Electrohydrodynamic Effects in Cholesteric Liquid Crystals under ac Electric Fields*

F. Rondelez and H. Arnould
Laboratoires d'Electronique et de Physique Appliquée, 94 Limeil-Brévannes, France

and

C. J. Gerritsma
Philips Research Laboratories, Eindhoven, The Netherlands

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When an electric field is applied perpendicularly to a cholesteric planar texture, periodic perturbations arise. The frequency dependence of the threshold of this instability is reported for nematic-cholesteric mixtures with both positive and negative dielectric anisotropy. In the latter case a "conduction" and a "dielectric" regime are observed, as in nematics. Our results are in agreement with a recent extension to ac excitations of Helfrich's theories for cholesterics.

The effects of electric fields on a cholesteric liquid crystal have been studied extensively since the pioneering work of Muller[1] and Harper.[2] The case of the field applied perpendicularly to the helix axis has been solved satisfactorily, both theoretically by de Gennes[3] and Meyer[4] and experimentally by Wysocki, Adams, and Haas[5] and by Baessler, Laronge, and Labes.[6] If the electric field is applied in a direction parallel to the helix axis, the effects are more complicated. In the experiments of Wysocki, Adams, and Haas,[7] one of the observations is a 90° rotation of the helical axis, the cholesteric liquid crystal going from the Grandjean or planar texture to the focal conic texture.[8] Baessler, Laronge, and Labes[6] reported a decrease in pitch accompanying a conical deformation, as predicted by Meyer,[4] to occur if the sample is a thin slab. Gerritsma and Van Zanten[9] observed successively a periodic pattern, pitch contraction, and 90° helix rotation at increasing voltages. However, the interpretation of these effects was troublesome. In the meantime, Heilmeier and Goldmacher discovered a "storage effect"[10] in nematic-cholesteric mixtures which could be useful for applications in displays. The situation has been recently clarified by Helfrich[11,12] who proposed a new type of periodic deformation of the planar structure based upon local variations of both the pitch and the direction of the helical axis. His first model[11] takes only a pure dielectric instability into account, whereas in the second model,[12] space charge effects also are included.

In order to check this theory more quantitatively, the dependence of the period of the pattern has been investigated as a function of pitch P and sample thickness L. The agreement is reasonable for small pitch and $\epsilon_a > 0$,[13] as well as for large pitch and $\epsilon_a < 0$,[14] $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ being the difference between the dielectric constants parallel and perpendicular to the preferred molecular axis.

In this Letter, we report the instabilities of a planar cholesteric structure induced by an ac field applied in a direction parallel to the helical axis for both $\epsilon_a > 0$ and $\epsilon_a < 0$. The results are compared with a recent approach by Hurault[15] who has extended Helfrich's theory to ac excitations, using essentially the formalism of Dubois-Violette, de Gennes, and Parodi developed for nematics.[16]

The experiments are carried out with mixtures[17] of di-*p*-*h*-butyl-azoxybenzene[18] (DIBAB, $\epsilon_a = 0.2$) or *N*-[*p*-methoxy-benzilidene]-*p*-*n*-butylaniline (MBBA, $\epsilon_a = -0.5$) with small amounts of cholesteryl nonanoate (CN). These mixtures are cholesteric at room temperature. The mixtures are sandwiched between two conducting semitransparent electrodes, the distances of which are varied from 12 to 250 μm by means of different Mylar spacers.

For $\epsilon_a > 0$ the planar structure is obtained by slowly cooling down from the isotropic phase,[13] while for $\epsilon_a < 0$ this texture is induced by dielectric alignment in an ac field.[19] In both cases rubbed electrodes are used. With increasing ac voltage, the uniform planar texture remains unperturbed up to a threshold voltage V_{th} (rms value). The onset of the perturbation is determined with a polarizing microscope as the optical appearance of a square grid of focals.[13,14] As in nematics, we find that the frequency behavior of V_{th} depends essentially on the sign of ϵ_a. Consequently, we shall report the measurements on these two cases separately.

