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A Driven Voltage-Controlled Reversible Electrooptic Effect in a Smectic A Phase II. PVA Anchoring

H. P. Hinov[a]; K. Avramova[a]
[a] Georgi Nadjakov Institute of Solid State Physics, Sofia, Bulgaria

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

II. PVA anchoring

by H. P. HINOV and K. AVRAMOVA
Georgi Nadjakov Institute of Solid State Physics, Boulevard Lenin 72, Sofia 1784, Bulgaria

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The driven voltage-controlled reversible electrooptic effect in a smectic A phase with a preceding nematic phase twisted by SiO anchoring, previously discovered (cf. the previous paper) has been studied with polyvinyl alcohol (PVA) anchoring. The unique feature of this novel electrooptic effect in smectic A phases is that it reverses by relaxing when the electric field is removed. For the case of PVA anchoring the reversibility of the effect only occurs near the smectic A–nematic phase transition in the smectic A phase. The temperature region of the reversibility of this effect can be widened with a higher voltage. A comparison with the case of a reversible electrooptic effect in a smectic A with a preceding twisted nematic phase and SiO anchoring is made. The possible application of this electrooptic effect in liquid crystal displays with storage is discussed briefly.

1. Introduction

At the present stage of experimental investigations, a specific reversible electrooptic effect in smectics A has been discovered, based on the planar-to-homeotropic smectic A transition [1–8]. This effect has been applied in large flat liquid crystal panel displays with a memory [9–15]. Their operation is connected with the existence of two stable structures in the smectic A phase, the one being transparent, and the other opaque, resulting in turn in one of the essential features of liquid crystal displays, namely its storage capability. The opaque and transparent structures in the smectic A phase are achieved by applying either a low-frequency electric field or a high-frequency electric field. Another type of 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 materials [16]. An important problem which still requires resolution is the achievement of a driven voltage-controlled reversible electrooptic effect in smectic A phases as stressed by Smith [17] (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 this novel electrooptic effect in smectic A phases).

The aim of this paper is to continue the study of the driven voltage-controlled reversible electrooptic effect observed and investigated for the first time in smectic A phases with a preceding twisted nematic or large-pitch cholesteric phase and SiO anchoring [18]. We have investigated a driven voltage-controlled reversible or partly reversible electrooptic effect near the smectic A–nematic phase transition in the smectic A phase, based on the reversible or partly reversible appearance or disappearance of textures created in the smectic A phase with a preceding nematic phase,

twisted by polyvinyl alcohol (PVA) anchoring excitated by an a.c. voltage above the threshold value and cooled down to the smectic A phase in the presence of the field. All of the smectic A textures observed exhibited a storage on the removal of the voltage. We describe our results by textural transformations of the smectic A phase and electrooptical transmission curves. A comparison is made with the cases when the preceding phase of the S_A is either a twisted nematic phase or a large-pitch cholesteric phase [18], both with SiO anchoring. The possibilities for the application of this effect for S_A displays are briefly discussed.

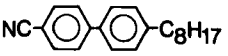
2. Description of the method

This method was described in detail in the preceding paper [18]. Nevertheless, we briefly mention the most important steps in the preparation of the S_A cells. First, there is a need from a liquid crystal with a small latent heat, comparable to thermal energies for the smectic A–nematic phase transition [19]. Secondly, the electric field applied should orient the preceding nematic phase in the middle of the sample and deform it in the boundary regions. With a relatively homogeneous temperature distribution across the nematic samples, the smectic A phase appears first in the middle part of the sample and then in the deformed boundary regions where the S_A–N transition temperature is considerably depressed [19]. Coinversely, in conventional S_A samples, the smectic A phase appears first at the glass plates where the nucleational energy is zero. This leads to uncontrolled formation of the smectic A phase. Our method permits first, to obtain good quality S_A scattering textures [19], secondly, to describe the matching of the surface and bulk smectic orientation, a much studied problem [20–24] and thirdly, to aid the calculation of the surface energy of interaction of smectics with the bounding walls [19, 25].

The possibilities of this novel method were confirmed again with the observation for the first time of a driven voltage-controlled reversible electrooptic effect in a smectic A phase with either a preceding twisted nematic phase or a preceding large-pitch cholesteric phase [18], both phases anchored by SiO. We demonstrate here the importance of the kind of anchoring which is closely related to the surface treatment of the glass plates. For instance, the replacement of the SiO orienting layer by polyvinyl alcohol (PVA), changes the previously observed electrooptic effect considerably, [18]. The S_A textures were changed drastically and the reversibility of the electrooptic effect was observed in the smectic A phase but only near the S_A–N transition.

