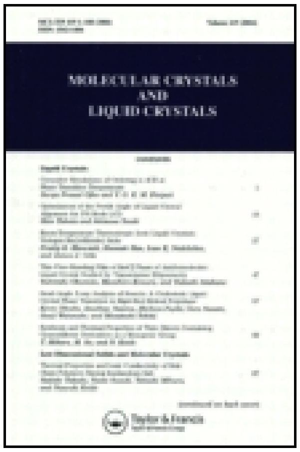

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A Novel Polar Electro-Optic Effect in Thin Large-Pitch Cholesteric Films

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A Novel Polar Electro–Optic Effect in Thin Large-Pitch Cholesteric Films

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Left-handed or right-handed spiral patterns have been observed in thin large-pitch cholesteric–nematic mixtures under the long time application of a DC voltage. The handedness of the winding of the spiral patterns was dependent on the polarity of the voltage, the type of the cholesteric–nematic mixture under study and the thickness of the cells. Their formation has been accounted for by the gradient flexoelectric splay-twist-bend deformation of point singularities formed in the electrode region. The gradient in the electric field was created by the accumulation of injected charges near the two electrodes. It was surprisingly observed that the adding of a small amount of a cholesteric to nematics favours very much the injection from the electrodes. This polar effect might be an important tool for the investigation of the gradient flexoelectric or injection phenomena in the thin large-pitch cholesterics.

I. INTRODUCTION

The realignment of the liquid crystal (LC) director and the deformation of the cholesteric (Ch) layers in the case of the typical polygonal textures in large-pitch Chs were investigated in detail by Bouligand.[1] The various types of the polygonal textures studied by this author have been obtained near the isotropic–cholesteric phase transition where the surface anchoring in general is weak with a conical degeneration in the φ-azimuthal orientation of the LC. The curving of the Ch layers in the polygonal textures usually is symmetric and points out towards the two glass plates which confine the LC. The position of the Ch layers and the orientation of the molecules in the polygonal textures are very complex. For the aim of our study however, only the spiral patterns being formed in the polygons are important. They are with a different handedness of the winding and different position near the two glass plates. Furthermore, single spiral patterns have been observed by Robinson and Ward on droplets of concentrated solution of polypeptides[2] and the explanation of the corresponding configuration has been given by Pryce and Frank.[3] Single spiral patterns have been observed also by Candau *et al.*[4] and by Mioskowski *et al.*[5] on Ch droplets. Finally, spiral patterns only with one handedness of the winding have been observed by Saupe near the free surface of small or large Ch droplets.[6]

We shall show that formation of spiral patterns is possible under the long time application of a DC voltage across a thin large-pitch Ch films as well. We have investigated this phenomenon under various circumstances including the study of left-handed or right-handed cholesteric–nematic (Ch–N) mixtures with a different thickness subjected under the action of AC or DC voltages with a different time duration, etc. Of special importance are the initial conditions with respect to the glass plate preparation, the initial Ch textures, the value of the cholesteric pitch relative to the thickness of the cells under study and especially the distribution of the electric field inside the Ch layers. All the experimental results obtained during our study unambiguously pointed out that the polar development of right-handed or left-handed spiral patterns is chiefly connected with the formation of space charge layers near the boundaries due to the injection from the electrodes. The very spiral patterns arise as a consequence of a symmetric splay-bend gradient flexoelectric deformation of some point singularities created in the electrode vicinity due to the strong nonhomogeneity of the electric field.

II. EXPERIMENTAL RESULTS

A. Compounds and sample preparation

We have investigated the following Ch–N mixtures:

a) 1% wt. CC (cholesteryl chloride), 89% wt. MBBA and 10% wt. 5CB

b) 2% wt. CC, 88% wt. MBBA and 10% wt. 5CB

c) 1% wt. CN (cholesteryl nonanoate), 89% wt. MBBA and 10% wt. 5CB

d) 1% wt. CC, 89% wt. of the LC 440 (a mixture of 2/3 *p-n*-butyl-*p'*-methyloxyazoxybenzene and 1/3 *p-n*-butyl-*p*-heptanoyloxybenzene) and 10% wt. 5CB. The dielectric anisotropy of these mixtures was measured to be between 1.5 and 2.[7] The Chs CC or CN were added to produce the right-handed or left-handed types of the mixture under study, respectively whereas the nematics with negative dielectric anisotropy MBBA or 440 were used to cause either nearly homeotropic (MBBA) or nearly planar (440) orientation of the LC under investigation.

The LC was confined between two semitransparent and conductive glass plates prepared by the usual rubbing technique which at appropriate direction of the rubbing and appropriate position of the glass plates relatively each other can ensure either a homogeneous high tilt of the Ch–MBBA mixtures or a homogeneous low tilt for the mixture which contains the LC 440, i.e. in the first case we obtained nearly homeotropic orientation of the molecules and in the second case nearly planar orientation. Some of the glass plates were additionally treated by soap with the aid of the simple technique already described in our previous work.[7] Nontreated glass plates were studied as well.

B. Experimental observations

First we have investigated the mixture of 1% wt. CC, 89% wt. MBBA and 10% wt. 5CB. The natural nondisturbed by the boundary conditions pitch was measured in thick samples to be around 12 μm in fairly good agreement with the theoretical formula given by Arnould and Rondelez[9]:

$$PC = 0.12\ \mu\text{m}$$

where P is the pitch of the Ch–N mixture and C is the concentration of the cholesteric component. This formula is valid only for small concentration below 5% in agreement with our experimental results. The initial state of such a Ch–N mixture with a high tilt at the boundaries is either Grandjean-like with a screw axis along Z, i.e. normal to the glass plates which usually terminates near the glass plates with two possible "scroll" textures due to the conflicting boundary conditions[10–14] or a complex confocal texture shown in Figure 1 which contains spiral patterns with both handedness of the winding, various dislocations of the Ch layers and many disclinations (see also Ref. 15). The first type of the "scroll" texture shown in

FIGURE 1 A complex confocal texture with left-handed and right-handed spiral patterns in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm; cross nicols, 10 divisions correspond to 45 μm.

