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A Driven Voltage-Controlled Reversible Electrooptic Effect in a Smectic A Phase I. SiO Anchoring

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A driven voltage-controlled reversible electrooptic effect in a smectic A phase

I. SiO anchoring

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A driven voltage-controlled reversible electrooptic effect in a smectic A phase with a preceding twisted nematic phase or a large-pitch cholesteric phase and SiO anchoring has been discovered. The unique feature of this novel electrooptic effect in a smectic A is that it reverses by relaxing when the electric field is removed. The conditions permitting the observation of such an effect are described in detail. On the basis of the smectic A textures observed a simple topological model is given. The influence of the polyvinyl alcohol anchoring is studied in the following paper. The main advantages and disadvantages of this novel electrooptic effect for a display device are briefly discussed.

1. Introduction

In a nematic layer, the competition between the alignment induced by the confining planes of the sample and an applied a.c. voltage leads to the observation of a driven voltage-controlled completely reversible electrooptic effect. Such an effect for the case of twisted nematic layers permitted the construction of various liquid crystal displays. In a smectic A (S_A) layer however, the competition between the alignment induced by the confining planes of the sample and an applied a.c. electric field leads only to the so-called ghost transition, predicted by de Gennes [1] and Rapini [2]. For higher fields, a visible transition is possible, resulting in a folding of the smectic layers made possible through the nucleation of a periodic array of defects [3]. Such an effect has been observed by Goscianski *et al.* [4] in planar S_A layers under a.c. voltage excitation. These authors have shown that the field can act on the orientation of the S_A samples several degrees below the nematic-smectic A transition temperature. On removal of the voltage, the regular arrays of the lines are broken down to form a texture of small focal conics which scatter light. It is evident that these effects do not lead to the observation of a driven electric field-controlled reversible electrooptic effect with characteristics necessary for the use in the liquid crystal displays.

The early experimental work of Tani [5] and the theoretical work of Geurst and Goossens [6] stimulated further efforts of researchers to use smectic A phases in liquid crystal displays. They have studied electrooptical effects in S_A phases with conductive dopants added and subjected to a low-frequency electric field [7-15]. Such electrooptic effects are mainly based on the turbulent local motion of the fluid and an electrohydrodynamic movement of dislocations. Simultaneously with the study of the low-frequency electrohydrodynamic effects researchers have investigated in detail the dielectric reorientations in smectic A phases without the utilization of conductive dopants [7, 8, 10-18]. All of these studies are connected with the investigation of the planar-to-homeotropic S_A transition or focal conics-to-homeotropic S_A transition. Useful remarks on these transitions have been made by Raynes [19, 20]. The planar-to-homeotropic S_A transition has been applied in large, flat liquid crystal panel displays with a memory [21–27]. Their operation is based on the existence of two stable structures in the S_A phase, the one being transparent, and the other diffusing, resulting in turn in one of the essential features of the liquid crystal display, namely its storage capability. The diffusing and transparent structures in the S_A phase are achieved by applying either a low-frequency electric field or a high-frequency electric field. The planar-to-homeotroic S_A transition is really the first reversible electrooptic effect within the smectic A phase which is very useful for application in liquid crystal displays with storage. Another type of a reversible electrooptic effect in smectic A phases can be found in the idea for a frequency reversal of the sign of the dielectric anisotropy in some S_A phases [28].

To summarize, at the present stage of the experimental investigations, a specific reversible electrooptic effect in smectic A phases has been discovered which is used in the liquid crystal displays with a storage. An important problem which still requires solution is the achievement of a driven voltage-controlled reversible electrooptic effect in smectic A phases which is also stressed by Smith [27] (by a driven voltage-controlled reversible electrooptic effect in a smectic A we mean that it reverses by relaxing when the electric field is removed, i.e. this is the unique feature of the novel electrooptic effect in smectic A phases).

The aim of our study, which is given in two separate papers, is to show the possibility of obtaining a driven voltage-controlled completely reversible electrooptic effect in smectic A phases which for the case of a preceding twisted nematic phase or a large-pitch cholesteric phase and SiO anchoring extends several degrees below the nematic–smectic A transition temperature while for the case of polyvinyl alcohol anchoring and a preceding twisted nematic phase the electrooptical effect is completely reversible very close to and below the nematic–smectic A transition. In the latter case, the smectic A scattering textures obtained can be used in displays with an electrical control of the storage close to the nematic–smectic A transition [30]. We start with an explanation of the driven voltage–controlled reversible electrooptic effect in a S_A phase with a preceding twisted nematic or large-pitch cholesteric phase, SiO anchoring and a high-frequency electric field excitation of the liquid crystal samples. The case of the electrically excited S_A with a preceding twisted nematic phase and polyvinyl alcohol anchoring will be given in the following paper [30].

2. A clarification of the method used to obtain a completely reversible electrooptic effect in smectic A phases

First we should focus our attention on the resolution of three main problems connected with the study of the smectic A phases. The first concerns the possible matching between the surface and bulk orientation of the liquid crystal in conventional smectic A samples which hitherto has been insufficiently studied. The second problem is connected with the scarcity of data for anchoring smectic A phases with the bounding walls of the cells (this problem will be discussed in detail later). The third problem shows that the smectic A textures in displays with storage are obtained under many influences, such as the rate of cooling and the presence of defects on the substrates or impurities in the bulk. The creation of S_A textures can be achieved by homogeneous or heterogeneous nucleation and depends crucially on the initial deformation of the preceding nematic phase. Finally, of importance is the thermomechanical equilibrium between the various defects [31]. All these causes often lead to uncontrollable and imperfect formation of the smectic A scattering centres. Evidently, it is necessary first, to obtain reproducible homogeneously-distributed S_A scattering centres which can be controlled either by appropriate treatment of the electrodes or by electrical forces and secondly, to discover smectic A scattering textures with novel electrooptical properties. All these problems can be successfully resolved by appropriate elaboration of the relevant experimental results obtained by Cladis and Torza [32] which clarify the formation of the smectic A phase from a previously deformed nematic layer (further insight on this problem is given in the paper by Chu and Jacobs [33]).

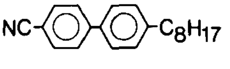
Recently, we have investigated the formation of a S_A phase from the strongly deformed surface regions of a nematic sample, created by a suitable application of an a.c. electric field across the preceding nematic phase and retained in the smectic A phase up to the formation of the S_A scattering textures [34, 35]. In the boundary regions, the nematic–smectic A transition temperature was depressed with a value which can reach 1°C [36] due to the strong deformations in these regions while in the middle oriented part of the cell it was unchanged. With the relatively homogeneous temperature distribution across conventional samples, the S_A phase is formed upon cooling, first in the middle oriented part of the sample and then in the boundary deformed regions. This new experimental observation permits first, the formation of regular smectic scattering textures, secondly, the determination of useful information, frequently unpredicted theoretically, about the matching between the orientation of the smectic A phase in the surface regions and that in the bulk [37–42], thirdly, the estimation of the surface energy of interaction of the S_A molecules with the bonding planes [34, 35] and fourthly, the observation of new smectic structures with novel electrooptical properties. For instance, the formation of smectic C dislocations with a large Burgers vector [43] was possible after the electrical excitation of the preceding twisted nematic phase followed by cooling in the presence of the electric field. The possibility of this novel method to form smectic A scattering centres in the thermally-addressed smectic displays with storage was also noted [44]. All the advantages and disadvantages of this method for the formation of the smectic phase have been discussed elsewhere [45].

The formation of the smectic A phase from the preceding nematic phase, twisted by SiO treatment of the electrodes, excited by an a.c. voltage with an appropriate amplitude and cooled down to the S_A phase in the presence of the electric field is discussed in § 3. The formation of the smectic A phase from the preceding large-pitch cholesteric phase is discussed in § 4. The possible application of this observation to display devices is briefly summarized in the Conclusion.

3. Formation of the smectic A phase with the preceding twisted nematic phase of the liquid crystal 8CB

(*a*) *Compounds and sample preparation*

We have used the liquid crystal 4-*n*-octyl-4′-cyanobiphenyl (8CB) with the structural formula



and the transition temperatures [15, 16, 46]

$$C\text{–}S_A\text{: } 20°C,\ S_A\text{–}N\text{: } 32°C,\ N\text{–}I\text{: } 39{\cdot}5°C.$$

It is clear that four phases are present: crystalline (C), smectic A (S_A), nematic (N) and isotropic (I). The smectic A–nematic transition is almost second order: this has been studied by thermal differential analysis [16]. The dielectric anisotropy is positive: $\Delta\varepsilon = 8{\cdot}2$; the dielectric constants are $\varepsilon_{\parallel} = 12{\cdot}8$ and $\varepsilon_{\perp} = 4{\cdot}6$ (the measurements were made at 22°C) [16]. It is important to note that the value of the latent heat is significantly different for the various phase transitions [46]:

$$\begin{aligned} \text{C–S}_A&: \quad 2{\cdot}52\,\text{kJ mol}^{-1}, \\ \text{S}_A\text{–N}&: \quad 0{\cdot}304\,\text{kJ mol}^{-1}, \\ \text{N–I}&: \quad 1{\cdot}232\,\text{kJ mol}^{-1}. \end{aligned}$$

It is evident that the latent heat at the S_A–N transition is very small which ensures the application of our method [32, 34, 35, 43–45]. The liquid crystal under study was very pure; the specific conductivity was measured to be about $4 \times 10^{-12}\,\Omega^{-1}\,\text{cm}^{-1}$.

The liquid crystal was placed between two tin oxide-coated glass plates separated by teflon spacers with a thickness of 20 μm. The substrates were treated by silicon monoxide under vacuum evaporation; this favours the planar orientation of the nematic director. The angle of evaporation was 30° to the surfaces. The director in the surface regions was oriented in such a way that initially they were twisted at an angle of 90°. The nematic layer was excited by an a.c. voltage with a frequency between 1 and 10 kHz and an amplitude between $3U_{\text{th}}$ and $25U_{\text{th}}$, where U_{th} is the threshold voltage which causes the appearance of the Freédericksz transition for the case of strong anchoring of the nematic layer. The threshold voltage in our experiment was measured to be approximately 1·6 V r.m.s. During the a.c. excitation the nematic phase was cooled into the smectic A phase. The S_A deformations obtained in this way, can be controlled electrically several degrees below the smectic A–nematic transition temperature where the elastic behaviour of the S_A phase still is manifest.

(*b*) *Experimental results*

(1) *Observation of three dimensional spherolites in the nematic phase*

All of the experimental results were obtained under a microscope with transmitted polarized white light. Sometimes we studied the liquid crystal without the use of polarizer or analyser or at appropriate non-crossed position of the two nicols.