Case 1, $\epsilon_a = \epsilon_\parallel - \epsilon_\perp > 0$.—Figure 1 shows the de-

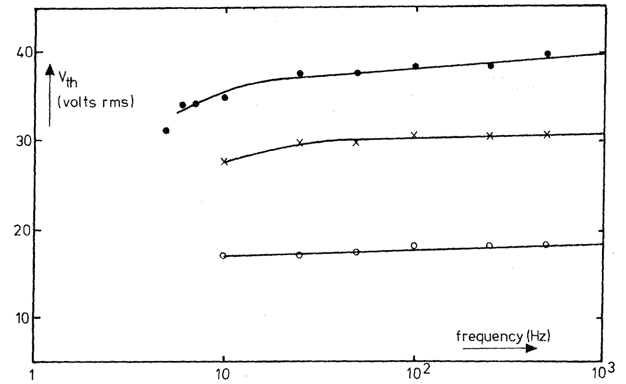

FIG. 1. Threshold voltage V_{th} for periodic perturbations as a function of frequency in DIBAB-CN mixtures. Sample thickness, 80 ± 5 μm. Closed circles, 2.5% CN; crosses, 1.0% CN; open circles, 0.5% CN.

pendence of the threshold voltage V_{th} as a function of frequency for cholesteric DIBAB-CN mixtures with CN concentrations of 0.5%, 1.0%, and 2.5% by weight. The corresponding pitches P were, respectively, 17, 9, and 4 μm; the sample thickness L was 80 ± 10 μm. From 0 to about 100 Hz, V_{th} increases somewhat with frequency, tending to saturation at higher frequencies. In Fig. 1, V_{th} values are given only for the frequency range 5–1000 Hz. From 1000 Hz up to frequencies of 100 kHz, V_{th} remains constant.

This result is the transposition to cholesterics of what has been theoretically predicted[15] and qualitatively observed[20,21] for nematics with $\epsilon_a > 0$. This analogy is furthermore supported by Hurault's approach which yields the following form for V_{th}:

$$V_{th}^2 = 8\pi^3 \frac{\epsilon_{\parallel} + \epsilon_{\perp}}{\epsilon_{\perp}} \frac{1 + \omega^2\tau^2}{\Theta_H + \epsilon_a \omega^2 \tau^2} (\tfrac{3}{2} K_{22} K_{33})^{1/2} \frac{L}{P}, \quad (1)$$

where K_{22} and K_{33} are the Frank elastic constants for twisting and bending, τ is the space-charge relaxation time given by $(\epsilon_{\parallel} + \epsilon_{\perp})/4\pi(\sigma_{\parallel} + \sigma_{\perp})$ in esu, and Θ_H is a dimensionless number characteristic of the material. Note that Θ_H is always positive. Equation (1) predicts that V_{th} tends to saturate for $\omega\tau \gg 1$, which is indeed observed (Fig. 1).

When the pitch P and the sample thickness L are varied, Eq. (1) predicts V_{th} to change proportionally to $(L/P)^{1/2}$. From Fig. 1, one can deduce that V_{th} is proportional to P^x with $x = -0.55 \pm 0.1$. The dependence of V_{th} on L was measured for the mixture with $P = 4$ μm only, in order to satisfy $P \ll L$, while L was varied between 50 and 100 μm. V_{th} is found to be proportional to L^x with $x = 0.45 \pm 0.1$. We conclude that within the measuring accuracy there is agreement between theory and experiment.

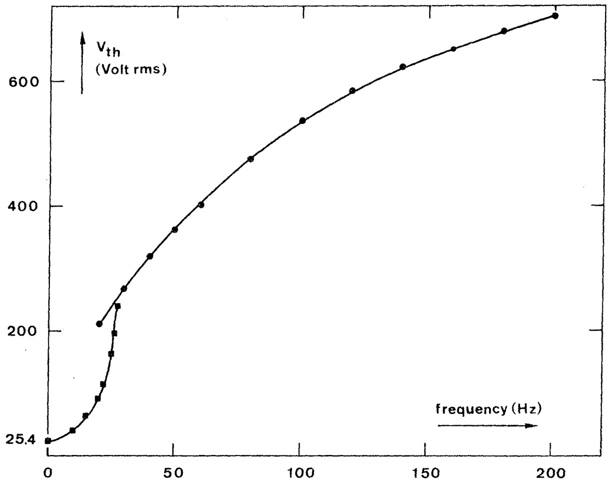

FIG. 2. Threshold voltage V_{th} for periodic perturbations as a function of frequency in an MBBA-CN mixture. Experimental points are for 5% CN; $L = 175$ μm. The solid line in the "conduction" regime is the theoretical curve according to Eq. (1), with $\zeta^2 - 1 = 6.2$. The solid line in the "dielectric" regime is the theoretical curve according to Eq. (2) with arbitrary coefficients.