3. Compounds and sample preparation

We have studied the liquid crystal 4-*n*-octyl-4′-biphenyl (8CB) with the structural formula:



and the transition temperatures [7, 9, 26]; C–S_A: 20°C, S_A–N: 32°C, N–I: 39·5°C; it is clear that four phases are present. The smectic A–nematic phase transition has been determined to be almost second order by a thermal differential analysis [7]. The dielectric anisotropy has been determined to be 8·2, with $\varepsilon_{\parallel} = 12{\cdot}8$ and $\varepsilon_{\perp} = 4{\cdot}6$, at a temperature of 22°C [7]. It is important to note that the value of the latent heat is

significantly different for the various phase transitions [26]:

$$C\text{–}S_A\text{: } 2{\cdot}52\,kJ\,mol^{-1},$$

$$S_A\text{–}N\text{: } 0{\cdot}304\,kJ\,mol^{-1},$$

$$N\text{–}I\text{: } 1{\cdot}232\,kJ\,mol.$$

It is clear that the latent heat at the S_A–N phase transition is very small which ensures the application of our method.

The liquid crystal was placed between two tin oxide-coated glass plates separated by teflon spacers with a thickness of 10 and 20 μm. The glass plates were dipped into a 1 per cent aqueous solution of PVA, removed slowly and dried in a oven at a temperature between 120°C–140°C [27, 28]. After the formation of the PVA layers they were rubbed to produce grooves which determine the uniform homogeneous alignment of the liquid crystal. The liquid crystal under study had a high purity; the specific conductivity of the cells was measured to be about $2\text{–}3 \times 10^{-12}\,\Omega\,cm^{-1}$. Consequently, the rubbing of the PVA layers does not contaminate the liquid crystal. The cell was constructed in such a way as to ensure a twist orientation of the nematic. The good twist orientation of the liquid crystal was observed under a microscope with a parallel position of the two nicols. Of course, a slight tilt of the molecules at the glass plates is possible. We have replaced the SiO orienting layer by a PVA in order to study the influence of the anchoring conditions and the various materials on the behaviour of the driven voltage-controlled reversible electrooptic effect discovered previously [18]. Furthermore, the substrates of the glass plates can be treated by PVA more easily, relative to the SiO orienting layers.