The first surprising experimental result was obtained in the nematic phase, close to the S_A–N transition. The twisted nematic layer broke up into many spherolites as shown in figure 1. The size of the spherolites varied between 6 and 12 μm although rarely did it reach 20 μm which is equal to the thickness of the liquid crystal cell. Under the application of a voltage with a large amplitude of 20–30 V r.m.s., the greater part of the deformation in the spherolites disappeared. It is clear that near to the smectic A–nematic transition, because of the non-linear elastic behaviour of the liquid crystal discussed by Chu and McMillan [47] and to the enhancement of the twist and bend elastic constants relative to the splay constant [32, 34, 48], the nematic one dimensional splay-twist-bend deformations broke up into three dimensional spherolites which evidently have a lower elastic energy. In a similar manner, a number of authors have investigated, both theoretically and experimentally, two dimensional domains due to twist-splay periodic deformations [49–53]. It is clear that the deformation inside the spherolites is predominantly of a splay-bend curvature of the director. Since this problem is beyond the scope of this paper, it will be studied in detail elsewhere.

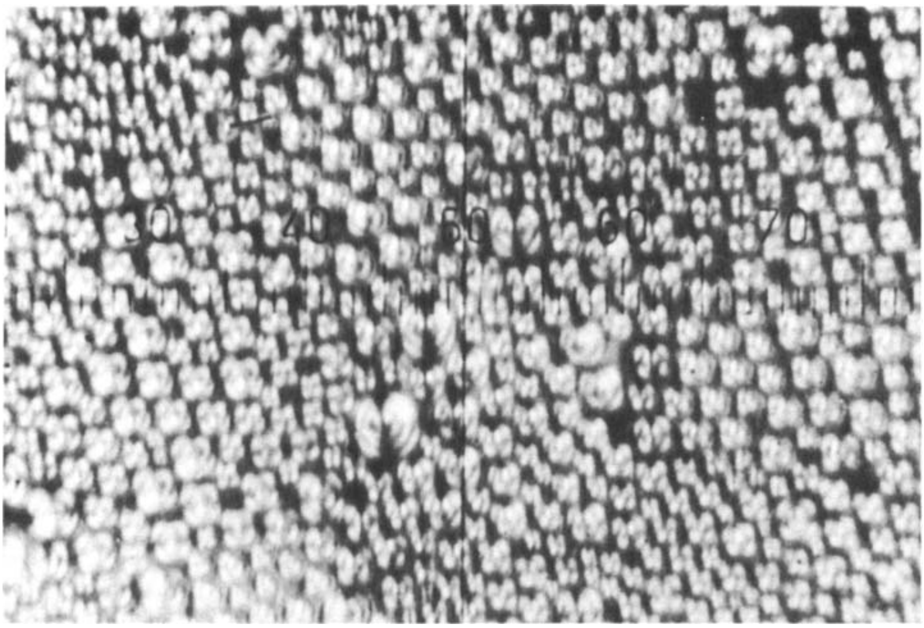


Figure 1. Spherolites obtained in a twisted nematic layer of 8CB close to the S_A-N transition, $P \perp A$, 10 small divisions correspond to 29 μm.

(2) *Electrooptric effect in a planar smectic A layer*

A planar nematic layer of 8CB, anchored by SiO treatment of the electrodes, was subjected to an a.c. voltage with a frequency of 10 kHz and an amplitude between 10 V r.m.s. and 40 V r.m.s. The threshold voltage was measured to be around 2 V r.m.s. which is slightly larger than the corresponding threshold voltage for the twisted nematic cell. For the case of a voltage lower than 10 V, we have observed regular S_A scattering textures reported elsewhere [34]. Under the application of a higher voltage, some of the confocal domains disappeared; this is shown in figure 2. It is important to mention that isolated focal conic circle-line pairs or groups of such pairs disappeared *irreversibly* into the homeotropic smectic A *due to the finite value of the surface anchoring*. The electrooptic effect is *irreversible* and has been obtained by many authors (see the references concerning the planar-to-homeotropic smectic A transition mentioned in the Introduction). The electrooptical behaviour of a S_A layer obtained from the electrically deformed twisted nematic layer, however, is different and useful for application of displays.

(3) *Electrooptic effect in smectic A layer obtained after cooling a twisted nematic layer in the presence of an a.c. voltage: experimental results and discussion*

The initially twisted 8CB nematic layer was subjected to a voltage with a frequency of 10 kHz and an amplitude of 10 V r.m.s. and cooled down to the smectic A phase in the presence of the voltage. The glass surfaces were treated with SiO, evaporated at an angle of 30° to the surface. The threshold voltage was measured to be about 1·6 V r.m.s. At the smectic A-nematic transition, the usual pretransition stripes observed by Cladis and Torza [32] were not formed. Instead, we obtained another texture shown in figures 3(*a*) and (*b*). It is a combination of cross-like domains

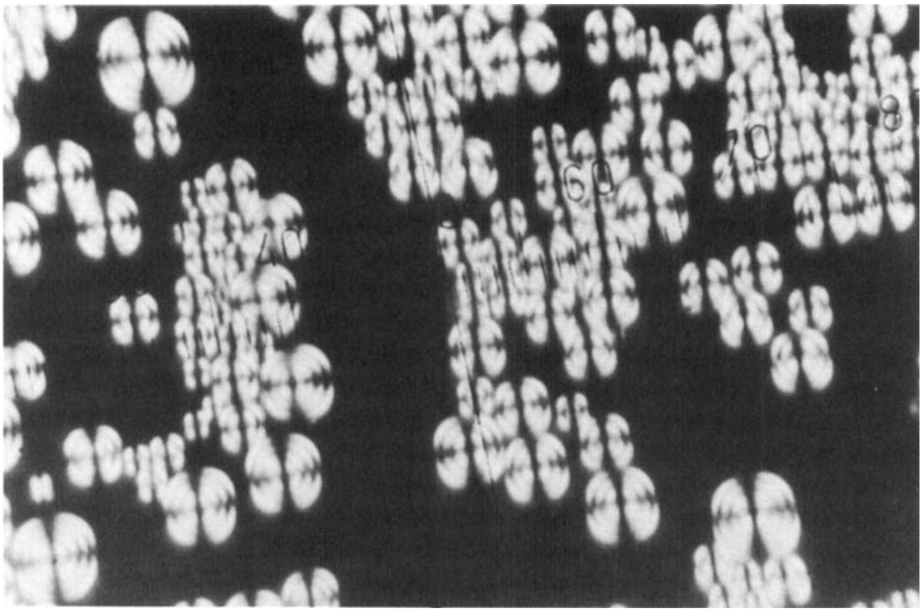
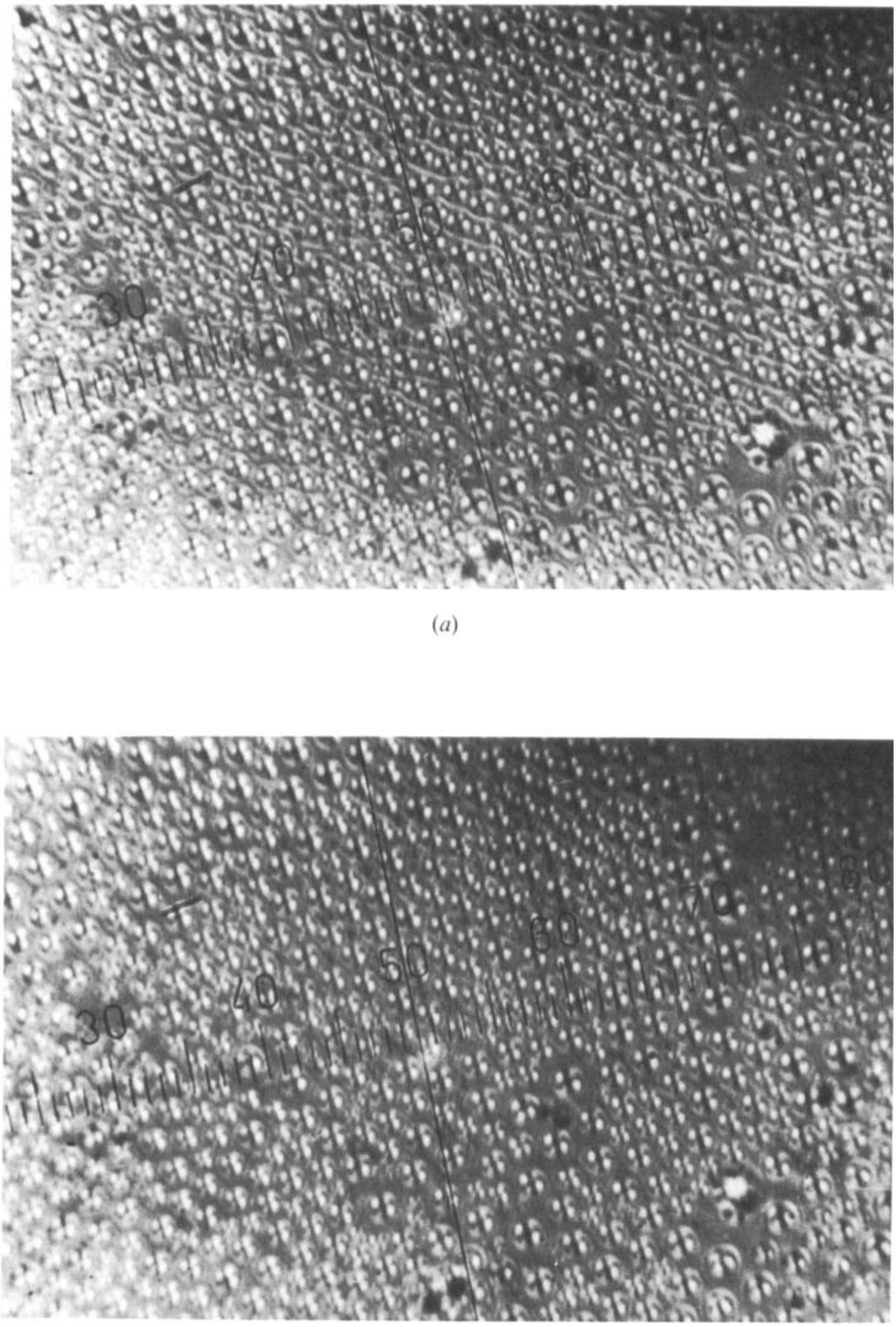


Figure 2. Focal conic circle-line pairs and a homeotropic smectic A obtained in a S_A layer of 8CB with a thickness of $20\,\mu m$ with a voltage of 10 V r.m.s., $f = 10\,kHz$, $P \perp A$.