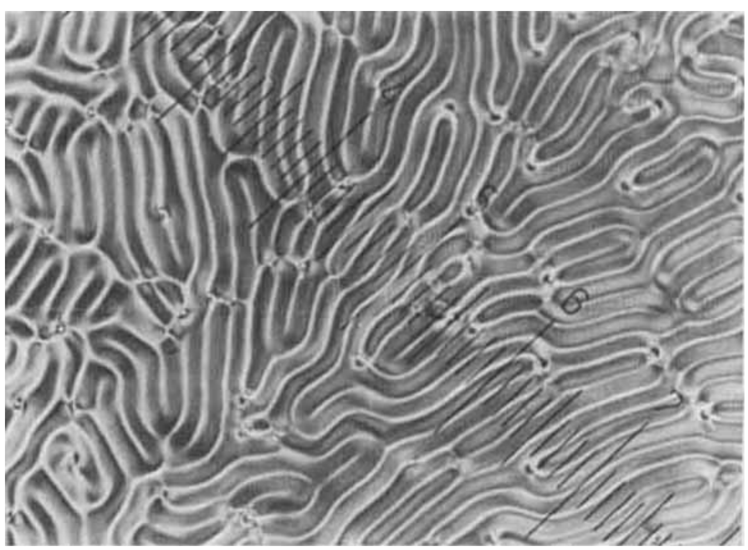

FIGURE 2 "Scroll" (or "disclination pattern") texture formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm after the application and removal of a high-frequency (20 kHz) electric field. The glass plates have been previously rubbed; crossed nicols, 10 divisions correspond to 45 μm.

Figure 2 may usually be obtained when the Ch layer initially is subjected under the action of an AC electric field with a high frequency to prevent the movement of the space charges which then is removed and the cholesterics relaxes to the initial voltageless state. The application of a DC voltage however, very often led to the formation of a second type of "scroll" texture illustrated in Figure 3 after the removal of the voltage. In accordance with the experimental results of Kawachi[13] and Gerber[14] the application of a low AC voltage, in our case several volts, may cause the development of complex "finger-print" or confocal textures like those shown in Figure 1 which finally disappear into a homeotropic pseudo-nematic. On the other hand, the application of a very low AC voltage, in our case 1 volt, was able to transform the initial complex "finger-print" or confocal textures with spiral patterns of both handedness of winding, various kinds of "fingers",[16] uniform branches of deformed stripe patterns and bumps,[17] etc. into the pseudo-nematic. Let us at this point clarify in accordance with Bouligand[1] that in the right-handed spiral patterns the screw of the Ch layers from the center of the spiral to the outer regions is counter-clockwise whereas for the left-handed spiral pat-

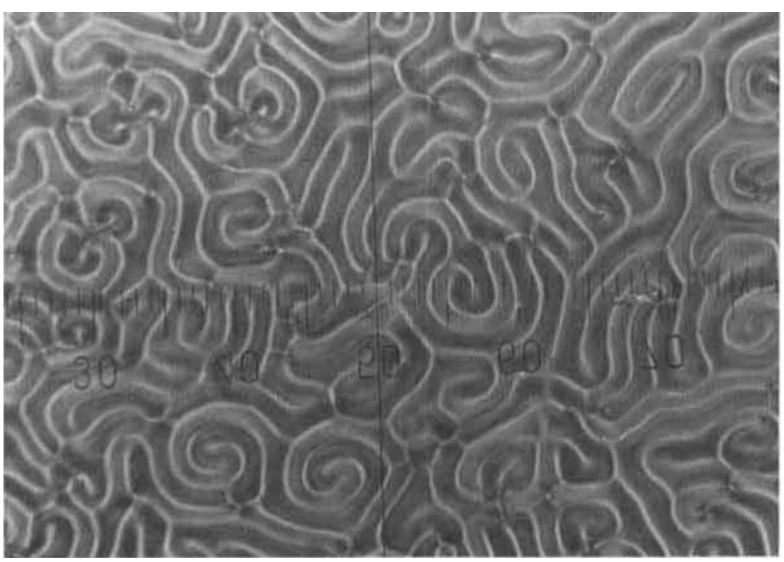

FIGURE 3 A "real scroll" texture formed in a 2% wt. CC-88% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm after the application and removal of a high DC voltage of 10–15 volts. Such a structure can be easily obtained after the relaxation of cross-like or other singularity-like domains; crossed nicols, 10 divisions correspond to 54 μm.

terns it is clockwise. The long time application of a DC voltage, for instance for minutes, however usually caused the formation of a system of spiral patterns with either left-handed or right-handed winding. Such a system of spiral patterns is illustrated in Figure 4. The increase of the voltage up to 10–15 V led to the creation of a strong hydrodynamics and various cross-like or other singularity-like domains. Some of them are shown in Figure 5. After 10–15 minutes the hydrodynamics was stabilized with the formation of many craters with a strong movement of the fluid (Figure 6). Sometimes, at lower voltage it was possible the complete suppression of the hydrodynamics with the formation of a texture like that shown in Figure 5. The decrease of the voltage from 10–15 V to 4–5 V usually was accompanied by the formation of many toric domains.[18]

The shape and size of the spiral patterns observed during our study were very different depending on the different anchoring and pitch of the Ch–N mixtures, the time duration of the DC voltage, the ionic impurity and the treatment of the glass plates. Several examples are shown in Figures 7 and 8. Various kinds of spiral patterns and defects including double spiral patterns were observed in weakly-anchored large-pitch Ch–N mixtures embedded into a pseudo-homeotropic N

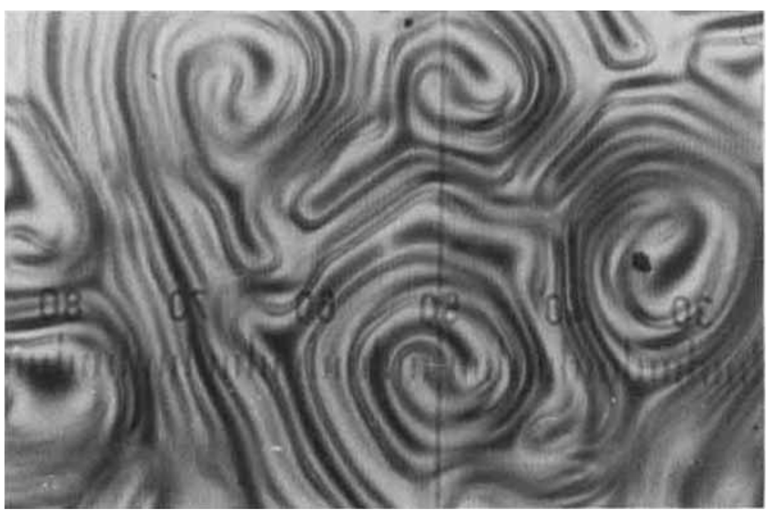

FIGURE 4 A system of spiral patterns with one handedness of winding formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm subjected under the action of a DC voltage of 4.2 V, room temperature; crossed nicols, 10 divisions correspond to 54 μm.