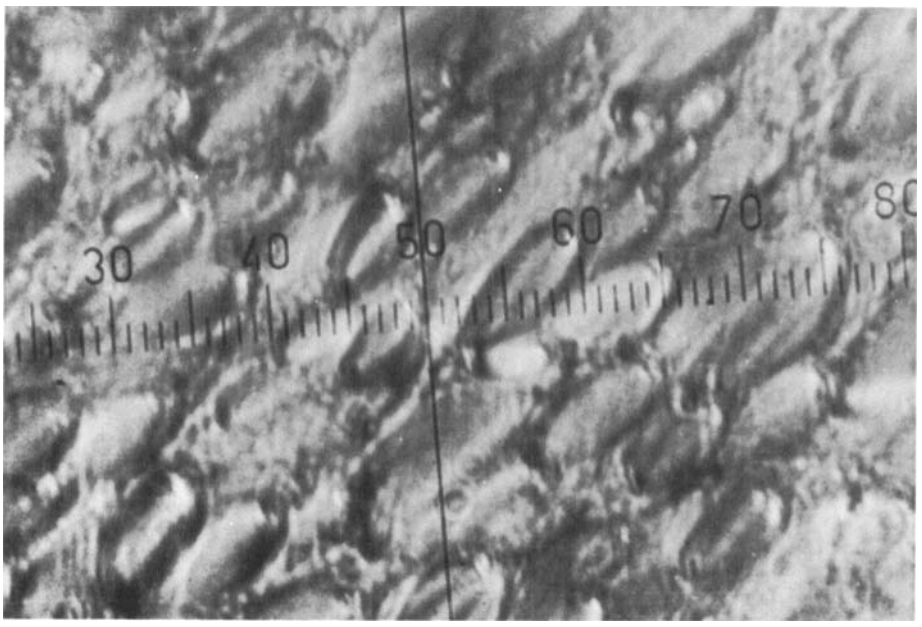
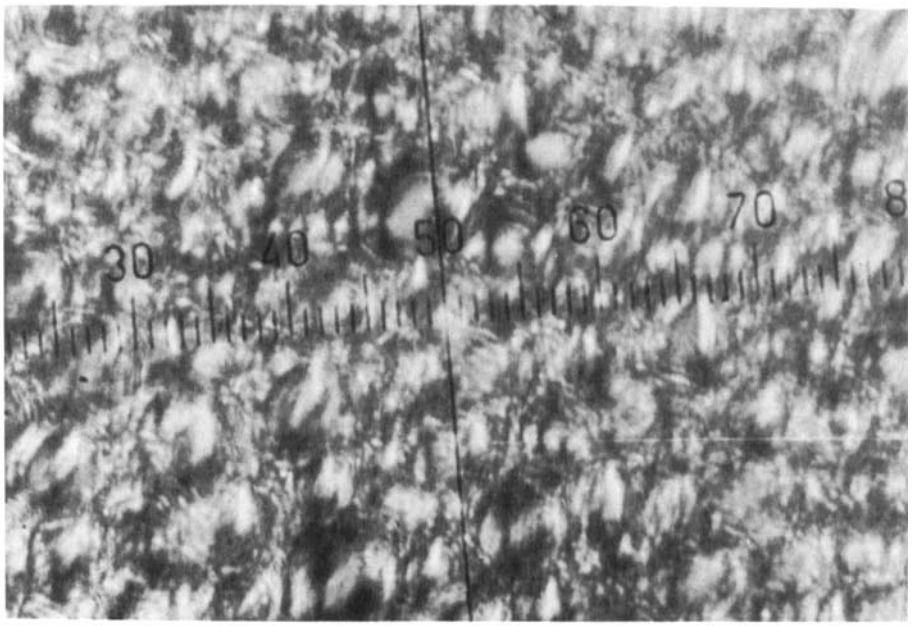
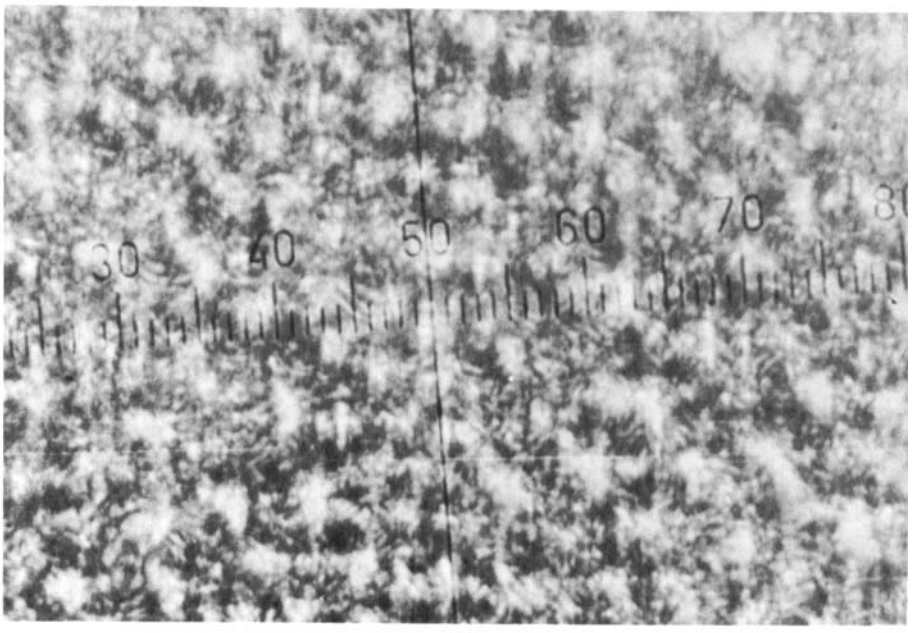