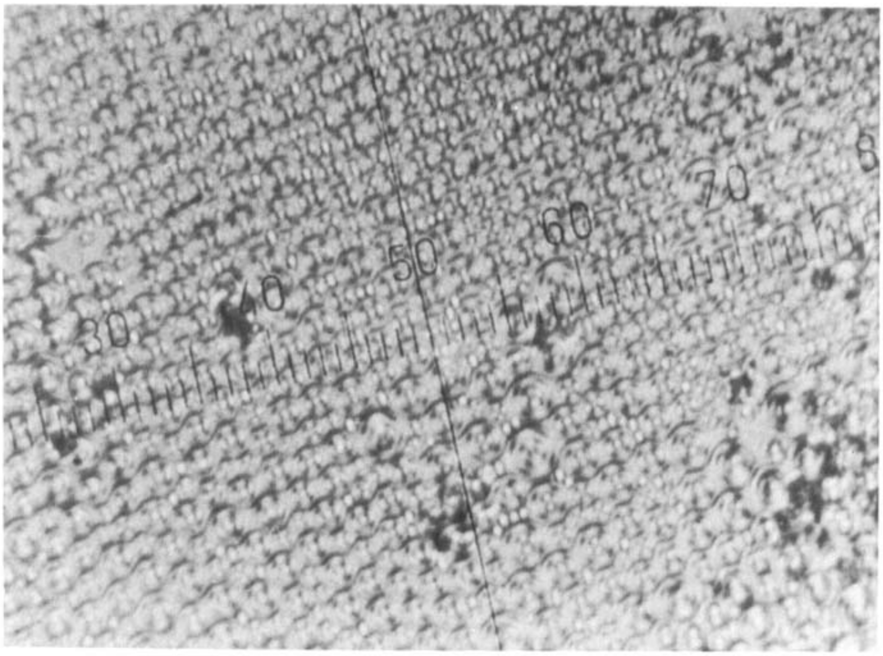
distributed in a number of arrays. Examination of the photographs shows unambiguously that the cross-like domains are small nematic droplets embedded into a slightly undulated smectic A layer. Because of the initial twist in the nematic phase, the usual smectic A–nematic boundary is unstable, in consequence it breaks up forming in this way the nematic spherolites. This growing process is accompanied by the minimization of the interfacial surface tension between the nematic and smectic A phases. In the S_A phase, the cross-like domains appear as spherolites with a rather complicated deformation of the S_A which is shown in figure 4(*a*). This photograph was taken with initially crossed nicols and a clockwise rotation of the polarizer at an angle of +30° and top focusing. The smectic A texture appears different for the case when the polarizer was rotated at an angle of −30° with the same focusing; this S_A texture is shown in figure 4(*b*). The most typical view is shown in figures 4 (*c*) and (*d*); these photographs were taken with crossed nicols using down and middle focusing, respectively. It is clear that all of these photographs can aid in the understanding of the possible arrangement of the smectic A planes and the possible orientation of the mesogenic molecules. We have examined carefully all of the S_A textures hitherto obtained and investigated, including arrays of focal conic domains known as double Grandjean walls studied in detail by Marignan *et al.* (see the references cited in [35]), or arrays of parabolic focal domains observed and investigated by many authors [54–57]. Our conclusions are based on the specific kind of smectic A textures which are illustrated in figures 3 and 4, and on the particular prehistory of the formation of the focal conics related to the existence of a twist both in the nematic phase and in the pretransitional smectic A–nematic region. We have assumed that the existence of an initial twist in the nematic phase is crucial and leads to the formation of circle-line focal conics which *are embedded into a deformed smectic A layer, more precisely they are embedded into an undulated S_A layer.* At this stage of the experimental



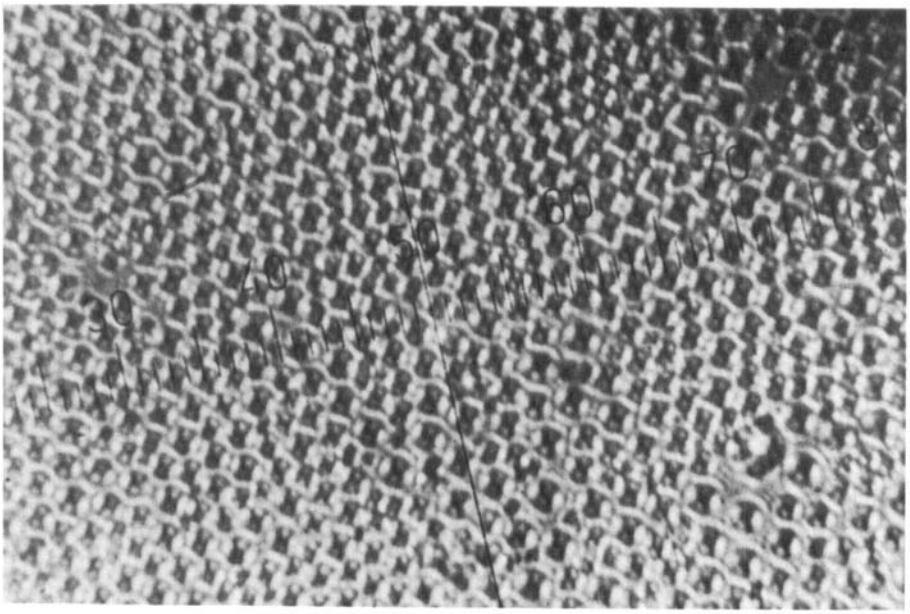
(*a*)

(*b*)

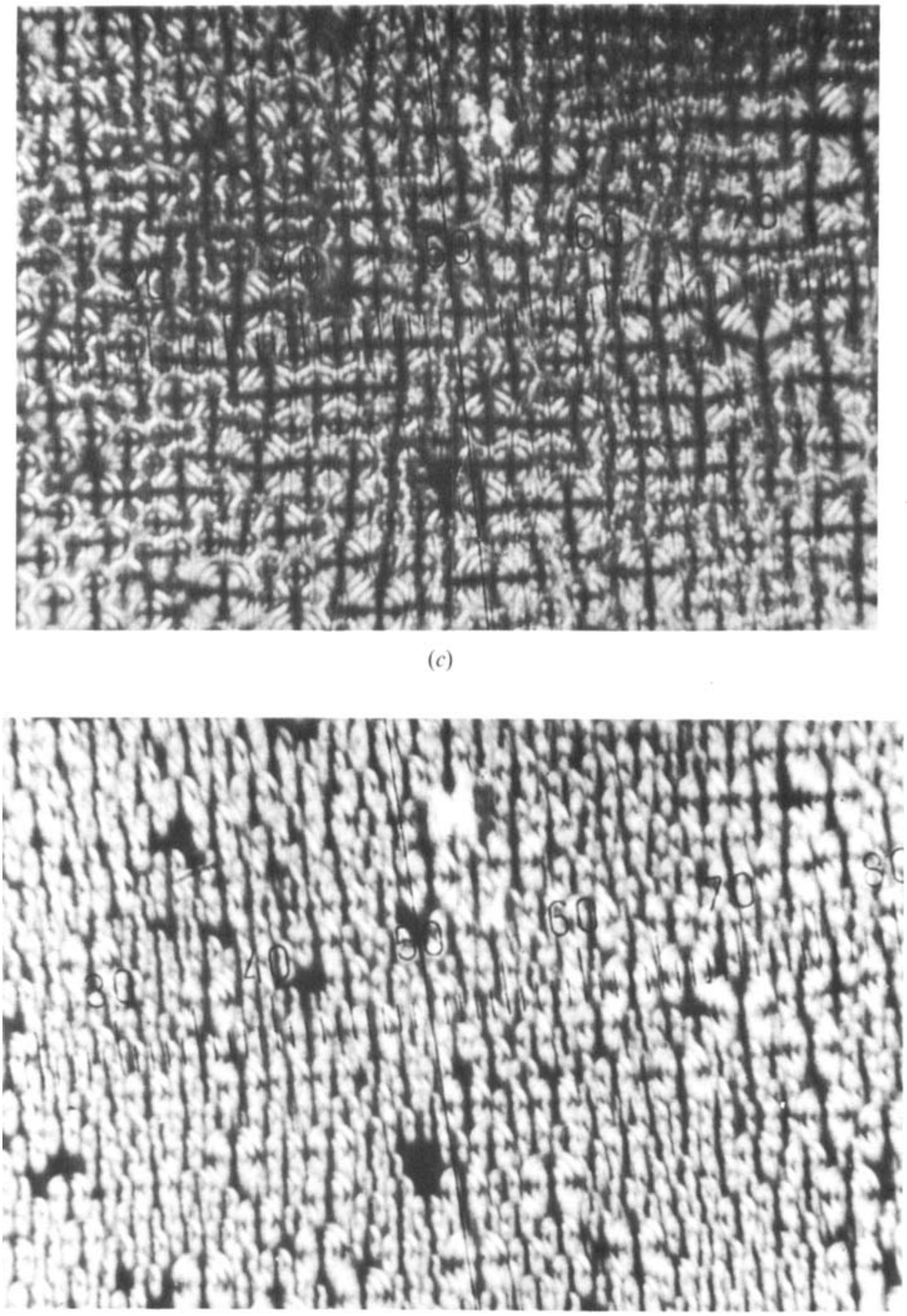
Figure 3. Pretransitional arrays of cross-like nematic domains and S_A undulations obtained in an initially twisted nematic layer of 8CB with a thickness of $20\,\mu$m on the cooling. A voltage of 10 V r.m.s., 10 kHz was applied across the nematic and smectic A phases, $P \perp A$, 10 small divisions correspond to $29\,\mu$m. (*a*) The beginning of the S_A undulations (*b*) After 15 s.



(*a*)



(*b*)



(c)

(d)

Figure 4. Arrays of circle-line focal conic domains obtained in a S_A layer of 8CB with a thickness of 20 μm. The preceding twisted nematic phase is excited with a voltage of 10 V r.m.s., 10 kHz which is retained in the smectic A phase up to the formation of the texture: (*a*) initially crossed nicols; the polarizer is rotated in a clockwise direction at an angle of +30°, top focusing; (*b*) initially crossed nicols; the polarizer is rotated in a counter-clockwise direction at an angle of −30°, top focusing; (*c*) crossed nicols, down focusing; (*d*) crossed nicols, middle focusing.

investigation however, due to the insufficient resolution of the focal conic domains and particularly of the deformation between the neighbouring focal conics, it is not possible to discuss in detail the undulations of the smectic A layers. Our conclusions are based on the following assumptions and ideas:

(*a*) the way the S_A phase appears from *a strongly deformed initially planar nematic layer* follows the scheme: *in the middle oriented part of the sample*—formation of a homeotropic smectic A; *in the strongly-deformed boundary regions:* stripe-like domains of Cladis–Torza [32] form namely smectic A edge dislocations —focal conic domains [58–60] embedded into a homeotropic S_A [34].

