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_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. © *1998 American Institute of Physics.* [S0003-6951(98)01114-0]

Antiferroelectric liquid crystals (AFLC) are prospective materials for the flat panel displays[1] for the reason that at least one additional stable state can be added to the bistable switching discovered by Clark and Lagerwall[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,[3–6] electro-optics,[4] and photon correlation spectroscopy.[7] 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 a AFLC. Though the nature of the relaxation process in SmC_A phase has somewhat been speculated in earlier experimental publications[3–5] and theoretical works,[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 μm. The sample used in experiments was AS-573 (Hull, UK) with the phase transition sequence being as follows:[6]

SmC_A 78 °C SmC_γ 81 °C AF 83 °C FiLC 90 °C

SmC^* 93 °C SmA 106 °C Is.

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_A phase have been found in the previous papers.[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_A phase and these

are denoted as Processes 0,1,2,3 with increasing of the relaxation frequency.[6] The lower frequency processes (Process 0 and Process 1) are found to exist[6] only in the two antiferroelectric phases SmC_A and AF phases. The frequency of Process 0 is ~2.5 kHz, whereas that of Process 1 lies between 10 and 70 kHz depending on the temperature.[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[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 φ, such that φ changing in the opposite sense[3] in the adjacent layers [Fig. 1(a)]. The mode concerning the fluctuation in φ of the type shown in Fig. 1(a) in the antiferroelectric phase was called antiferroelectric Goldstone mode by Hiraoka *et al.*[4] However, rotations of the directors in the opposite directions is termed as ''the antiphase motion'' by Buivydas *et al.*[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.
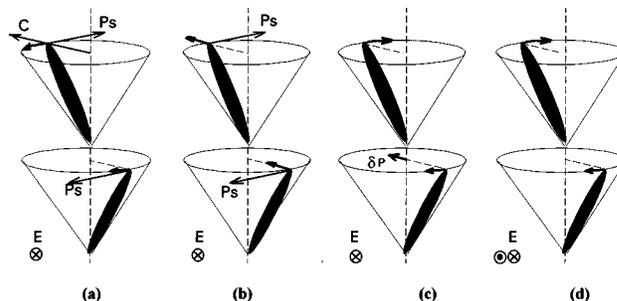

FIG. 1. Four different physical mechanisms for the molecular rearrangements in the antiferroelectric SmC_A phase under the applied voltage. P_s is spontaneous polarization vector, C being the C director.

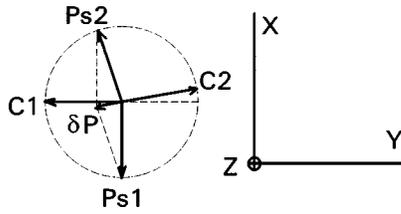[a)]Author for correspondence.

FIG. 2. Schematic presentation of the arrangement of the *C* directors (*C*1,*C*2) local spontaneous polarization (P_{s1}, P_{s2}) of two neighboring smectic layers in helical antiferroelectric phase with respect to the laboratory frame of reference.

(ii) Fluctuations in the tilt angle (θ) or the antiferroelectric soft mode as depicted in Fig. 1(b).

(iii) Helical Goldstone mode due to the existence of ''antiferroelectric'' polarization $\delta\mathbf{P}$ [as shown in Fig. 1(c) and also see Fig. 2]. The explanation for the existence of the antiferroelectric polarization is given later, and

(iv) A disturbance of antiferroelectric helix due to the dielectric anisotropy, $\Delta\epsilon E^2$, Fig. 1(d).

Origin of Process 0: The *C* directors in the adjacent smectic layers are not completely antiparallel to each other even in the antiferroelectric phases.[3] This will give rise to the ''antiferroelectric spontaneous polarization'' $\delta\mathbf{P}$ as shown in Fig. 1(c). This is found to be almost parallel to the *C* directors (Fig. 2). The magnitude of such an ''antiferroelectric polarization'' $\delta\mathbf{P}$ is estimated as follows: Taking into account the typical value of the helical pitch ≈ 2000 Å and the smectic layer thickness ≈ 40 Å, a calculation shows that the angle between the spontaneous polarization vectors in the two adjacent smectic layers is $\sim 176° - 177°$ and the magnitude of $\delta\mathbf{P}$ is approximately 3% of the spontaneous polarization P_s. Such an ''antiferroelectric polarization'' will spiral along the helical axis as does the polarization in a ferroelectric phase. Hence we can expect the dielectric relaxation process to arise from the distortion of the antiferroelectric helix similar to that of a ferroelectric helical Goldstone mode.

Origin of Process 1: The relaxation frequency of Process 1 is higher than that of Process 0. The mechanism can either be the antiphase motion of the type shown in Fig. 1(a) or soft mode [Fig. 1(b)] Hiraoka *et al.*[4] suggested ''antiferroelectric-like'' Goldstone mode for this type of motion, a misleading terminology as mentioned before. In certain investigations of the samples having a direct SmC$_A$–SmA transition, this process was also assigned[10] to the soft mode for the reason that it followed a typical behavior for this mode close to the transition temperature, i.e., relaxation frequency increased with temperature on either side of the transition temperature. Nevertheless, 20 °C below this temperature, the relaxation frequency was found to decrease with decreasing temperature. Although a decrease in the relaxation frequency can be explained with an increase in the rotational viscosity by decreasing temperature, nevertheless an unusual dependence of $\Delta\epsilon$ such as that observed[6] has got no proper explanation, i.e., $\Delta\epsilon$ decreasing instead of increasing close to the transition temperature. Therefore we rule out the ''antiferroelectric soft mode'' as a possible physical mechanism for the Process 1. The relaxation Process 1 is therefore tentatively assigned to the distortion of the antiferroelectric order[4] caused by the antiphase motion [Fig. 1(a)]. The mechanism will later be confirmed through electro-optic spectroscopic investigations.