under long time, 10–30 minutes, duration of the DC voltage. On the other hand, the treatment of the glass plates with soap is able to remove the formation of many defects and in particular the double spiral patterns. These experimental findings clearly show the importance of the glass plate topography.

The Ch–N mixtures containing the LC 440 did not show any polar effect possibly due to the strong tendency of the N molecules of this LC to lie in planes parallel to the electrodes. The additional treatment of the glass plate with lecithin however, permitted the formation of nice spiral patterns like those shown in Figure 9.

In thin LC cells, the spiral patterns were very clear visible either under arbitrary position of the two nicols or even without their utilization.[19] The change of the focusing in the depth of the spiral patterns changes very slightly the image of these patterns whereas the optical image of the spiral patterns from the polygons has been drastically dependent on the depth of the focusing.[1] Furthermore the spiral patterns can be obtained more easily from initially "finger-print" texture when the Ch layers are vertical.[15,16,18] On the other hand, it is impossible to form such spiral patterns in initially Grandjean-like

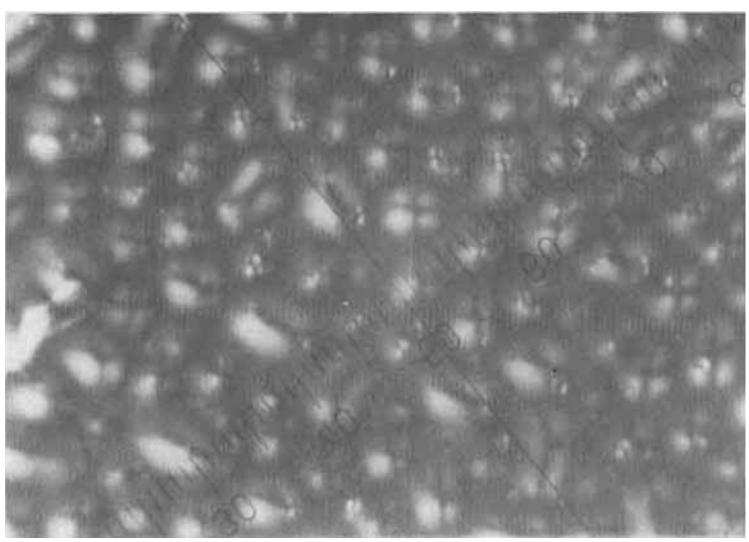

FIGURE 5 A system of cross-like and singularity-like domains formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm subjected under the action of a DC voltage of 10–15 V. The hydrodynamics has been suppressed after 10–15 minutes from the initial excitation of the LC; crossed nicols, 10 divisions correspond to 54 μm.

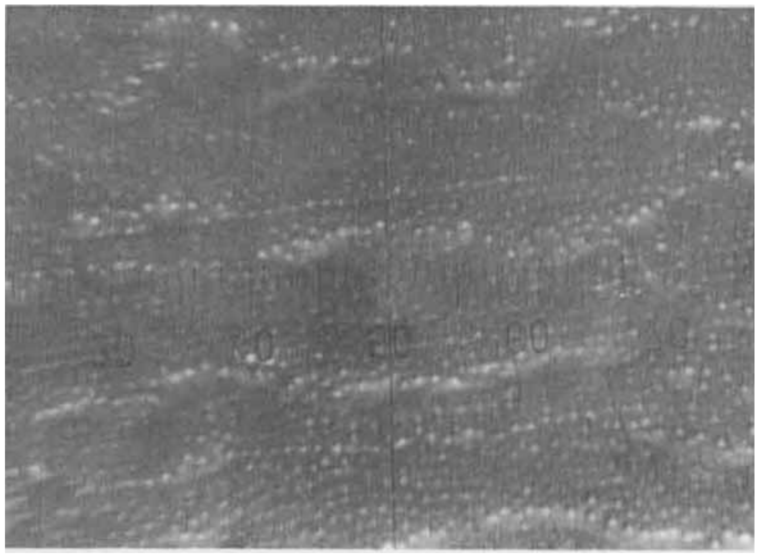

FIGURE 6 A system of cross-like domains and many craters with a strong hydrodynamics in a 2% wt. CC-88% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm subjected under the action of a DC voltage of 10–15 V. This photo has been taken 30 minutes after the initial excitation of the LC; crossed nicols, 10 divisions correspond to 54 μm.

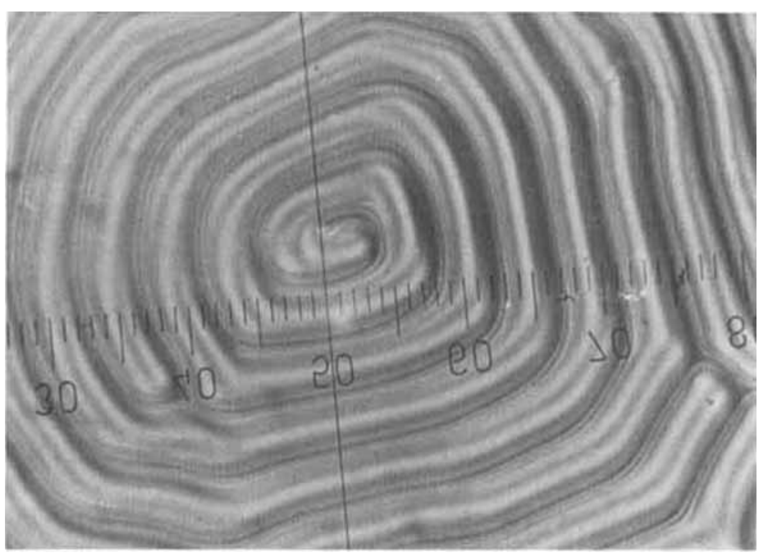

FIGURE 7 A giant spiral pattern formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm under the action of a DC voltage of 4 V; crossed nicols, 10 divisions correspond to 54 μm.