(*b*) the way the S_A phase appears from *a strongly-deformed initially twisted nematic layer* according to our experimental results follows a different scheme: *in the middle oriented part of the sample*—formation of a homeotropic S_A which undulates after the appearance of the S_A phase in the boundary regions; *in the strongly-deformed boundary regions*—nematic cross-like domains (spherolites) embedded into a slightly undulated S_A phase—arrays of focal conics embedded into an undulated S_A.

These conclusions are based on a number of experimental and theoretical results for smectic A undulations obtained by de Gennes [1], Durand [6], Clark and Meyer [62], and Delaye *et al.* [63]. According to the theoretical results of Durand [61], a local undulation of the smectic A phase at the boundary with an amplitude of 15 Å and a length of one S_A layer can penetrate into nearly 1000 S_A layers (see also the Thése of Ribotta [54]). In other words, the undulations of the smectic A layers being in the boundary regions do penetrate into the whole S_A sample. Our assumptions were found surprisingly in the paper of Friedel [65] who has pointed out '. . . it seems clear also that defects—translation dislocations and focal conics—strongly interfer with the oscillations of the layers, in a way that has not been completely elucidated.' Consequently we can make the following reasonable assumptions supported by our experimental results:

(*a*) the arrays of the focal conics are embedded into one undulated S_A layer;
(*b*) the undulations of the S_A planes are extended into the whole sample;
(*c*) dislocations play a possible role in the dynamics of the electrooptic effect reducing in this way the strains
(*d*) the S_A textures cannot be electrically transformed into a homeotropic S_A phase.

The electrooptic transmission curves obtained with an electronic recorder are shown in figure 5 for the case of a voltage with a frequency of 10 kHz and an amplitude of 20 V r.m.s., 25 V r.m.s., 30 V r.m.s., 35 V r.m.s. and 40 V r.m.s. The shape of these curves shows first, that the electrooptic effect *starts with a threshold* and second, that the electrooptic effect is *completely reversible* in the temperature range of 3°C to 5°C below the smectic A-nematic transition temperature, depending on the strength of the voltage, where the elastic behaviour of the S_A phase still is manifest [15–17]. Below this temperature range, the plastic character of the S_A phase prevails [66] and S_A textures are stored.

Under the microscope we saw that after the application of a voltage with an amplitude above threshold the focal conic domains gradually disappear without any visible hydrodynamic movement of the fluid (see figure 6). At larger voltages the S_A deformations were condensed around the linear disclinations which are perpendicular

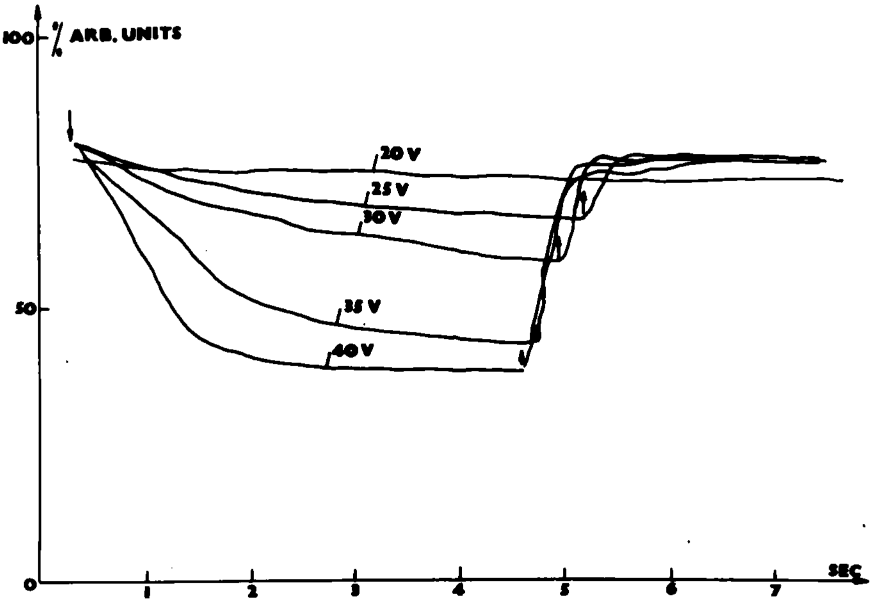


Figure 5. Electrooptic transmission curves obtained with an electronic recorder for a S_A layer of 8CB with a thickness of 20 μm; crossed nicols.

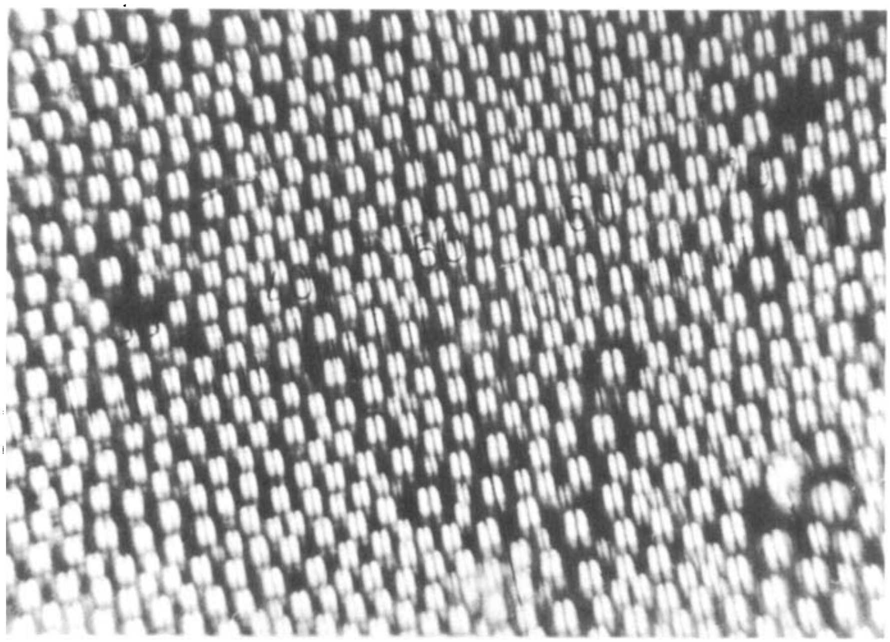


Figure 6. The focal conic domains shown in figure 4 (*a*) at a voltage of 30 V r.m.s., $f = 10$ kHz.

to the glass plates and appearing as many bright spots with a dimension below 1 μm. After the removal of the voltage the focal conic domains reappear smoothly; it seemed that the S_A texture was not changed. Evidently on the application of the voltage the dielectric reorientation of the smectic A, probably including a motion of dislocations,

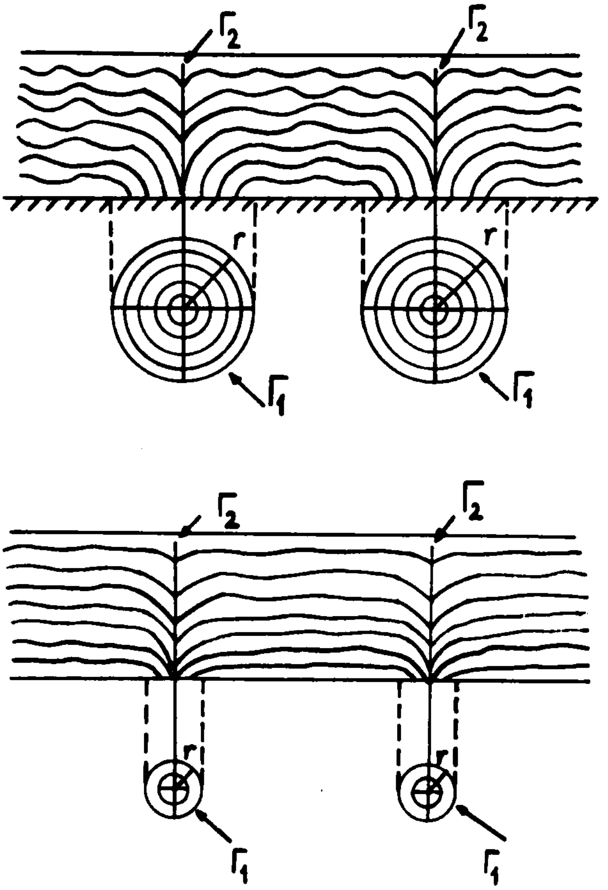


Figure 7. A schematic representation of focal conic domains embedded into an undulated smectic A: (*a*) without the application of a voltage; (*b*) after the application of a voltage with an amplitude above threshold.

is from the undulated part of the sample towards the centre of the focal conics. Conversely, on the removal of the voltage the dielectric reorientation is in the opposite direction; this is illustrated in a naive manner in figures 7 (*a*) and (*b*). Such behaviour of the smectic A is provoked by the peculiar character of the S_A deformations: symmetric focal conic domains embedded in a deformed smectic A. On the other hand, such a dielectric reorientation is possible when there is appropriate pinning of the S_A defects on the surface irregularities of the glass plates [31, 67]. According to Pershan [68], the position of the S_A defects with respect to the boundaries is important for their interaction with this boundary. For instance, the anchoring of the S_A structure with the boundary is evidently of significance when the S_A defects are pinned on the boundary whereas in the case of S_A defects parallel to the boundary, the S_A layer can be regarded as a free layer. In this case anchoring of conventional liquid crystals is not important. Further, the nucleation of the S_A phase from the deformed nematic phase should be heterogeneous [31, 65]. The value of the dilation constant B, depending on the density of the S_A defects, is also of importance [31, 67, 68]. Lower values of B will aid the observation of the novel reversible electrooptic effect.