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 $\delta\mathbf{P}$, the equation for the director motion in the antiferroelectric phase can be written as follows:

$$\gamma\frac{\partial\varphi}{\partial t} = K\frac{\partial^2\varphi}{\partial z^2} + \delta P E_0 \cos\omega t \cdot \cos\varphi$$

$$+ \Delta\epsilon^* E_0^2 \cos^2\omega t \sin 2\varphi, \tag{1}$$

where $\gamma = \gamma_\varphi \sin^2\theta$, $K = K_\varphi\sin^2\theta$, $\Delta\epsilon^* = \Delta\epsilon \sin^2\theta/8\pi$, γ_φ is rotational viscosity, K_φ is elastic constant, θ is molecular tilt angle, φ is the azimuthal angle, $\Delta\epsilon$ is the dielectric anisotropy. On using the formula $\cos\varphi\sin\varphi = \sin(2\varphi)/2$, Eq. (1) can be written in complex form as

$$\gamma\frac{\partial\varphi}{\partial t} = K\frac{\partial^2\varphi}{\partial z^2} + \delta P E_0 e^{j\omega t}\cos(\varphi)$$

$$+ \frac{\Delta\epsilon^*}{2} E_0^2(e^{j2\omega t} + 1)\sin(2\varphi). \tag{2}$$

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

$$\varphi(z,t) = qz + f(z,t) = qz + \cos(qz)f_{11}e^{j\omega t} + \sin(2qz)$$

$$\times(f_{22}e^{j2\omega t} + f_{20}), \tag{3}$$

where f_{11} and 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}, and f_{20}:

$$f_{11} = \frac{\delta P E_0}{Kq^2}\frac{1}{(j\omega\tau_1 + 1)}, \quad f_{22} = \frac{\Delta\epsilon^* E_0^2}{8Kq^2}\frac{1}{(j\omega\tau_2 + 1)},$$

$$f_{20} = \frac{\Delta\epsilon^* E_0^2}{8Kq^2}, \tag{4}$$

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 $\sim 20-30$ 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 φ arising from the type of motion shown in Fig. 1(a). This may also be called ''antiphase
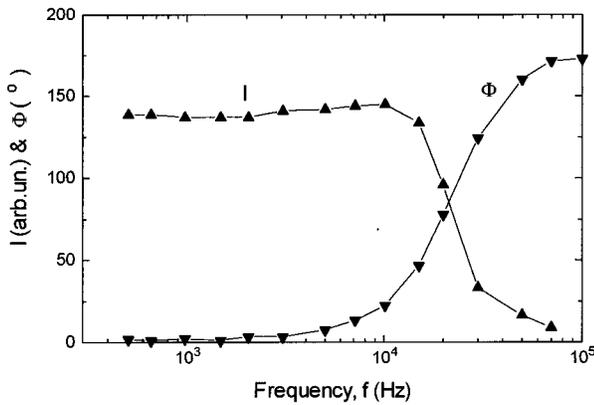
FIG. 3. Frequency dependence of intensity (I) and the phase part (Φ) of the linear response for a well homogeneously-aligned 20 μm cell at 75 °C.

Goldstone mode.'' We rule out the assignment due to the soft mode [Fig. 1(b)] 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 ~6 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[3] or only under the bias voltage.[4] The nonlinear electro-optic response appears to be caused by the distortion of the helix
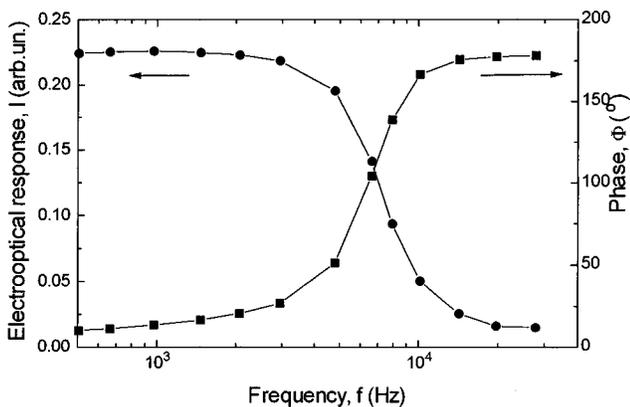
due to the dielectric anisotropy. The relaxation frequency for this response being approximately two times that for Process 0 in the dielectric spectra is in a good agreement with theoretical predictions [see Eq. (5)]. It may be reemphasized that the helical distortion is caused by two mechanisms: polar interactions $\delta\mathbf{P}.\mathbf{E}$ [Fig. 1(c)] and the interactions due to the dielectric anisotropy $\Delta\epsilon.E^2$ [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.

FIG. 4. Frequency dependence of the intensity (I) and the phase (Φ) at twice the frequency of the applied signal for an unaligned 20 μm cell at 75 °C.

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