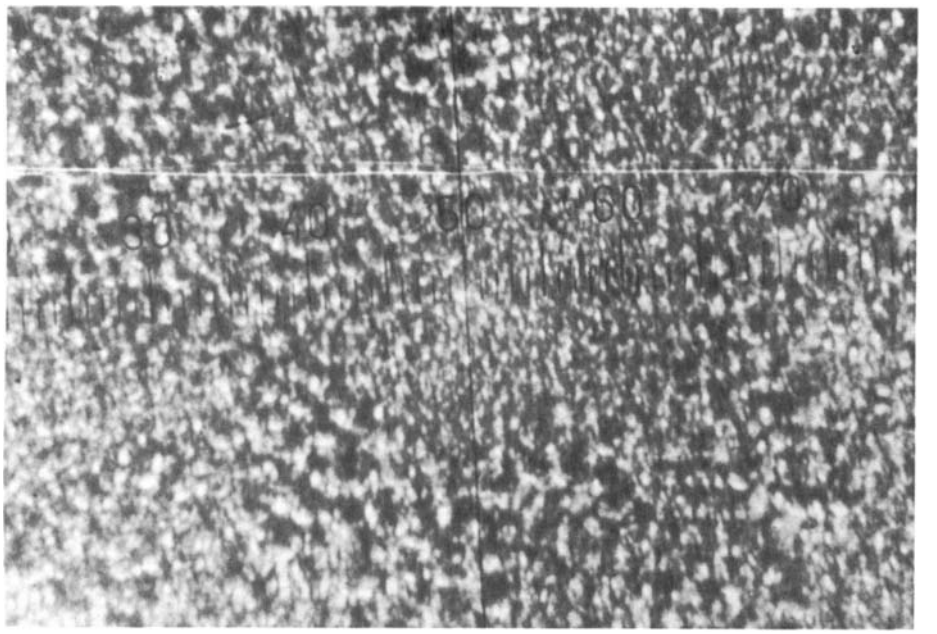
Figure 1. Grandjean walls obtained in S_A layer of 8CB with a thickness of 20 μm at a voltage excitation of the preceding nematic phase twisted by PVA anchoring which was cooled to the smectic A phase in the presence of the voltage; $U = 5\,V$ r.m.s. $f = 10\,kHz$, $P \perp A$, the 10 small divisions correspond to 29 μm.



(*a*)



(*b*)



(*c*)

Figure 2. Strongly-scattering textures stored in a S_A layer of 8CB with a thickness of 20 μm with an excitation voltage of the preceding nematic phase twisted by PVA anchoring which has been cooled to the smectic A phase in the presence of the voltage, $P \perp A$, the 10 small divisions correspond to 29 μm. (*a*) $U = 10$ V r.m.s., $f = 10$ kHz, (*b*) $U = 20$ V r.m.s., $f = 10$ kHz, (*c*) $U = 40$ V r.m.s., $f = 10$ kHz.

The nematic layer was subject to an a.c. voltage with a frequency between 1 and 10 kHz and an amplitude between $3U_{th}$ and $25U_{th}$, where U_{th} is the threshold voltage which causes the appearance of the Fréedericksz transition for strong anchoring of the nematic layer. The threshold voltage in our case was measured to be approximately 1·4 r.m.s. On the other hand, the threshold voltage for the case of SiO anchoring was approximately 1·6 r.m.s. It is clear that the θ-polar anchoring, which is defined later, for the SiO treatment of the glass plates is slightly larger [29]. During the a.c. voltage excitation, the nematic phase was cooled to the smectic A phase. The S_A deformations, which were very different from those obtained by SiO anchoring [18], could be controlled electrically but only close to the S_A–N transition in the smectic A phase. We now describe this electrooptical behaviour.

4. Experimental results

The S_A textures obtained were studied with the aid of a microscope with transmitted polarized white light. The application of an a.c. voltage with an amplitude of 5 V r.m.s. and a frequency of 10 kHz led to the observation of very well formed Grandjean walls as shown in figure 1 and studied by Williams [30] and by Williams and Kléman [31]. On the application of a higher voltage of 10 V r.m.s. we observed the well-known pretransitional stripe-like domains observed by Cladis–Torza [32] which were transformed in the smectic A phase into isolated circular-line focal conics embedded in a homeotropic S_A matrix. On the removal of the voltage however, we have observed strongly-scattering S_A textures which are shown in figures 2 (*a*) to (*c*) for a voltage of 10 V r.m.s., 20 V r.m.s. and 40 V r.m.s., respectively. Similar S_A