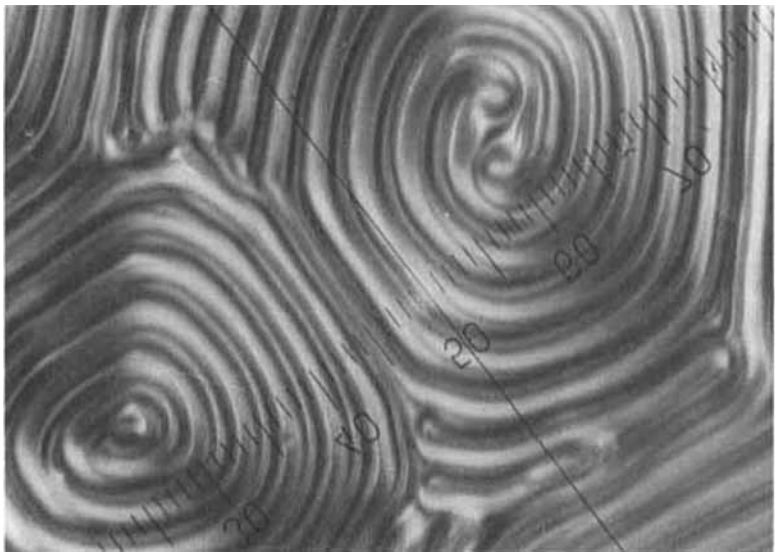

FIGURE 8 Single and double spiral patterns in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB with a thickness of 15 μm under the action of a DC voltage of 5 V. The glass plates have been rubbed and treated by lecithin; crossed nicols, 10 divisions correspond to 54 μm.

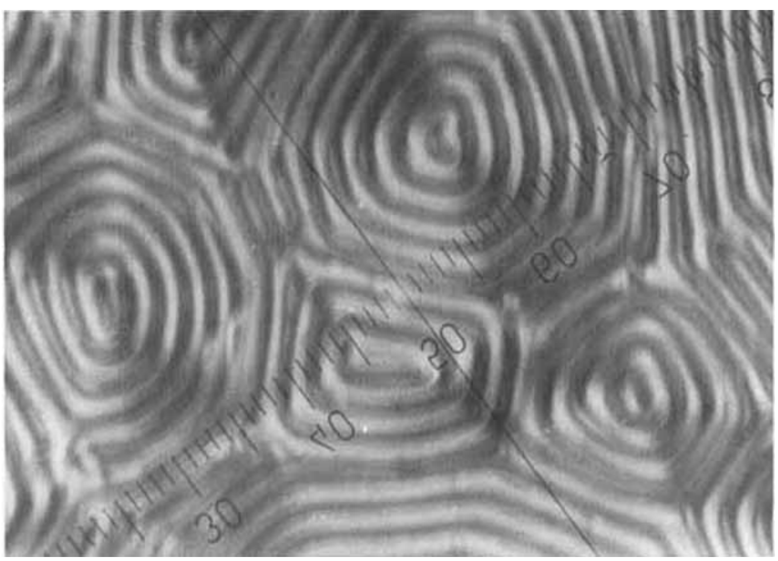

FIGURE 9 A texture with unidirectional spiral patterns formed in a 1% wt. CC-89% wt. 440-10% wt. 5CB mixture with a thickness of 15 μm under the action of a DC voltage of 4.5 V. The glass plates have been rubbed and treated by lecithin; crossed nicols, 10 divisions correspond to 54 μm.

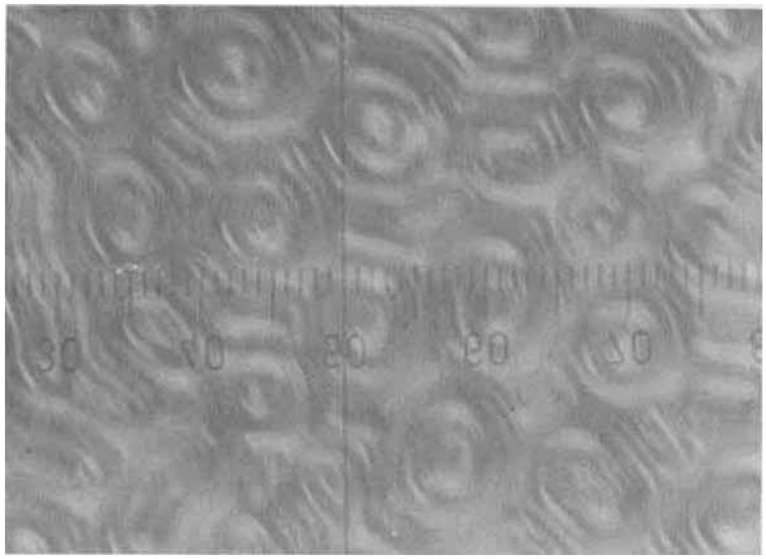

FIGURE 10 A texture with unidirectional spiral patterns formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 55 μm under the action of a DC voltage of 6 V; crossed nicols, 10 divisions correspond to 54 μm.