It is worth mentioning that the voltage threshold which, according to the experimental results shown in figure 5, is approximately 21 V r.m.s., can be calculated exactly from the equation [1]

$$U_{\text{th}}^2 = (2\pi d/\Delta\varepsilon)(BK_{11})^{1/2},$$

with $K = 10^{-6}$ dyn, $B = 10^7$ dyn/cm^2, $d = 20\,\mu$m and $\Delta\varepsilon = 8$. Indeed, this voltage has been calculated for a destabilizing action of the electric field whereas in our case it orients the smectic A. Nevertheless, it seems that due to the non-linear elastic effects this transition is somewhat similar to the planar-to-homeotropic transition in S_A materials [24]. *The second important remark* concerns the dynamic characteristics of the electrooptic effect under study. The dynamic electrooptic curves shown in figure 5 clearly indicate that the turn-on time is much longer relative to the turn-off time. Evidently this experimental result is connected with different physical reasons. In our opinion, the turn-on time is connected chiefly with the movement of dislocations which accompany dielectric reorientation. Accordingg to Ribotta and Durand [69], the relaxation of the local stresses with the aid of the creation or disappearance of dislocations is in the range of 50 ms whereas for dislocations coming from the bulk, the transit time can be many seconds. The experimental results of Bartolino and Durand have shown that the short decay time τ_1 (a few tens of ms) is followed by a plateau with a decay time τ_2 of the order of a few seconds. Our experimental results show that the turn-on time is in the range of a second. Evidently it is connected with the movement of dislocations which travel however a very short distance (a few microns). The turn-off time is much shorter and is controlled by the bounding plates. *The third important remark* concerns the type of the anchoring of the smectic A structure. The alignment of smectics on SiO, treated substrates under vacuum evaporation, has been investigated mainly for the bulk of the liquid crystal [71]. The φ-azimuthal anchoring of the S_A director which controls its rotation in the plane of the electrodes and the θ-polar anchoring which controls the rotation of the director in planes containing the normal to the glass plates and intersecting the glass plates have been introduced in a way, similar to that for anchoring of the nematic director. For instance, the θ-polar anchoring of the S_A director has been estimated from the experiments by Proust and Perez [72, 73] for a free S_A film (4×10^{-3} erg/cm^2) or for a smectic A–water interface ($2{\cdot}5 \times 10^{-2}$ erg/cm^2). The θ-polar anchoring of the S_A director interacting with a glass plate, evaporated with a SiO thin film, has been estimated to be 4×10^{-2} erg/cm^2 [34, 73]. The φ-azimuthal surface energy unfortunately has not been measured. The importance of this energy for the form of the focal conics which are pinned on the glass plates has been pointed out by Le Berre and Hareng [8, 15]. Since the driven voltage-controlled reversible electrooptic effect is connected directly with the formation of focal conic domains embedded in an undulated S_A layer, we can conclude in agreement with Le Berre and Hareng [8] that the φ-azimuthal surface energy must be smaller relative to the bulk elastic energy of the focal conics, calculated for the first time by Kléman [75]. On the other hand, the θ-polar anchoring is very important for pinning the focal conics. From the literature we know that the various dislocations and focal conics can glide easily between the layers [69, 70, 76–80]. At the boundary, the situation is quite different. According to Friedel [65], the regions of focal conics have a solid friction of the order of the elastic energy stored in the production of the domains which is possible due to the surface anchoring of the liquid crystal. Consequently, the θ-polar surface energy must be larger than the stored elastic energy in the focal conics. Some of the other requirements which permit the formation of focal conics when the boundary is covered by SiO can be found in the paper of Chou *et al.* [31]. For instance, due to the heterogeneous nucleation of the focal conics, the net liquid crystal-substrate interfacial energy must be negative:

$$\Delta\sigma_{\mathrm{int}} = \sigma_{S_A\text{-sub}} - \sigma_{N\text{-sub}} < 0.$$

By virtue of their topographical features and chemical properties, SiO_x alignment layers formed at various deposition angles yield different $\Delta\sigma_{\mathrm{int}}$ with the liquid crystal [31]. Chou *et al.* have proved experimentally that there is a strong correlation between the deposition angle, the tilt bias angle of the S_A director, and the number of focal conics being created. They showed that the focal conics can be created at a small tilt bias surface angle which is below 20°. For a higher tilt, the focal conics cannot be created. The nearly planar S_A layer facilitates very much the creation of focal conic domains. We have confirmed this experimental finding unambiguously.

Another interesting preliminary experimental result is the observation of a hysteresis which was not possible to record for technical reasons; a detailed investigation of this hysteresis will be published later. It is similar to the mechano-optical hysteresis of a smectic A observed by Adomenas *et al.* [81] who investigated the structural transition of a homeotropic smectic A into a focal conic one. The nature of the hysteresis observed in our experiment can be textural [81] or may be due to the non-linear character of the focal conic domain transformations.

4. Formation of the smectic A phase from a preceding large-pitch cholesteric phase

In this section we demonstrate that smectic A phases with a preceding large-pitch cholesteric phase can also show such a driven voltage-controlled reversible electro-optic effect [82].

(*a*) *Compounds and sample preparation*

We have studied 99 per cent wt of the liquid crystal 4-nitrophenyl-4′-octyloxybenzoate (NPOB) with the transition temperatures:

$$\text{C–S}_A\text{: 49°C, S}_A\text{–N: 61·5°C, N–I: 68°C}$$

with 1 per cent of cholesteryl chloride (CC). The pitch of the cholesteric mixture was measured to be approximately 12 μm [83]. The properties of the liquid crystal NPOB have been well studied in a number of papers, collected in [84]. The dielectric anisotropy is positive in both the nematic and smectic A phases and changes from 4 near the nematic–isotropic transition to 11–12 near the crystal–smectic A phase transition [85]. It is important to note that the latent heat is different for the various phase transitions [86]:

$$\begin{aligned} &\text{C–S}_A: && 2{\cdot}76\,\mathrm{kJ\,mol^{-1}},\\ &\text{S}_A\text{–N}: && 0{\cdot}84\,\mathrm{kJ\,mol^{-1}},\\ &\text{N–I}: && 0{\cdot}54\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

It is clear that the latent heat for the S_A–N transition is small enough to permit the application of our method. Furthermore, we accept that the dielectric constant of CC does not change the value of the dielectric constants of NPOB significantly.

The cholesteric–nematic mixture was placed between two tin oxide coated glass plates separated by teflon spacers with a thickness of 20 μm. The substrates were treated with silicon monoxide under vacuum evaporation which favours the planar orientation of the molecules in the boundary regions: the angle of evaporation was 30° to the surface. Some samples were constructed in such a way that the directors at the two boundaries were twisted by an angle of 90°. The initially formed Grandjean-like texture was excited by an a.c. voltage with a frequency of between 1 and 10 kHz. The value of the voltage applied across both the large-pitch cholesteric and smectic A phases was between $3U_{\mathrm{th}}$ and $25U_{\mathrm{th}}$, where U_{th} is the threshold voltage which causes the appearance of the Helfrich undulations of large-pitch cholesteric phases. In our case U_{th} was measured to be approximately 2·5 V r.m.s.

(*b*) *Electrooptic effect in a smectic A layer obtained after cooling a large-pitch cholesteric layer in the presence of an a.c. voltage: experimental results and discussion*

The application of a low voltage with an amplitude of 5 V r.m.s. and a frequency of 10 kHz across the large-pitch cholestic layer followed by slow cooling to the S_A phase in the presence of the voltage led to the creation of an unoriented S_A texture shown in figure 8; this scatters light strongly. Such S_A texture can be electrically controlled only around the smectic A–nematic transition and is only of interest for liquid crystal displays with a storage [30]. The application of a higher voltage of 30 V r.m.s. led to the creation of a pseudo-nematic in the boundary regions which on cooling to the S_A phase in the presence of the voltage was transformed in many focal conic circle-line pairs as shown in figure 9. The different position of the nicols and the kind of focusing being top, middle or down can help in understanding the exact picture of the focal conic domain distribution. For instance, the photograph shown

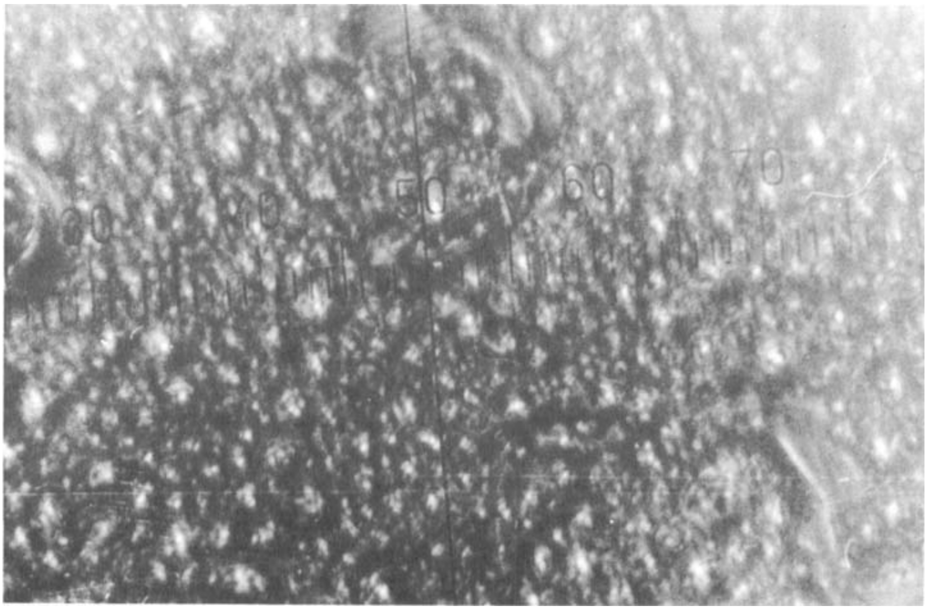


Figure 8. A strongly-scattering unoriented S_A texture obtained in a smectic A layer of 99 per cent wt NPOB and 1 per cent wt CC with a thickness of 20 μm; crossed nicols.