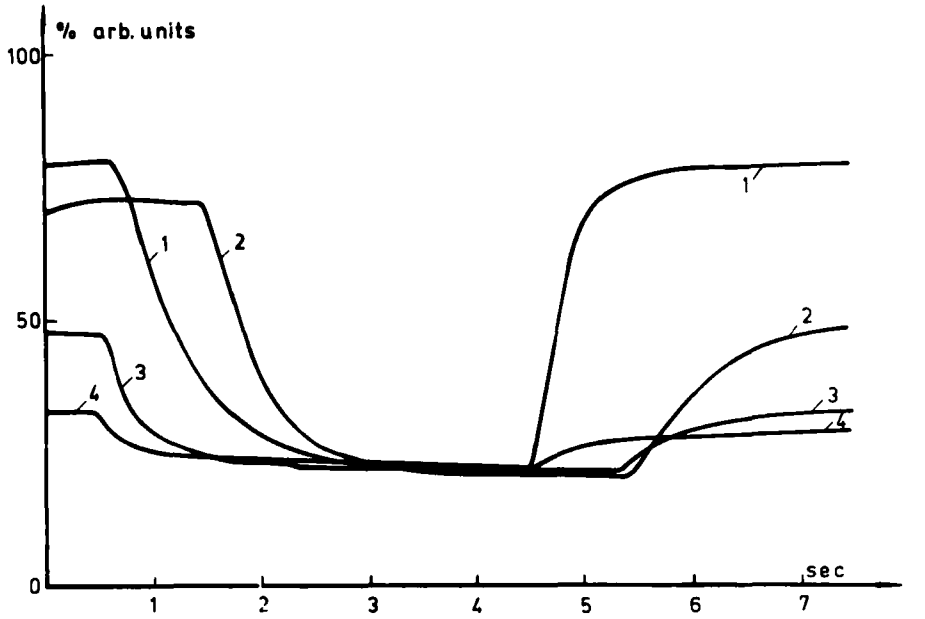


Figure 3. Electrooptic transmission curves obtained with an electronic recorder for an 8CB smectic A layer with a thickness of 10 μm. The applied voltage had an amplitude of 20 V r.m.s., f = 10 kHz. The curve, designated by 1, was recorded at the S_A–N phase transition in the smectic A phase. The temperature interval between each two successive curves is approximately 0·5°C.

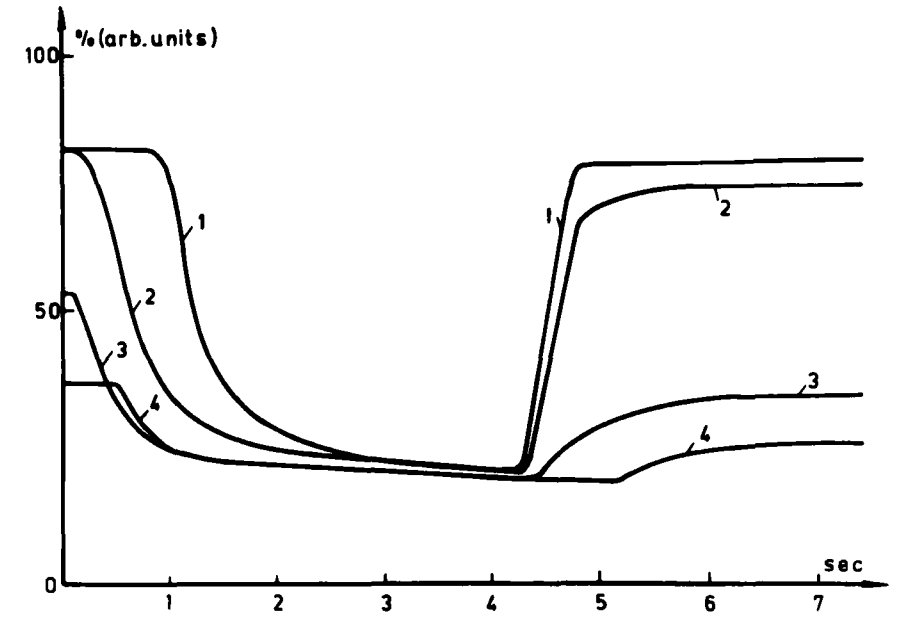


Figure 4. Electrooptic transmission curves obtained with an electronic recorder for an 8CB smectic A layer with a thickness of 10 μm. The applied voltage had an amplitude of 32 V r.m.s., f = 10 kHz. The curve, designated by 1, was recorded at S_A–N transition in the smectic A phase. The temperature interval between each two successive curves is approximately 0·5°C.