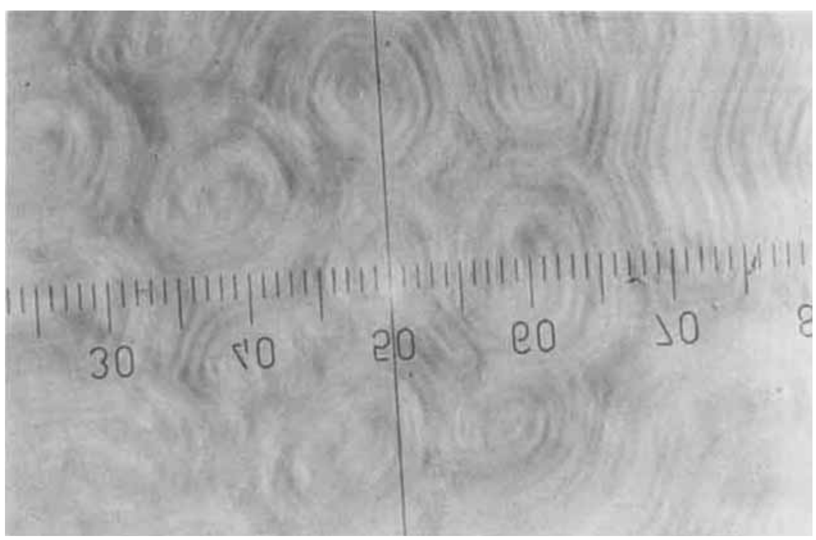

FIGURE 11 A texture with unidirectional spiral patterns formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 55 μm under the action of a DC voltage of 5 V. The photo has been taken without nicols, 10 divisions correspond to 54 μm.

texture, complex confocal (Figure 1) or polygonal textures.[1] The observation of the spiral patterns is especially complicated for thick cells with a thickness above 40 m. It was very difficult to understand the possible handedness of the winding of the spiral patterns due to the complex birefringence of the two optical rays, the additional focusing and the multiplied scattering of the light. This is evident from the pictures shown in Figures 10 and 11. This optical problem can be successfully resolved by the application of an additional AC electric field after the removal of the initially applied DC voltage. In this way, the spiral patterns were more visible due to the unwinding effect of the dielectric torques.

The degree of the unwinding of the spiral patterns after the removal of the DC voltage depends strongly on the thickness of the LC layer under study. For instance, the relaxation of spiral patterns embedded into a homeotropic matrix was always realized by the undulation of the Ch layers in direction parallel to the screw axis and this type of unwinding is shown in Figure 12. This manner of relaxation is typical for nearly all "fingers" embedded into a homeotropic matrix. When the "fingers" are adjacent, the relaxation crucially depends on the

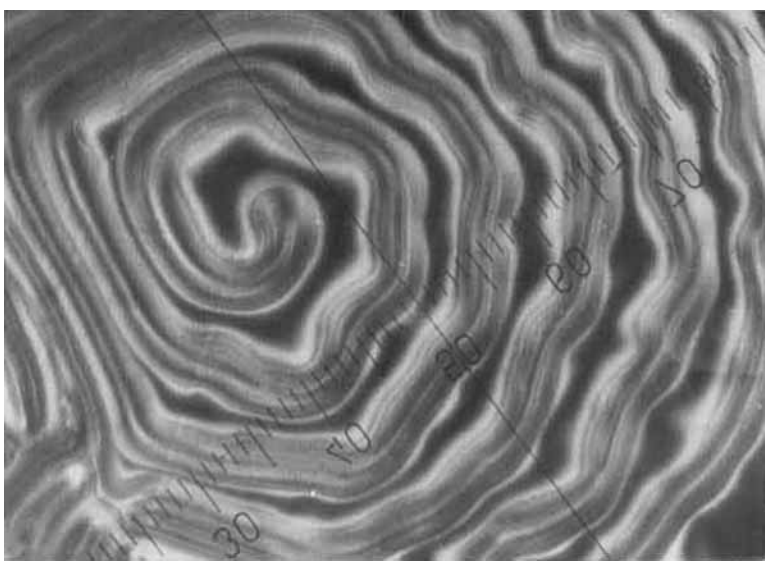

FIGURE 12 Relaxation of a giant spiral pattern embedded into a homeotropic matrix and formed in a 1% wt. CC-89% wt. MBBA-10% wt. 5CB mixture with a thickness of 15 μm under the action of a DC voltage of 4.5 V and its removal; crossed nicols, 10 divisions correspond to 54 μm.

thickness of the layer under study. In case of thin samples only part of the deformation relaxes. In case of thick samples the spiral patterns stay for days after the removal of the voltage as storage patterns.

B. Influence of various physical parameters on the formation of the spiral patterns

a) Influence of the cell thickness. The handedness of the winding of the spiral patterns depends on the value of the thickness and the type (left-handed or right-handed) of the Ch–N layer under study as well as on the polarity of the DC voltage. All these dependences are schematically shown in Figure 13. The position of the spiral patterns has been confirmed by optical measurements in fairly good agreement with the Bouligand's considerations.[1] The application of a DC voltage of 3–5 V across a CC-MBBA-5CB mixture of 30 μm surprisingly led to the formation of *right-handed* and *left-handed* spiral patterns with random position near the two electrodes. The study of the CN-MBBA-5CB mixture, however, *did not show* such a critical thickness. The spiral patterns arose only in relatively thick cells with a thickness above 30 μm (see Figure 13). The increase of the cell thickness up to 110 μm for the case of both Ch–N mixtures removes the formation of the spiral patterns under consideration: in thick cells we have ob-

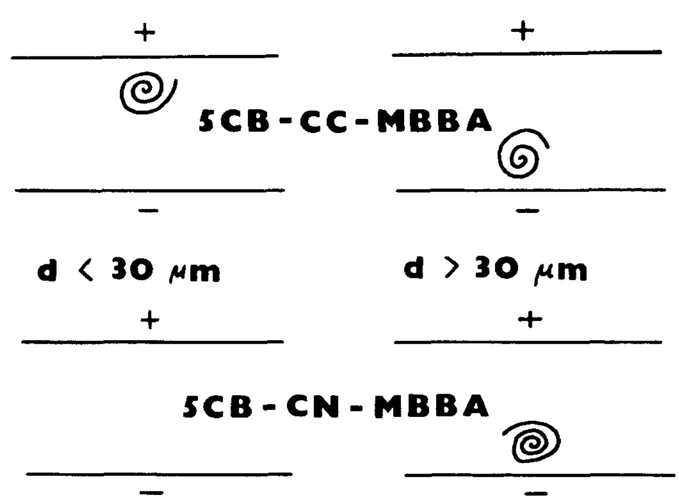

FIGURE 13 A schematic illustration of the formation of the spiral patterns near the cathode and anode depending on the thickness and the type of the Ch–N mixture under study.

served only usual "finger-print", confocal or polygonal textures and spiral patterns with both handedness of the winding.