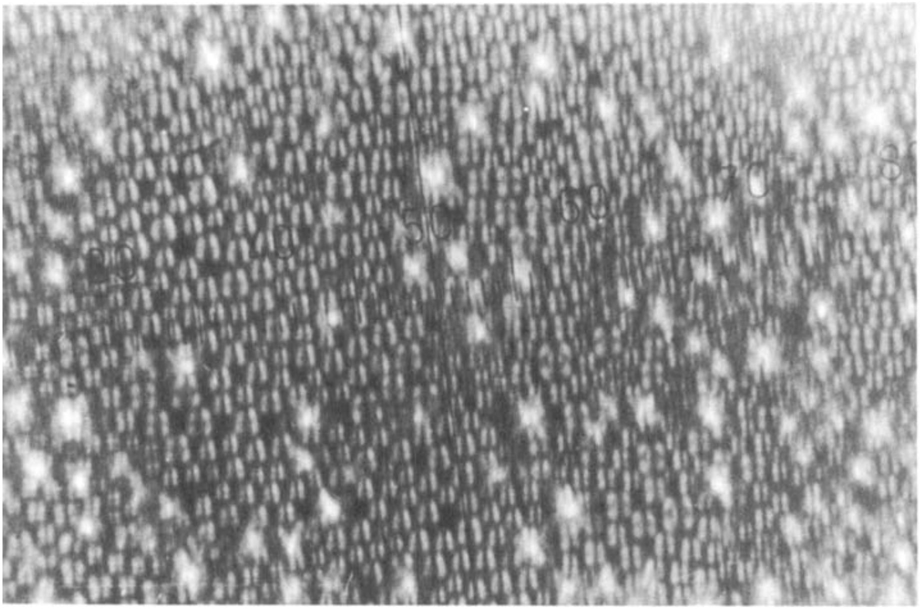


Figure 9. Circle-line focal conic pairs obtained in a S_A layer of 99 per cent wt NPOB and 1 per cent wt CC with a thickness of 20 μm after the application of a voltage of 30 V r.m.s., 10 kHz across the preceding large-pitch cholesteric phase which is cooled to the smectic A in the presence of the voltage. After the formation of the S_A texture, the voltage is removed; top focusing, $P \perp A$, 10 small divisions correspond to 29 μm.

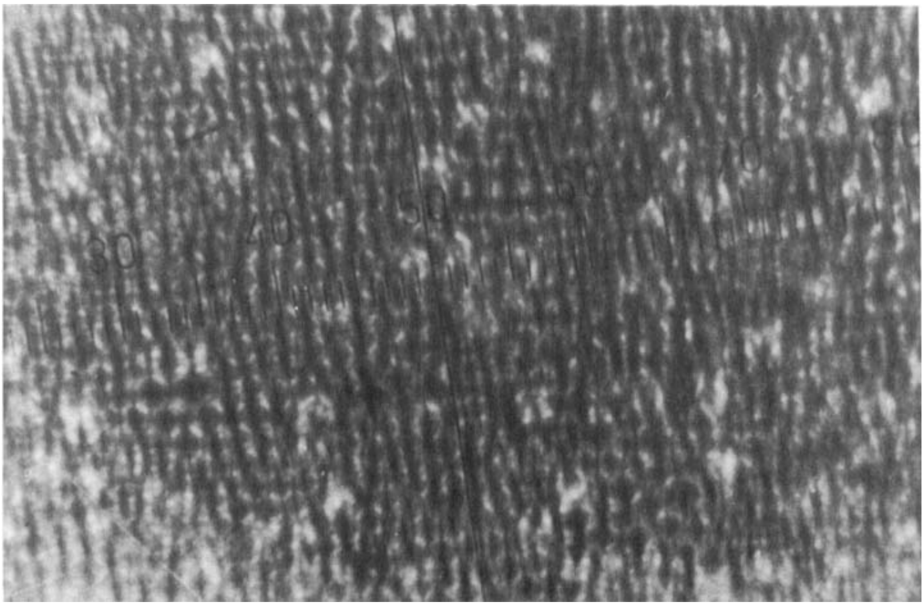


Figure 10. Details in the region around the focal conic domains shown in figure 9; down focusing, $P \perp A$.

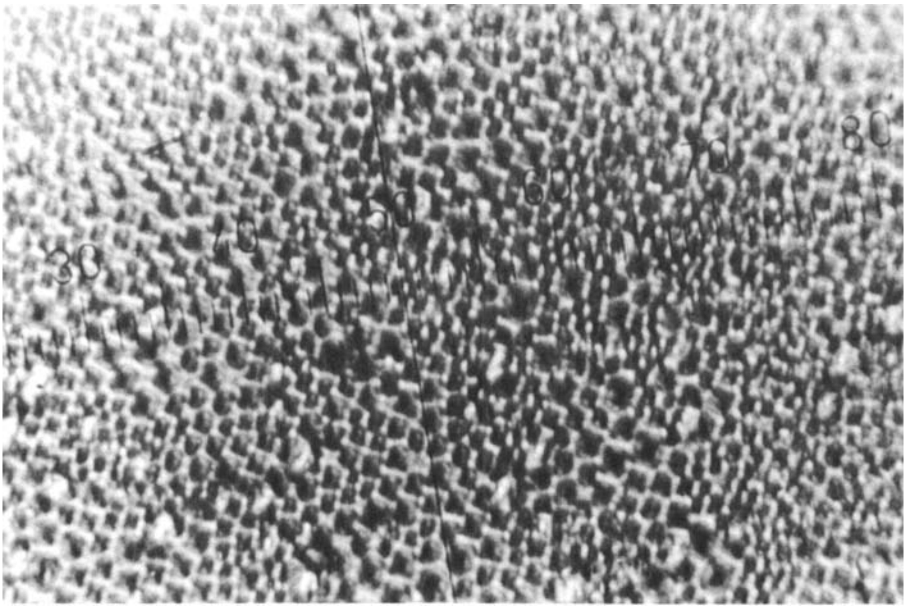


Figure 11. Details in the region around the focal conic domains shown in figure 9; down focusing, *P* 45° A.

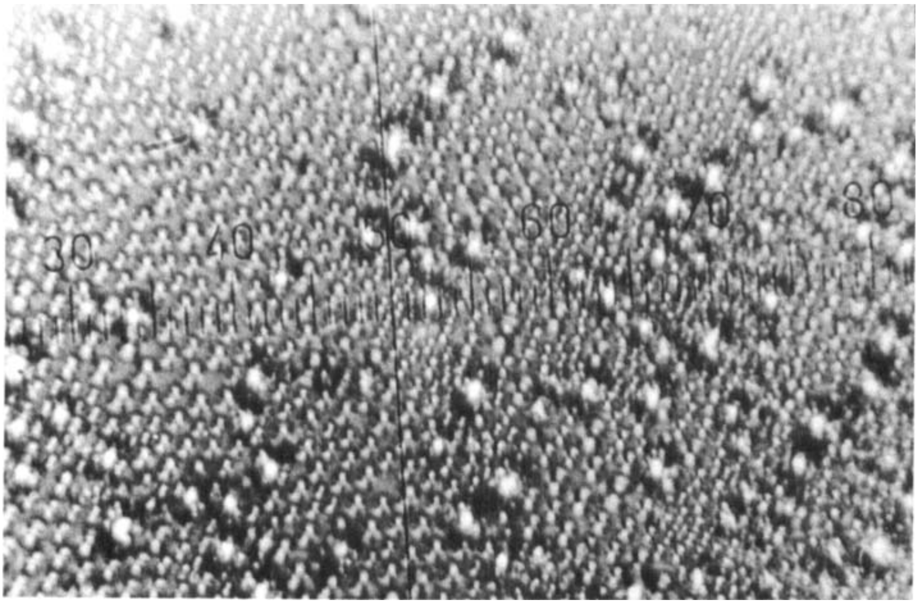


Figure 12. The region around the focal conic domains shown in figure 11 with top focusing.

in figure 9 was taken with crossed nicols and top focusing while the down focusing of the same S_A texture shows details of the environment of the focal conic domains, cf. figure 10. This environment is more clearly visible with a 45° position of the two nicols and down focusing, as shown in figure 11. Another interesting S_A texture is shown in figure 12 at a 45° position of the nicols and top focusing of the light. Photographs 8 to 12 were taken on the removal of the voltage.

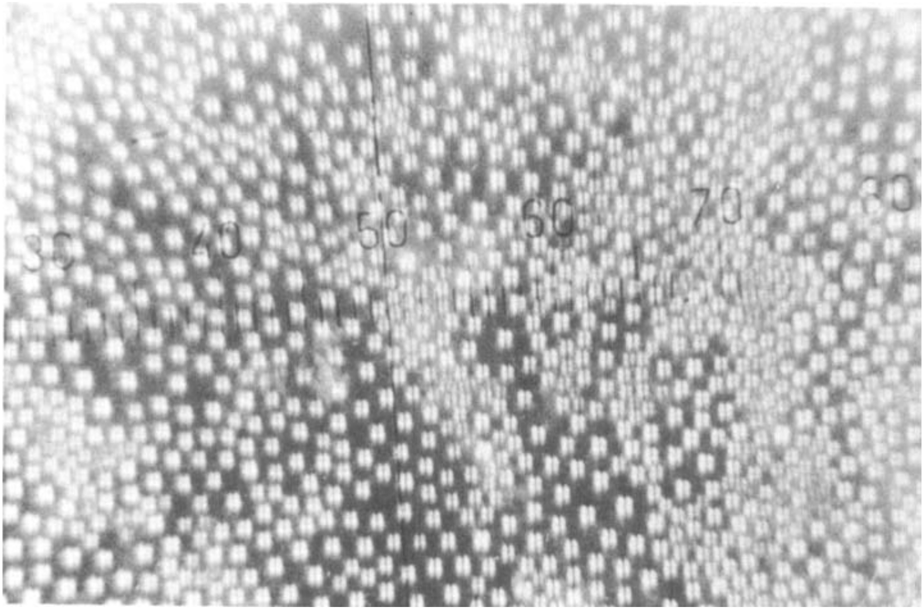


Figure 13. The focal conics shown in figure 9 under a voltage at 25 V r.m.s., 10 kHz, $P \perp A$, 10 small divisions correspond to 29 μm.

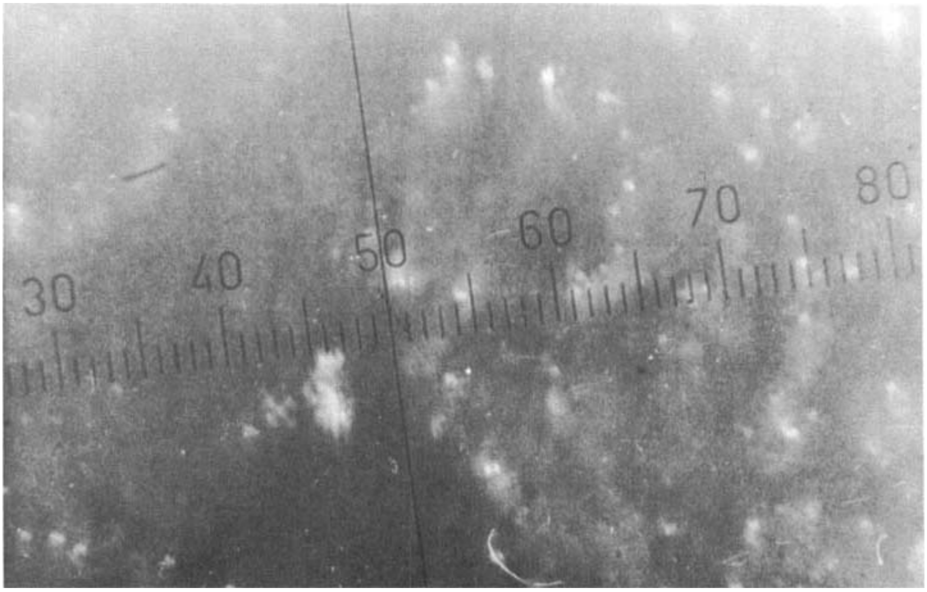


Figure 14. Disappearance of the focal conic domains shown in figure 13 at a voltage of 32 V r.m.s., 10 kHz, $P \perp A$.