scattering textures have been obtained by many authors and particularly by Le Berre and Hareng [2] who have investigated their electrooptical behaviour in detail. However, the reversible electrooptical behaviour, illustrated in figures 3 and 4 is new. The electrooptic transmission curves obtained with an electronic recorder, are the electrooptic response of a S_A cell, illuminated with a He–Ne laser, followed by the detection of light with a special photodiode. The curves 1 to 4, shown in figure 3, were obtained with a excitation voltage of 20 V r.m.s., 10 kHz, applied in the smectic A phase up to the formation of the S_A scattering textures. The four curves were obtained with free cooling of the sample in a time interval of 30 s. The first curve was obtained in the smectic A phase near the S_A–N transition. The fourth curve was obtained at a temperature which according to our temperature controller was about 30°C. The curves 1 to 4, shown in figure 4, were obtained at a larger voltage of 32 V r.m.s. with the same conditions of cooling. It is seen that the larger voltage widens the temperature interval where the electrooptic effect is completely reversible. On the other hand, the electrooptic effect starts with a threshold. For instance, a voltage which is below 10 V r.m.s., cannot change the S_A textures. At a voltage of 10 V r.m.s. we observed only a small oscillation of the light transmitted through the S_A cell.

5. Discussion

We discuss our experimental results with respect of the surface anchoring of both the nematic and smectic A phases. From the literature it is well known that the kind of the anchoring: SiO, PVA or an other type, is very important for the electrooptical behaviour of a smectic A phase. For instance, Le Berre and Hareng [2, 6, 8] have studied the planar-to-homeotropic S_A transition for SiO anchoring. The silane treatment of the glass substrates however, has determined the homeotropic orientation of the S_A director [7]. Such an orientation of the director in the boundary regions permits the observation of focal conic-to-homeotropic S_A transition [7]. On the other hand, according to Dunmur and Walton [33], the SiO and PVA anchoring lead to identical experimental results. We first clarify the problem concerning the anchoring of the nematic and smectic A director [18]. The alignment of smectic phases on SiO treated substrates prepared with vacuum evaporation has been investigated mainly for bulk liquid crystals [34]. The φ-azimuthal anchoring of the smectic A director which controls the rotation of the director in the plane of the electrodes, and the θ-polar anchoring which controls the rotation of the director in planes which contain the normal to the glass plates and intersect the planes of the electrodes, were introduced in a way similar to that for the anchoring of the nematic director. The θ-polar anchoring energy has been measured by a number of authors [19, 25, 35, 36, 37] who obtained a value in the range of 10^{-3}–10^{-2} erg/cm^2. Very important remarks about the penetration of the smectic torques have been made by Meirovitch and Freed [38]. According to these authors one and the same substrate can create a strong anchoring of the nematic director and a weak anchoring of the smectic A director. This difference is naturally related to the peculiar character of the nematic and smectic A phases.

Let us compare the electrooptic effect obtained earlier for a preceding nematic phase twisted by SiO anchoring [18] with that obtained for the PVA anchoring. First, there is a large difference in the type of the S_A textures observed. With the SiO anchoring the S_A textures are very regular with the presence of many focal conic domains which are embedded into a deformed smectic A phase. With PVA anchoring the S_A textures are very irregular with the presence of many defects which evidently

leads to the observation of many irregular bright spots. Secondly, there is a large difference in the manner of the appearance or disappearance of the S_A textures. With SiO anchoring the S_A textures appear or disappear very smoothly without any visible electrohydrodynamic movement. We have suggested that this behaviour is connected with the dielectric reorientation of the S_A director, accompanied by a non-observable movement of dislocations. With PVA anchoring the appearance or disappearance of the S_A textures is accompanied by a visible movement of the fluid in the plane of the electrodes. As mentioned, the liquid crystal after the preparation of the cells had a high purity; the conductivity was measured to be in in the range of $2\text{–}3 \times 10^{-12}\,\Omega^{-1}\,\text{cm}^{-1}$. It is evident that such a movement is caused by essentially transverse movement of the defects [2, 8, 33, 39] which are not pinned on the glass plates [40] (for details see [18]). It is seen that the drastic change in the electrooptical behaviour is due to the type of anchoring and has its origins in both the value of the anchoring energy and the nature of the SiO or PVA covering layers. Evidently the SiO layer has many irregularities which on the one hand can pin the S_A defects [40] and on the other hand aids the heterogeneous nucleation of the focal conic domains [41]. The rubbed PVA layer is, however, smooth and the great part of the dislocations and disclinations are parallel to the glass plates. Since for such a position of the S_A defects the value of the surface energy is not important [41] (it is much less than $400\,\text{erg/cm}^2$), the smectic A phase is free and the electrohydrodynamic movement of the dislocations is in the plane of the electrodes. We stress that after the appearance or disappearance of the S_A scattering textures the movement stops. Electrohydrodynamic movement of a smectic A phase due to the conductivity mechanism is usually local and continuous in time. For SiO anchoring the greater part of the dislocations and disclinations are pinned on the glass plates and the anchoring of the smectic can influence the deformation or orientation of the smectic A phase. Finally, the difference in the two electrooptic effects might be due to the change in the elastic properties of the smectic A phase in the presence of many defects. This effect called diaelasticity has been suggested by Pershan [41] and by Pershan and Prost [40]. Due to the very different type of S_A textures, the electrooptic transmission curves are quite different. For PVA anchoring the contrast is higher and the response times are smaller.