b) Influence of the boundary conditions and the value of the cholesteric pitch. The treatment of the glass plates which confine the Ch–N mixture under study has no crucial role for the creation of the spiral patterns. The only important requirement is the obtaining of homeotropic or nearly homeotropic orientation of the molecules in the boundary regions. For instance, we have observed spiral patterns with one handedness of the winding in cells with soap-treated, rubbed or nontreated glass plates. The value of the pitch, on the other hand, is of crucial importance. We have observed spiral patterns with one handedness of winding in cells with a thickness between 15 μm and 55 μm and a Ch–N mixture with a pitch between 12 μm and 6 μm. It is easy to obtain such spiral patterns or other defects in the large-pitch Chs when the pitch is comparable to or larger than the thickness of the mixture under study. In addition, when the "fingers" are embedded into a homeotropic matrix, the spiral patterns and all the other defects are formed easily and repeatably, i.e. this texture facilitates very much the obtaining of the polar effect under consideration. The utilization of a Ch–N mixture with a pitch below 10 μm cumbers the creation of the spiral patterns and in the case of mixtures with a pitch below 6 μm, the obtaining of the spiral patterns was impossible. It is evident that the formation of the spiral patterns or the other defects is easier for the case of the large-pitch Chs when the torques which govern their formation are comparable to the weak forces which create the very Ch structure.

c) Role of the DC voltage and the distribution of the electric field inside the LC layers under study. During our experimental investigations we noted the threshold character in the appearance of the spiral patterns or other defects. The threshold voltage was different depending on the current-voltage prehistory of the cells, the conductivity of the Ch–N mixtures and especially on the treatment of the electrodes. It was typically between 3 and 5 volts. This voltage raised up to 7 V only for cells with soap-treated electrodes. All the experimental findings clearly pointed out that the current-voltage characteristics of the Ch–N mixture under study and the electric field distribution are extremely important for the formation of the spiral patterns. Unfortunately the current-voltage problem for the case of the cholesterics or Ch–N mixtures hitherto is insufficiently investigated.[20,21] Now we only know that the mobility of the space charges of these liquid crystals is between 10^{-5} and 10^{-7} cm^2 V/sec. This mobility is in the same order of magnitude as that of the charge carriers of the nematics, and particularly of MBBA.[22,23] The current-voltage characteristics of the Ch–N mixtures under study, which are not published here due to their preliminary character, unambiguously pointed out that from a very low voltage well below 1 V up to 10–15 V a pronounced *injection* from the electrodes exist. It was confirmed by the existence of "inverse potential" due to the accumulation of negative charges near the cathode and positive charges near the anode. The value of this "inverse potential" was between 0.8–1 V for thin cells with a thickness below 15 μm and around 1.5 V for thick cells. The "inverse potential" was typical for the low conducting Ch–N mixtures with a resistivity of MΩ resulted in the weak current which was in the range from several to several tens μA. Let us stress that a small amount of a cholesteric additive can drastically change the DC current-voltage characteristic of the nematic. For instance, our experimental measurements performed only on MBBA clearly have shown the existence of well defined double electric layers with a saturation potential of 1.5 V when the applied DC voltage across the whole MBBA layer has been 4–5 V (see also the results and comments in Refs. 24–28). Evidently, the small additive of a cholesteric facilitates very much the injection and the double electric layers are replaced by injection charge carriers layers. The current-voltage characteristics of our cells were very strongly dependent on the cell thickness. The application of a high DC voltage between 10 and 15 volts across thin Ch–N mixtures for seconds and even for minutes led to the sudden increase of the current from 100 to 500 times and to the sudden decrease of the "inverse potential" due to the injected space charges to zero. All these experimental observations together with the strong linear dependence between the enlarge current and the voltage clearly pointed out the Ohmic character of such cells for the case of a high DC voltage. We *did not observe* in this case any formation of spiral patterns. Consequently, the polar appearance of the spiral and the other defects is directly related to the strong *nonhomogeneity* of the electric field near to the electrodes. It is interesting to note that the appearance of the spiral patterns depends very strongly on the state and nature of the electrodes. For instance, the long time duration of the applied high DC voltage (10–15 V) can lead to irreversible changes of the electrodes which remove completely the spiral patterns. However, when the DC voltage is applied for a short time, the electrodes might be returned to their initial state by short time application of a high frequency electric field. The appearance of the spiral patterns depends crucially on the existence of space charge layers not only near to the electrodes but rather in depth of the Ch–N mixture under study. It is well known that space charges can be generated from the electrodes by the injection mechanism[29–32] or by field-assisted dissociation.[27]

III. DISCUSSION

We see from the experimental observations that it is not possible to attribute the formation of the spiral and the other patterns only to the existence of surface defects. After the long time application of a DC voltage with a threshold or abovethreshold value the spiral and other defect patterns can cover the whole area of the Ch–N mixture under study. For the case of the spiral patterns one notes a distinct symmetry in the winding. In our opinion, all the patterns observed including the spiral ones represent gradient flexoelectric induced large-pitch cholesteric defects. However, they can arise only under many requirements which shall be pointed out below.