Case 2, $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} < 0$.—Measurements were performed on MBBA-CN mixtures with 0.1% to 5% by weight of CN. These concentrations correspond to pitches varying from 112 to 4 μm. Figure 2 shows the dependence of the threshold V_{th} with frequency. Two distinct regimes are observed, separated by a critical frequency f_c. The analogy with the behavior of nematics is even more striking here than in the case of positive ϵ_a. Therefore we shall call the low-frequency regime the "conduction" one and the high-frequency regime the "dielectric" one.

In the conduction regime, V_{th} is observed to change proportionally to $(L/P)^x$, with $x = 0.50 \pm 0.09$ when L is varied from 12.5 to 250 μm, and with $x = 0.49 \pm 0.10$ when P is varied from 4 to 112 μm. These results agree quantitatively with Helfrich's predictions and with Eq. (1) which is still valid in that regime. The best fit between the experimental frequency dependence of V_{th} and the theoretical curve is obtained for $\zeta^2 - 1 = 5.0 \pm 1.8$, where $\zeta^2 - 1 = \Theta_H / \epsilon_a$. Knowing the ratio K_{22}/K_{33} from the expression $\Lambda^2 = \frac{3}{2}(K_{33}/K_{22})PL$, where Λ is the period of the distortion pattern at threshold, we get then, with K in dynes,

$$K_{22} = (4.4 \pm 1.7) \times 10^{-7},$$

$$K_{33} = (1.3 \pm 0.6) \times 10^{-6}.$$

The relative inaccuracy of these data is due to the poor determination of ζ^2 by that method. The above values of K_{22} and K_{33} are in reasonable agreement with other data reported in the literature.[22] On the other hand, from Eq. (1), the critical frequency is proportional to the conductivity according to $f_c = (\zeta^2 - 1)^{1/2}/2\pi\tau$. Doping our samples with a quaternary ammonium salt (0.01% to 0.1% by weight of tetrabutyl ammonium bromide), we get another determination of $\zeta^2 - 1$. When the doping concentration increases, the anisotropy of conductivity σ_a decreases.[23] Taking this effect into account, we obtain

$$\zeta^2 - 1 = 4.2 \pm 2.3$$

which represents the value for undoped samples.

Above the critical frequency f_c, we observe the so-called "dielectric" regime. Using samples of different thickness, we find here a *field* threshold $E_{\rm th}$ independent of the pitch. $E_{\rm th}$ varies with the excitation frequency according to a parabolic law: $E_{\rm th} \propto f^{1/2}$. These experimental features are supported by the work of Hurault,[15] where

$$E_{\rm th} = 2(\omega/\lambda)^{1/2}/\zeta, \qquad (2)$$

λ^{-1} having the dimension of a viscosity in esu.

In the dielectric regime, the optical pattern at threshold appears also as a square grid of focals. The period is now much shorter than in the "conduction" regime. This is reminiscent of the "chevrons" period compared with that of the Williams's striations in nematics. However, the situation remains intricate for, in some samples, other patterns appear that are not yet presently understood.

In summary, electrohydrodynamic instabilities have been observed in cholesteric liquid crystals with positive and negative dielectric anisotropy. The frequency dependence of the threshold voltage is very similar to that of nematics. The sign of the dielectric anisotropy is a determining factor.

Good agreement has been found between the experimental results of threshold as a function of frequency and the predictions of a recent theory.[15] Therefore the experimental determination of the parameter ζ and of the period Λ leads to reasonable values of the elastic constants of MBBA + CN mixtures.

Systematic determinations of the various parameters are in progress, together with a more complete study of the dielectric regime. Both will be published in detail elsewhere.

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