), such that \(\varphi\) changing in the opposite sense\textsuperscript{3} in the adjacent layers [Fig. 1(a)]. The mode concerning the fluctuation in \(\varphi\) of the type shown in Fig. 1(a) in the antiferroelectric phase was called antiferroelectric Goldstone mode by Hiraoka et al.\textsuperscript{4} However, rotations of the directors in the opposite directions is termed as “the antiphase motion” by Buivydas et al.\textsuperscript{3} The terminology “antiphase motion” or the distortion of the antiferroelectric order caused by the antiphase motion is more appropriate for the reason that it depicts the mechanism more clearly. The antiferroelectric Goldstone mode in our view be reserved for another relaxation process [Fig. 1(c)], the mechanism of which is similar to that of a ferroelectric Goldstone mode.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Four different physical mechanisms for the molecular rearrangements in the antiferroelectric SmC\textsubscript{A} phase under the applied voltage. \(P_s\) is spontaneous polarization vector, \(C\) being the C director.}
\end{figure}
However, in the literature no direct evidence for the mechanism is given before. Note that among the four proposed mechanisms for the collective relaxation processes, the first three [Fig. 1(a)–1(c)] can be shown to be dielectrically active. The first two [Figs. 1(a), 1(b)] are also electrooptically active at the fundamental frequency and the forth mechanism is electrooptically active at twice the frequency (second harmonic) of mode shown in Fig. 1(c). Therefore a comparison of the results of the dielectric spectroscopy with electrooptics can clarify the origin of the two collective relaxation processes in SmC_A phase seen in the dielectric spectra.

On assuming the existence of the antiferroelectric polarization \( \mathbf{P} \), the equation for the director motion in the antiferroelectric phase can be written as follows:

\[
\frac{\partial \mathbf{P}}{\partial t} = K \frac{\partial^2 \mathbf{P}}{\partial z^2} + \Delta \mathbf{P} E_0 \cos \omega t \cos \phi + \Delta \mathbf{P} \cos^2 \omega t \sin 2\phi, \tag{1}
\]

where \( \gamma = \gamma \sin^2 \theta, K = K \sin^2 \theta, \Delta \mathbf{P} = \Delta \mathbf{P} \sin^2 \theta \beta \pi, \gamma \phi \) is rotational viscosity, \( K \phi \) is elastic constant, \( \theta \) is molecular tilt angle, \( \phi \) is the azimuthal angle, \( \Delta \mathbf{P} \) is the dielectric anisotropy. On using the formula \( \cos \phi \sin \phi = \sin(2\phi)/2 \), Eq. (1) can be written in complex form as

\[
\frac{\partial \mathbf{P}}{\partial t} = K \frac{\partial^2 \mathbf{P}}{\partial z^2} + \Delta \mathbf{P} E_0 \cos(\omega t + \sin(2\phi)). \tag{2}
\]

On assuming \( E_0 \) to be sufficiently small, and on applying the standard perturbation technique, let the solution be of the following form:

\[
\mathbf{P}(z,t) = \mathbf{P}_0(z) + \mathbf{P}_1(z,t) = \mathbf{P}_0(z) + \cos(qz) f_{11} e^{j\omega t} + \sin(2qz) \times (f_{22} e^{j\omega t} + f_{20}), \tag{3}
\]

where \( f_{11}, f_{20}, f_{22} \) are the coefficients of Fourier series proportional to \( E_0 \) and \( E_0^2 \). On substituting Eq. (3) into Eq. (2), we find the coefficients \( f_{11}, f_{22}, f_{20} \):

\[
f_{11} = \frac{\Delta \mathbf{P} E_0}{Kq} \frac{1}{(j\omega \tau_1 + 1)}, \quad f_{22} = \frac{\Delta \mathbf{P} E_0^2}{8Kq^2} \frac{1}{(j\omega \tau_2 + 1)}, \tag{4}
\]

\[
f_{20} = \frac{\Delta \mathbf{P} E_0^2}{8Kq^2},
\]

where

\[
\tau_1 = \gamma / Kq^2, \quad \tau_2 = \gamma / 2Kq^2. \tag{5}
\]

Figure 3 shows the dependence of the amplitude part and the phase part of the electro-optic response at the same frequency as the applied signal for a homogeneously aligned cell. The relaxation frequency is found to be \( \sim 20–30 \text{kHz} \) and is almost of the same magnitude as for the dielectric relaxation Process 1. Therefore we can unambiguously assign this relaxation process in the antiferroelectric phase to the distortion of antiferroelectric order by the electric field caused by a change of angle \( \phi \) arising from the type of motion shown in Fig. 1(a). This may also be called "antiphase
Goldstone mode. We rule out the assignment due to the soft mode [Fig. 1(a)] due to the reasons already given in the previous section.

Figure 4 presents the dependence of the amplitude and the phase part of the second-harmonic electro-optic response at twice the frequency of the signal for an unaligned cell. The relaxation frequency for this process is found to be $6 \text{ kHz}$, which is two times the frequency of Process 0 in the dielectric spectra. As mentioned before, the relaxation Process 0 is found to exist in the dielectric spectra without bias voltage or only under the bias voltage. The nonlinear electro-optic response appears to be caused by the distortion of the helix due to the dielectric anisotropy. The relaxation frequency for this response being approximately two times that for Process 0 in the dielectric spectra is in a good agreement with theoretical predictions [see Eq. (5)]. It may be reemphasized that the helical distortion is caused by two mechanisms: polar interactions $\delta \mathbf{P} \cdot \mathbf{E}$ [Fig. 1(c)] and the interactions due to the dielectric anisotropy $\Delta e \cdot E^2$ [Fig. 1(d)]. The latter cannot be detected dielectrically but is clearly observed in the absence of bias voltage in the electro-optic response at the second harmonic frequency of the applied field for Process 0.

We summarize the findings as follows:

1. The higher frequency relaxation process (Process 1) is due to the distortion of the antiferroelectric order caused by the antiphase motion shown in Fig. 1(a). This may also be called the antiphase antiferroelectric Goldstone mode. It is also observed in the electro-optic response at the fundamental frequency.

2. The lower frequency relaxation process (Process 0) in the dielectric relaxation spectra is the helical distortion mode. Antiferroelectric Goldstone mode is suggested to be the appropriate terminology as its mechanism is similar to that of a helical Goldstone mode. The distortion of the helix caused by the dielectric anisotropy gives rise to an electro-optic response at twice the frequency of the applied field for this process. The reasons for having different frequencies for Process 0 using different techniques are provided by solving a equation that governs the motion of the director of an antiferroelectric helix subject to a weak alternating field.

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