Let us start with the possible explanation of the most simple single spiral patterns. It is evident *apriori* that such defects can arise only in large-pitch cholesterics with initially homeotropic orientation of the molecules at the bounding surfaces. The slight degeneration in the symmetry by any arbitrary inclination of the molecules in these regions shall lead to the appearance of many other defects not described here. The second our conclusion is that the symmetrical splay-twist-bend distortions in the boundary regions are induced by gradient flexoelectric mechanism already observed and clarified in the case of nematics.[33,34] This idea indirectly is supported by the observation of spiral patterns on Ch droplets arising from complex splay-twist-bend deformations of the N director around different point singularities.[2–5,35–39] On the other hand, the strong flexoelectric torques can induce different singularities even in the unwinded pseudonematic shown in Figures 5 and 6 or in nematics.[40] The spiral patterns can be obtained after the symmetrical deformation of initially homeotropic orientation[37] which in our case is imposed by the strong dielectric torques acting immediately after the application of the DC voltage. On the other hand, the symmetrical splay-twist-bend of the molecules leading to the complex curving of the Ch layers is caused by the gradient flexoelectric torques due to the nonhomogeneity of the electric field in Z direction perpendicular to the glass plates.[33,34] Consequently, for the single spiral patterns we propose the topological model shown in Figure 14 for the case of the point singularity $n = +2$ ($S = +1$). It is clear that the inclusion of other point singularity defects shall lead to other curving and position of the Ch layers and to other orientation of the molecules. Let us point out that the curving of the Ch layers is near to the glass plates in agreement to our optic observations. In addition the topological model clearly shows that spiral patterns can be easily formed from the initial vertical position of the Ch layers, for instance of the "finger-print" texture. As noted, the spiral patterns cannot be formed from Grandjean-like orientation of the Ch layers or from already formed polygonal textures. On the other hand, the flexoelectrically generated spiral patterns are very different from the spirals in the so-called "scroll" texture shown in Figure 3. Such spirals match the symmetrically inclined orientation of the molecules at the boundaries with the Grandjean-like orientation of the Ch in the depth of the layer. The explanation can be easily obtained from the detailed investigations of Bouligand.[1,43] It is much more difficult to explain why the spiral patterns change their handedness of winding with the increase of the thickness of the Ch–N mixture. As noted, it is evident that the appearance of the spiral patterns is directly linked with the nonhomogeneity of the electric field and the formation of thick space charge layers at the electrodes. Our experimental observations have clearly shown that the nonhomogeneity of the electric field is created by the injection from the electrodes.[44,45] It is necessary to stress that the polar effect investigated in this study is due to the *double injection* from the electrodes. This claim is based on the reversal in the sign of the spiral patterns with increasing of the thickness of the Ch–N mixture. Having in mind that the formation of the spiral patterns is needed first, from a relatively high electric field which should orient the molecules in the boundary regions homeotropically and second, from a gradient in the electric field with a given sign because the other sign is connected with flexoelectric torques which orient the molecules homeotropically, we have assumed the existence of injection from the two electrodes with a *different strength*. According to Turnbull[46] when the electrodes are too near, in our case around and below 30 μm, prevails the more stronger injection, while in the relatively thick cells the injection from the two electrodes is important. For the case of CC–MBBA-5CB mixture our assumption is illustrated in Figure 15. It is clear that the injection from the cathode is more stronger than the injection from the anode and in case of thin cells the spiral patterns are formed near the anode where the electric field is more stronger. In addition, it seems that the flexoelectric deformation in this mixture is favoured by the negative sign of the derivative of the amplitude of the

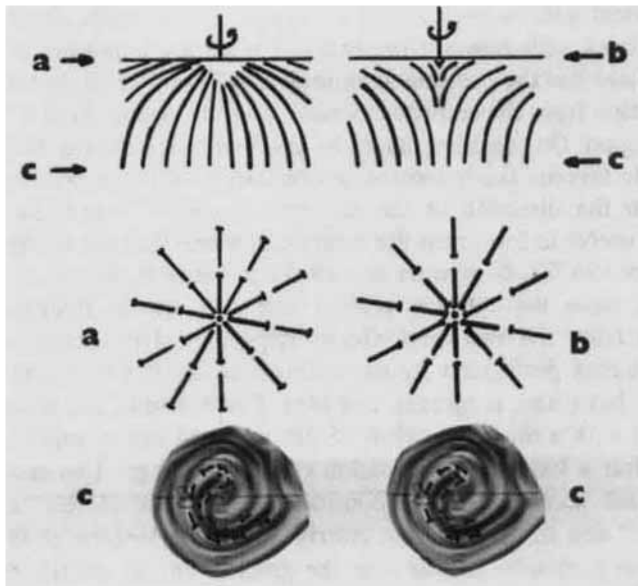

FIGURE 14 A possible topologic model for the creation of single spiral patterns in large-pitch cholesteric with a point singularity $n = +2$ ($S = +1$).

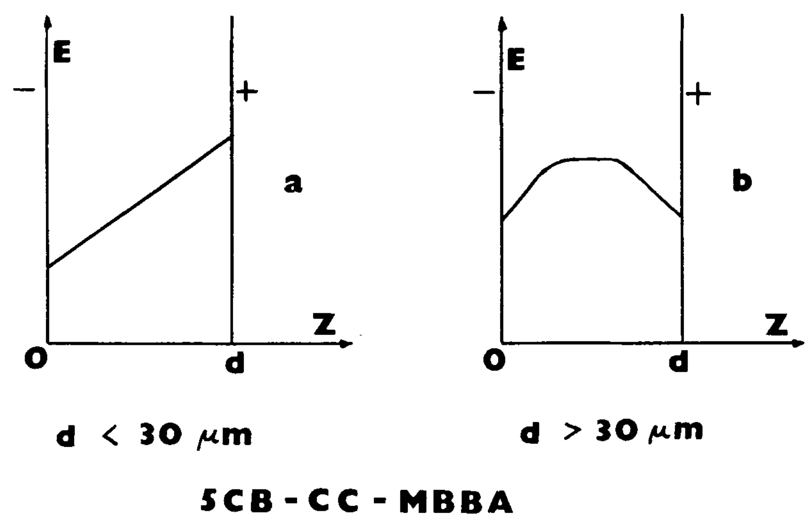

FIGURE 15 A schematic illustration of the electric field distribution in the CC–MBBA-5CB mixture with a different thickness. In thin LC cells prevails the injection from the cathode while for the case of thick cells the injection from the two electrodes is important.