The application of a voltage with an appropriate amplitude across such S_A textures can lead to the complete disappearance of the domains. For instance at a voltage of 25 V r.m.s., the greater part of the focal conic domains are still visible which is evident from figure 13. A voltage of 40 V r.m.s. is sufficient however, for the complete disappearance of all the S_A deformations visible in figure 13; this is shown in figure 14.

Only some bright spots can be seen around the largest S_A deformations. After the decrease or removal of the voltage the S_A deformations reappear and are visible under the microscope. The electrooptic transmission curves obtained with an electronic recorder for such smectic A cells, are shown in figure 15 for the case of a voltage with a frequency of 10 kHz and amplitudes of 20 V r.m.s., 25 V r.m.s., 30 V r.m.s., 35 V r.m.s. and 40 V r.m.s. Careful scrutiny of the S_A textures shown in figures 8 to 14 and the comparison with the similar photos taken for the study of the electrooptical behaviour of a smectic A phase with a preceding twisted nematic phase led us to the same conclusions: *the focal conic domains are embedded in an undulated smectic A layer.* After the application of a voltage with an amplitude above-threshold, as noted previously the S_A deformations are condensed around the linear disclinations which are perpendicular to the glass plates. For example, a voltage with an amplitude of 25 V r.m.s. significantly changes the S_A deformations while the total electrooptic response is weak. This experimental finding is evident from a comparison of figures 13 and 15. A voltage with an amplitude of 40 V r.m.s. is sufficient however, to remove nearly all the visible S_A deformations which is shown in figure 14.

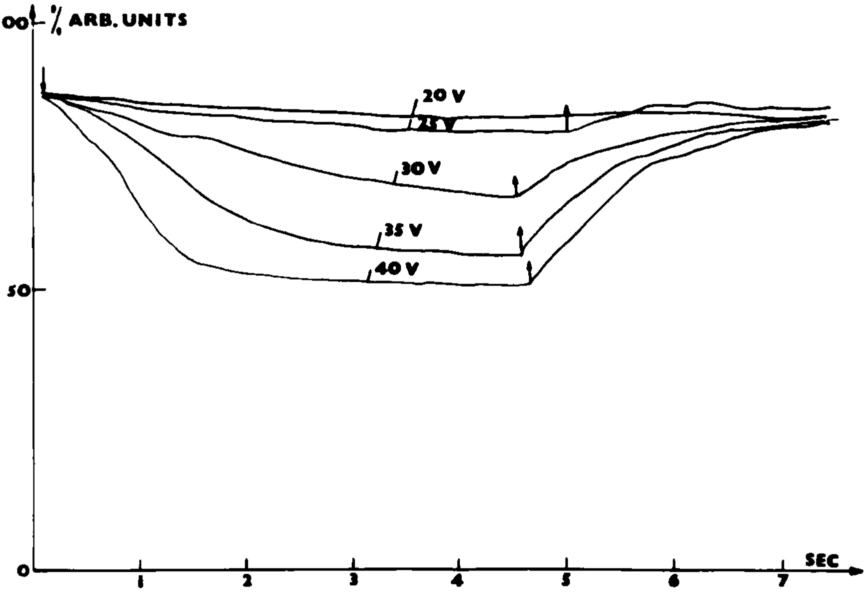


Figure 15. Electrooptic transmission curves obtained with an electronic recorder for a smectic A layer of 99 per cent wt NPOB and 1 per cent wt CC with a thickness of 20 μm; crossed nicols.

Comparison of the experimental results shown in figures 8 to 15 with the experimental results concerning the electrooptical behaviour of a smectic A with a preceding twisted nematic phase clearly points out *some similarities.* Both electrooptic effects are not accompanied by an observable electrohydrodynamic movement of the smectic A. There is a dielectric reorientation of the smectic A which is accompanied by a non-observable movement of dislocations which relax the strains. Such an electrooptic behviour of the smectic A is provoked for both classes under study by the peculiar character of the S_A deformations: symmetric focal conic domains embedded into a deformed smectic A. On the other hand, such dielectric reorientation is possible with the appropriate pinning of the S_A disclinations and/or dislocations on the surface irregularities of the glass plates [31, 65, 67], as mentioned previously. Both effects are reversible in a temperature range of 3°C to 5°C below the nematic or the cholesteric to smectic A transition. The extent of this temperature interval depends on the strength of the applied voltage. There are *some differences* as well. For example, the turn-off relaxation times of the smectic A phase, with a preceding twisted nematic phase, are faster relative to those of the smectic A phase with a preceding large-pitch cholesteric phase. The turn-on times however, are nearly equal in both cases. Secondly, the relative change in the transmitted light is larger for the case of a smectic A phase with a preceding twisted nematic phase. These differences are evidently connected with the details of the S_A textures in both cases. In our opinion, the S_A textures obtained in a smectic A phase with a preceding twisted nematic phase are more typical and are connected with the stronger influence of the boundaries. For the case of a smectic A with a preceding large-pitch cholesteric phase, the S_A textures are connected rather with the particular character of the large-pitch cholesteric phase, e.g. the electrooptic effect in this type of smectic A does not depend significantly on the initial orientation of the director at the boundaries. For instance, the electrooptic transmission curves shown in figure 15 are obtained for a twisted orientation of the pseudo-nematic. For the case of a planar orientation of the pseudo-nematic, the electrooptic transmission curves are slightly different.

The observation of a driven voltage-controlled electrooptic reversible effect in a smectic A phase with a preceding large-pitch cholesteric phase demonstrates that such a behaviour is typical for many smectic A phases with the only requirement being a small latent heat of the smectic A–nematic or large-pitch cholesteric phase transition in comparison with the thermal energy.

5. Conclusions

We have discovered for the first time a driven voltage-controlled completely reversible electrooptic effect in smectic A liquid crystals which can be used in displays [82]. Such a reversible electrooptic effect can be obtained with the following conditions for the case of a preceding twisted nematic phase:

(*a*) a liquid crystal with a small latent heat for the smectic A–nematic transition at least in comparison with thermal energies is needed [32].

(*b*) the glass plates of the cells which contain the liquid crystal should be treated by silicon monoxide to achieve a strong θ-polar anchoring of the S_A structure which must be sufficient to support the focal conic domains being created; the φ-azimuthal anchoring of the S_A director should be smaller relative to the energy stored in the focal conic domains;

(*c*) the nematic director must be twisted at an angle of 90° in the direction of the electric field;

(*d*) the twisted nematic phase must be electrically excitated by a voltage greater than $5U_{\mathrm{th}}$, where U_{th} is the threshold voltage which causes the appearance of the Fréedericksz transition in the twisted nematic for the case of strong anchoring, and then cooled to the smectic A phase in the presence of the voltage.

For the case of a smectic A phase with a preceding large-pitch cholesteric phase conditions (*a*), (*c*) and (*d*) must be replaced by (*e*), (*f*) and (*g*) respectively:

(*e*) a liquid crystal with a small latent heat for the smectic A–cholesteric transition, that is small in comparison with the thermal energies [32];

(*f*) the large-pitch cholesteric should have a Grandjean-like orientation and the helix axis must be along the direction of the electric field;

(*g*) the Grandjean-like texture of the large-pitch cholesteric must be electrically excited with a voltage greater than $5U_{th}$, where U_{th} is the threshold voltage which causes the appearance of the Helfrich undulations of the large-pitch cholesteric planes for strong anchoring and cooled down to the smectic A phase in the presence of the voltage.

This electrooptic effect is completely reversible in the smectic A phase, in a narrow temperature interval 3°C to 5°C below the S_A–N transition temperature where the elastic behaviour of the smectic A phase is still manifest. In the temperature region with plastic behaviour, the S_A scattering centres cannot be controlled by the voltage. There is no need to reheat to the nematic phase since the electrooptical effect is completely reversible in the smectic A phase.

The reversibility of the electrooptic effect is probably connected with the dielectric reorientations of the smectic A phase accompanied by a non-observable movement of dislocations and provoked by the peculiar character of the S_A deformations: symmetric focal conic domains embedded in a deformed smectic A.

We mention the more important advantages and disadvantages of this novel electrooptic effect. The main advantages are in our opinion:

(*a*) for the first time a driven voltage-controlled reversible electrical switching of S_A deformations has been achieved;

(*b*) for the first time electrical reversibility of a storage effect in the smectic A phases has been demonstrated.

The main disadvantages are in our opinion

(*a*) the relaxational times are rather slow, although they can be made faster with the use of larger voltages;

(*b*) the driven voltage-controlled reversible electrooptic effect exists in a narrow temperature interval which is typical for nearly all controlled electrooptic effects in the smectic A phases [7, 8, 16, 17]. This temperature interval can be made larger when a higher voltage excites the smectic A phase;

(*c*) the contrast is insufficiently high due to the specific character of the textural transformations.

Nevertheless, the observation of the driven voltage-controlled reversible electrooptic effect in smectic A phases is the first step and it will probably stimulate the effort of other researchers in this direction. Some electrooptical characteristrics, important for the technical application of this novel electrooptic effect, will be published elsewhere.

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References

[1] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Oxford University Press).
[2] Rapini, A., 1972, *J. Phys., Paris*, **33**, 237.
[3] Parodi, O., 1972, *Solid St. Commun.*, **11**, 1503.
[4] Goscianski, M., Léger, L., and Mircea-Roussel, A., 1975, *J. Phys. Lett., Paris*, **36**, L-313.

[5] Tani, C., 1971, *Appl. Phys. Lett.*, **23**, 241.

[6] Geurst, J. A., and Goossens, W. J. A., 1972, *Physics Lett.* A, **41**, 369.

[7] Le Berre, S., and Hareng, M., 1976, *Étude des effects electrooptiques et thermooptiques dans les cristaux liquides smectiques en vue de leur application à la visualisation,* Raport Final DGRST No. 74.7.1408, Thomson-CSF.