The very well formed Grandjean walls shown in figure 1 were oriented along the bisectrix of the 90° twisted nematic. The type of Grandjean wall [30, 31] shows that the φ-azimuthal anchoring which hitherto has not been measured, is sufficiently strong to support the formation of such a wall. For SiO anchoring however [18] we did not observe the formation of such Grandjean wall nor asymmetric focal conics which would indicate a strong azimuthal anchoring of the smectic [2]. We saw only many circle-line focal conics which indicates the complete degeneration of the φ-azimuthal anchoring of the smectic A layer. We have observed such focal conics in the S_A phase which was obtained from a nematic phase strongly-deformed and twisted by PVA anchoring with a sufficiently high a.c. voltage. The removal of the voltage however, led to the observation of strongly-scattering S_A textures shown in figures 2 (*a*) to (*c*). Consequently, we can conclude that boundaries covered by a rubbed PVA layer cannot support focal conics embedded into a homeotropic S_A matrix, i.e. the φ-azimuthal anchoring of such boundaries is stronger relative to that of SiO treated boundaries whereas the θ-polar anchoring is weaker. It seems that all these causes led to the different formation of the smectic A phase; stripe-like pretransitional domains instead of small nematic droplets embedded into a undulated S_A layer [18], and as a consequence to the very different electrooptic behaviour.

We now describe the problem concerning the orientation of the liquid crystal director at the substrates treated by PVA layers. The electrooptic behaviour of the twisted nematic layers clearly shows that rubbing the PVA layers ensures a good planar orientation of the nematic director i.e. the relatively strong θ-polar surface energy at the two walls supports the formation of a well-defined 90° twisted nematic layer (a relatively strong φ-azimuthal surface anchoring). The situation is quite different however in the smectic A phase. The formation of well-defined Grandjean walls which are oriented at an angle of 45° with respect to the orientation of the S_A director at the two boundaries clearly indicates a strong φ-azimuthal anchoring of the S_A director whereas the θ-polar anchoring is weak and cannot support the initial planar alignment of the director achieved in the nematic phase. The sufficiently large surface tilt of the molecules cannot support the formation of focal conics embedded into either a homeotropic or a deformed smectic A phase [42]. On the other hand, Le Berre and Hareng [2] have obtained similar S_A textures as that shown in figures 2 (*a*) to (*c*) at T_N–T of 0·2°C in cells with surfaces treated by SiO. It seems that SiO anchoring in the experiments of Le Berre and Hareng cannot support the planar orientation of the S_A director near the smectic A–nematic transition.

6. Conclusions

We now comment briefly on the possibilities of the driven voltage-controlled electrooptic effect in smectic A phases investigated here for applications. Because of the higher contrast and the smaller relaxation time relative to the driven voltage-controlled reversible effect in S_A cells with boundaries treated by SiO [18] this electrooptic effect can be used in the liquid crystal devices with storage. Furthermore, the S_A scattering textures obtained are very stable with respect to temperature even near the smectic A–nematic transition (this is clear from the details of the electrooptic transmission curves). On the other hand, the reversibility of the effect can be widened considerably by applying a voltage which is sufficiently high (for instance in the range 150–200 V r.m.s.). Various levels of contrast can be achieved by several applications of one and the same voltage (see the experimental transmission curves). This is possible because of the partly reversible character of this electrooptic effect in a certain temperature interval. The contrast can be changed and by application of a voltage with a different amplitude in the twisted nematic phase by PVA anchoring and going into the smectic A phase on cooling. This way however, is more applicable in laser-addressed liquid crystal displays.

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