electric field with respect to the coordinate Z, i.e. when $dE/dz < 0$. For the thick cells however the two injections are important and the electric field has the possible form shown in Figure 15, b. In this case the injection from the cathode is weaker and the electric field is higher in this region. On the other hand, the gradient in the electric field near the anode favours the homeotropic orientation of the molecules since it acts in the direction of the dielectric torques[33,34] and the spiral patterns prefer to form near the cathode. It seems that the thickness of 30 μm for this Ch–N mixture is critical and below it prevails only the injection from the cathode while above this critical thickness the injection from the two electrodes is important. The current-voltage measurements performed by us in thin and thick CC–MBBA-5CB mixtures have also supported this idea. For example, the current in thin cells with a thickness below 15 μm as noted can increase significantly after a long time application of a DC voltage. This raising in the current accompanied by considerable decrease of the "inverse potential" due to the injection clearly shows overlapping of the two space charge clouds. In this case the gradient in the electric field is weak. The very spiral patterns can form even in the case when the potential due to the electrode charge layers is in the range of 50–100 mV. The further decrease of the value of this potential however, led to the disappearance of the spiral patterns. Inversely, the current in thick cells was very stable and not dependent on the time duration of the DC voltage. In addition, it seems that the threshold voltage necessary for the creation of the spiral patterns has been apparently linked with the *saturation* of the charge layers near the two electrodes. For thin cells this voltage was between 3–4 volts while for thick cells it was about 6–7 volts. Furthermore, the raising of the voltage above this value did not change considerably the "inverse potential" due to the injected charges which evidently shows the saturation of the injection phenomenon. The strength of the injection either from cathode or from anode was strongly dependent on the small amount of the Ch added to the Ns. For instance, the LC CC favours the injection from the cathode while the CN favours the injection from the anode as is schematically illustrated in Figure 16. Our assumption has been supported by the disappearance of the spiral patterns with one handedness of the winding in thin CN–MBBA-5CB mixtures. In thick mixtures however, the spiral patterns have existed near the cathode. In general, surprisingly we observed that the add of a small amount of a certain Ch to the Ns drastically changes their current-voltage characteristics. It can decrease considerably the saturation voltage which shows the separation of the impure ions and the corresponding

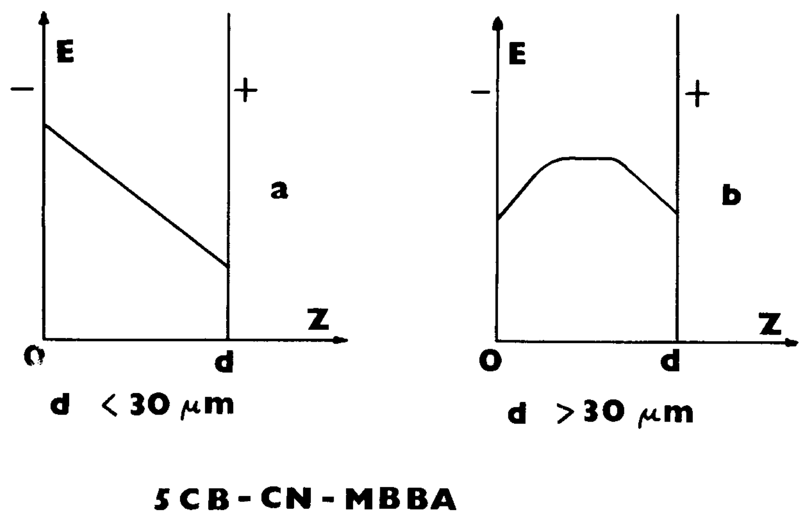

FIGURE 16 A schematic illustration of the electric field distribution in the CN–MBBA-5CB mixture with a different thickness. In thin LC cells prevails the injection from the anode while for the case of thick cells the injection from the two electrodes is important.

saturation of the two double electric layers and can extremely favour the injection from the two electrodes. The injection phenomenon was also supported by the strong electric field accompanied the spiral pattern formation being between 2×10^3 V/cm and 10^3 V/cm, the strong dependence of the space charge layer formation with respect to the electrode treatment, the current-voltage prehistory of the sample under study and the role of the impurity content, etc. In addition, the application of a very low frequency AC voltage between 0.1 Hz and 1 Hz did not show any formation of the spiral patterns. The formula for the cutting frequency of the injection has been given, for instance, by Honda[48] and includes the charge quantity Q, the conductivity σ, the maximal voltage applied across the cell $U_{\max}$ and the thickness of the cell d:

$$f_c = (\sigma/2Q)(U_{\max}/d)$$

It seems that this frequency for our experimental investigations lies below 0.001 Hz which was not achievable with our equipment.

It is possible to give some quantitative explanation for the connection between the appearance of the spiral patterns and the degree in the nonhomogeneity of the electric field, and the accumulation of the space charges. For this purpose, it is sufficient to use the dimensional number C_0 introduced by Atten.[47] Using the simple expression for C_0 given by Honda[48] we can ascertain in accordance with Honda and Sasada[49] that the spiral patterns appear when

$$C_0 = (Q/\epsilon)(d^2/U_{max})$$

where Q is the density of the space charges, d is the depth of the surface spiral patterns, ϵ is the mean dielectric constant of the large-pitch cholesteric under study and U_{max} is the applied DC voltage is around unity. For $C_0 > 1$, the space charge layer is very thin, the current becomes Ohmic. For $C_0 < 1$, the density of the space charge is low which leads to a weak gradient in the electric field.

CONCLUSION

We have observed either left-handed or right-handed spiral patterns in thin large-pitch Ch–N mixtures under the long time application of a DC voltage. The handedness of the winding of the spiral patterns depends crucially on the polarity of the voltage and the thickness of the cells under study. They can be destroyed first, after the heating of the Ch layer to the isotropic phase, second after the reversal of the polarity of the applied DC voltage and third, after the short time application of a high-frequency electric field. The spiral patterns can reappear after several minutes when the layer again is subjected under the action of the DC voltage. The degeneration in the initial homeotropic orientation of the LC layer in the boundary regions led to the formation of many other Ch defects not considered here.

The appearance of the spiral patterns has been explained by possible gradient flexoelectric generation of point singularities. A topological model for the most simple case of single spiral patterns was given by introducing of a flexoelectrically generated singularity point $n = +2$ ($S = +1$).

The handedness of the winding of the spiral patterns permitted the determination of the electrode where they are formed which is closely related to the injection and the sign in the gradient of the electric field crucial for the development of the spiral patterns. From the position of the spiral patterns for the case of different cell thickness we concluded that a strong injection from the two electrodes exist. In addition, we surprisingly observed that the adding of a small amount of CC or CN to MBBA or the LC 440 led to the significant change in the current-voltage characteristics of the nematics and replaced the two double electric layers by corresponding injected charge carriers layers. The experimental results have shown that the CC favours the injection from the cathode while the CN the injection from the anode.

The first in our knowledge polar electric field effect in thin large pitch cholesteric films is interesting for industrial applications. However, in our opinion it is also an important tool for the investigation of the gradient flexoelectric and injection phenomena in the large-pitch cholesterics.

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