[8] Le Berre, S., and Hareng, M., 1977, *Étude des phenomenes basse frequence dans les smectiques A*, Raport Final DGRST No. 76.7.0117, Thomson-CSF.

[9] Dazai, F., Uchida, T., and Wada, M., 1977, *Molec. Crystals liq. Crystals Lett.*, **34**, 197.

[10] Chirkov, V. N., Aliev, D. F., and Zeinally, Z. Kh., 1977, *Pis'ma Zh. Tekh. Fiz.*, **3**, 1016.

[11] Coates, D., Crossland, W. A., Morrissy, J. H., and Needham, B., 1978, *J Phys.* D, **11**, 2025.

[12] Chirkov, V. N., Aliev, D. F., Radshabov, G. M., and Zeinally, A. Kh., 1979, *Molec. Crystals liq. Crystals Lett.*, **49**, 293.

[13] Pichikjan, N. A., Slepkov, I. A., and Sonin, A. A., 1980, *Kristallografia*, **25**, 187.

[14] Aliev, D. F., Chirkov, V. N., and Zeinally, A. Kh., 1981, *Kristallografia*, **26**, 144.

[15] Le Berre, S., and Hareng, M., 1978, *Ann. Phys.*, **3**, 327.

[16] Hareng, M., Le Berre, S., and Thirant, L., 1974, *Appl. Phys. Lett.*, **25**, 683.

[17] Hareng, M., Le Berre, S., and Metzger, J., 1975, *Appl. Phys. Lett.*, **27**, 575.

[18] Dunmur, D. A., and Walton, T. W., 1985, *Molec. Crystals liq. Crystals Lett.*, **2**, 7.

[19] Raynes, E. P., 1980, *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag) p. 176.

[20] Raynes, E. P., 1983, *Phil. Trans. R. Soc.* A, **309**, 167.

[21] Hareng, M., Le Berre, S., and Hehlen, R., 1977, *Rev. Tech. Thomson-CSF*, **9**, 373.

[22] Crossland, W. A., and Ayliffe, P. J., 1982, *Proc. Soc. Inf. Disp.*, **23**, 9.

[23] Crossland, W. A., and Canter, S., 1985, *Soc. Inf. Disp. Int. Symp. Digest*, Orlando, Florida, p. 124.

[24] Crossland, W. A., and Canter, S., 1985, *Electron. Engng*, **57**, 35.

[25] Walker, C. J., and Crossland, W. A., 1985, *Displays*, **6**, 207.

[26] Canter, S., and Crossland, W. A., 1986, *Electric. Commun.*, **60**, 87.

[27] Coates, D., Crossland, W. A., Morrisy, J. H., and Needham, B., 1978, *Molec. Crystals liq. Crystals Lett.*, **41**, 151.

[28] Coates, D., 1978, *Molec. Crystals liq. Crystals Lett.*, **49**, 83.

[29] Smith, K., 1985, *Elektronika*, **58**, 13, a Russian translation of *Electronics*, **58**, Nos. 28 and 29.

[30] Hinov, H. P., and Avramova, K., 1988, *Liq. Crystals*, **3**, 1505.

[31] Chou, N. J., Depp, S. W., Eldrige, J. M., Lee, M. H., Sprokel, G. J., Juliana, A., and Brown, J., 1983, *J. appl. Phys.*, **54**, 1827.

[32] Cladis, P. E., and Torza, S., 1975, *J. appl. Phys.*, **46**, 584.

[33] Chu, W. H., and Jacobs, J. T., 1978, *IBM Jl. Res. Dev.*, **22**, 40.

[34] Hinov, H. P., 1981, *J. Phys., Paris*, **42**, 307.

[35] Hinov, H. P., Shonova,, N., and Avramova, K., 1983, *Molec. Crystals liq. Crystals*, **97**, 297.

[36] Madhusudana, N. V., and Strikanta, B., 1983, *Molec. Crystals liq. Crystals*, **99**, 375.

[37] Bidaux, R., Boccara, N., Sarma, C., de Seze, L., de Gennes, P. G., and Parodi, O., 1973, *J. Phys., Paris*, **34**, 661.

[38] de Gennes, P. G., 1972, *Solid St. Commun.*, **10**, 753.

[39] Langevin, D., 1976, *J. Phys., Paris*, **37**, 755.

[40] Sethna, J. P., and Kléman, M., 1982, *Phys. Rev. A*, **26**, 3037.

[41] Ktorides, P. I., and Uhrich, D. L., 1982, *Molec. Crystals liq. Crystals*, **87**, 69.

[42] Meirovitch, E., and Freed, J. H., 1980, *J. phys. Chem.*, **84**, 2459.

[43] Hinov, H. P., and Petrov, M., 1983, *Molec. Crystals liq. Crystals*, **100**, 223.

[44] Hinov, H. P., 1983, *Jap. Display*, p. 360.

[45] Hinov, H. P., and Derzhanski, A. I., 1984, *Molec. Crystals liq. Crystals*, **114**, 119.

[46] Cox, R., and Johnson, J., 1978, *IBM Jl. Res. Dev.*, **22**, 51.

[47] Chu, K. C., and McMillan, W. L., 1977, *Phys. Rev.* A, **15**, 337.

[48] Karat, P. P., and Madhusudana, N. V., 1977, *Molec. Crystals liq. Crystals*, **40**, 239.

[49] Longberg, F., and Meyer, R., 1985, *Phys. Rev. Lett.*, **55**, 718.

[50] Kini, U. D., 1986, *J. Phys., Paris*, **47**, 693.

[51] Oldano, J. C., 1986, *Phys. Rev. Lett.*, **56**, 1091.

[52] MIRALDI, E., OLDANO, C., and STRIGAZI, A., 1986, *Phys. Rev.* A, **34**, 4348.
[53] KINI, U. D., 1986, *J. Phys., Paris*, **47**, 1829.
[54] ROSENBLATT, CH., PINDAK, R., CLARK, N. A., and MEYER, R. B., 1977, *J. Phys., Paris*, **38**, 1105.
[55] ASHER, S. A., and PERSHAN, P. S., 1979, *J. Phys., Paris*, **40**, 181.
[56] BENTON, W. J., TOOR, E. W., HILLER, C., and FORT, JR., T., 1979, *J. Phys., Paris*, **40**, 107.
[57] OSWALD, P., BÉHAR, J., and KLÉMAN, M., 1982, *Phil. Mag.* A, **46**, 899.
[58] WILLIAMS, C. E., and KLÉMAN, M., 1974, *J. Phys. Lett., Paris*, **35**, L-33.
[59] WILLIAMS, C. E., and KLÉMAN, M., 1975, *J. Phys., Paris, Coll.*, **36**, C1-315.
[60] WILLIAMS, C. E., 1976, Thése Dr. Sci., Orsay, Université de Paris-Sud.
[61] DURAND, G., 1972, *C. r. hebd. Séanc. Acad. Sci., Paris B*, **275**, 629.
[62] CLARK, N. A., and MEYER, R. B., 1973, *Appl. Phys. Lett.*, **22**, 493.
[63] DELAYE, M., RIBOTTA, R., and DURAND, G., 1973, *Phys. Lett.* A, **44**, 139.
[64] RIBOTTA, R., 1975, Thése Dr. Sci., Orsay, Université de Paris-Sud.
[65] FRIEDEL, J., 1979, *J. Phys., Paris, Coll.*, **40**, C3-45.
[66] DURAND, G., 1983, *J. Chim. phys.*, **80**, 119.
[67] PERSHAN, P. S., and PROST, J., 1975, *J. appl. Phys.*, **46**, 2343.
[68] PERSHAN, P. S., 1974, *J. appl. Phys.*, **45**, 1590.
[69] RIBOTTA, R., and DURAND, G., 1977, *J. Phys., Paris*, **38**, 179.
[70] BARTOLINO, R., and DURAND, G., 1977, *Molec. Crystals liq. Crystals*, **40**, 117.
[71] URBACH, W., BOIX, M., and GUYON, E., 1974, *Appl. Phys. Lett.*, **25**, 479.
[72] PROUST, J. E., and PEREZ, E., 1977, *J. Phys. Lett., Paris*, **38**, L-91.
[73] PEREZ, J. E., and PROUST, J. E., 1977, *J. Phys. Lett., Paris*, **38**, L-117.
[74] HOCHBAUM, A., and LABES, M. M., 1982, *J. appl. Phys.*, **53**, 2998.
[75] KLÉMAN, M., 1977, *J. Phys., Paris*, **38**, 1511.
[76] DE GENNES, P. G., 1974, *Physics Fluids*, **17**, 1645.
[77] ORSAY GROUP ON LIQUID CRYSTALS, 1975, *J. Phys., Paris, Coll.*, **36**, C1-305.
[78] KLÉMAN, M., and WILLIAMS, C. E., 1974, *J. Phys. Lett., Paris*, **35**, L-49.
[79] MARIGNAN, J., and PARODI, O., 1979, *J. Phys., Paris, Coll.*, **40**, C3-78.
[80] MARIGNAN, J., MALET, G., and PARODI, O., 1978, *Ann. Phys.*, **3**, 221.
[81] ADOMENAS, P. V., VISTIN', L. K., MESROPYAN, A. N., TUBELITE, A. A., CHISTYAKOV, I. G., CHUMAKOVA, S. P., EIGENBROT, V. M., and YAKOVENKO, S. S., 1977, *Zh. eksp. teor. Fiz.*, 1903, English translation in *Sov. Phys. JETP*, **46**, 999.
[82] HINOV, H. P., 1988, *Bull. Patents and Trade Marks*, Certificate of authorship, N 76021.
[83] HINOV, H. P., and KUKLEVA, E., 1984, *Molec. Crystals liq. Crystals*, **90**, 203.
[84] DEMUS, D. (editor), 1978, *Forschungen über flüssige kristalle 1: 4-n-Octyloxybenoesäure-4-nitrophenyl-ester*, Vol. 21 (Martin-Luther Univ., Halle-Wittenberg, Wiss. Beitrage).
[85] BARNIK, M. I., BELJAEV, S. V., RUMJANSEV, V. G., ZWETKOFF, V. A., and SHITKOV, N. M., 1978, *Wiss. Beitrage*, **21**, 95.
[86] DEMUS, D., DEUTSCHER, H. J., KONIG, S., KRESSE, H., KUSCHEL, F., PELZL, G., SCHUBERT, H., SELBMANN, CH., WEISSFLOG, W., WIEGELEBEN, A., and WULF, J., 1978, *Wiss. Beitrage*, **21**, 9.