Comparison of the characteristics of the chiral analog of the de Vries type of smectic-*A** phase

O. E. Panarina,[1] Yu. P. Panarin,[2] J. K. Vij,[1,*] M. S. Spector,[3] and R. Shashidhar[3]
[1]*Advanced Materials Laboratory, Department of Electronic and Electrical Engineering, Trinity College, University of Dublin, Dublin 2, Ireland*
[2]*School of Electronic and Communications Engineering, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland*
[3]*Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Code 6900, 4555 Overlook Avenue SW, Washington, D.C. 20375*

(Received 23 January 2002; revised manuscript received 15 July 2002; published 28 May 2003)

In this paper we compare the results of three ferroelectric materials that exhibit unusual smectic-*A* (Sm*A*) phases. These phases have been assigned to chiral analogs of the de Vries Sm*A* phase. Several experimental techniques have been employed for this investigation. The possible molecular structures of de Vries Sm*A** phases are discussed.

DOI: 10.1103/PhysRevE.67.051709 PACS number(s): 42.70.Df, 61.30.Gd, 77.80.−e, 78.30.−j

INTRODUCTION

It is well known that the smectic layer spacing in the tilted smectic phases is lower than in the orthogonal smectic phases due to the molecular tilt. Nevertheless, in 1972, Diele *et al.* [1] reported a smectic-*A* (Sm*A*) phase with the same layer spacing as a nonchiral Sm*C* phase. Later on, the unusual Sm*A*-Sm*C* phase transition without a smectic layer shrinkage was observed in several publications both in the nonchiral [2–4] and recently in the chiral smectic liquid crystals (LCs) [5–9].

To explain the nature of the Sm*A*-Sm*C* transition without alteration in the smectic layer spacing, de Vries suggested [2] in 1974 a new type of Sm*A* phase, where the molecules are tilted similar to those in the Sm*C* phase. In one possible structure, the tilted Sm*C*-like smectic layers are stacked in a random fashion [3]. In other words, the molecules are tilted with respect to the smectic layer normal, similar to those in the Sm*C* phase, but the tilt directions in different smectic layers are randomly oriented or, strictly speaking, there is no long-range correlation in the azimuthal angle of the smectic layers. In this phase, the local symmetry of the smectic layer (C_{2h}) is the same as for the Sm*C* phase and in the case of chiral molecules the smectic layers possess a local spontaneous polarization. The overall symmetry of such a structure is $D_{\infty h}$ due to an averaging on all smectic layers and is the same as in the conventional orthogonal Sm*A* phase.

On the other hand, the same property (unshrinkable layer spacing) can be explained by another possible structure, where the molecules are tilted but there is no long-range order in the azimuthal angle within each smectic layer and only a short-range correlation in the tilting sense [4]. Hence, due to the averaging on any smectic layer, the uniaxial symmetry of the Sm*A* phase is observed. The overall symmetry of this arrangement as well as the local symmetry is $D_{\infty h}$, as of a conventional orthogonal Sm*A* phase.

In other words, to explain the unshrinkable smectic layers in Sm*A*-like phases, de Vries suggested two possible structures [3,4]: where the molecules are tilted with respect to the smectic layer normal, similar to those in the Sm*C* phase but the tilt directions in different smectic layers are randomly oriented [3], or uncoupling of the tilt directions in every single smectic layer occurs [4].

For the case of nonchiral liquid crystalline molecules, and consequently due to the absence of the local spontaneous polarization, both possible structures cannot be distinguished from each other and from the orthogonal Sm*A* phase.

For chiral materials, it was found that under the application of an external electric field, the behavior of this type of Sm*A** phase is different from the orthogonal Sm*A** phase, namely, the high electroclinic effect and the manner in which the saturation of the induced tilt angle with voltage is achieved. Such materials may or may not exhibit the field-induced Sm*A**-Sm*C** phase transition. The *macroscopic* behavior of the materials with the field-induced Sm*A**-Sm*C** phase transition was initially explained by a large high-order coefficient Θ^6 in the Landau free-energy expansion [10,11]. This explanation may probably be correct for the previously studied materials; nevertheless, this contradicts the recent Fourier transform infrared (FTIR) [12] and electro-optic [9,13,14] results on different samples. The dichroic ratio and birefringence in this type of Sm*A* materials are considerably lower than in the unwound Sm*C** phase and these show pronounced voltage dependencies.

The chiral de Vries materials exhibit a pronounced electroclinic effect [8]. Moreover, other Sm*A* materials with large electroclinic coefficients [10,11] may possess the de Vries structure. Two properties: the unshrinkable smectic layers at the Sm*A**-Sm*C** transition and a large electroclinic coefficient appear to be the essential features of de Vries materials, though differing explanations have been given. The first possible structure of the tilted Sm*A** phase suggested by de Vries [3] is similar to a new class of phase [15], *sliding phase*, predicted to occur in weakly coupled, three-dimensional stacks of two-dimensional *XY* systems. This structure is also supported by the recent computer simulations of smectic ordering in liquid crystals [16,17] that are composed of bent-rod strongly angled molecules interacting

*Author to whom correspondence should be addressed. Email address: jvij@tcd.ie

through only a soft repulsive potential, arising from the steric interactions. The existence of the structures similar to the sliding phase is also predicted by the axial nearest next neighbor interaction model [18], where the correlation between the neighboring smectic layers is weakened by a competition between the ferroelectric and antiferroelectric orderings, and finally the correlation is suppressed by a disordering effect of the thermal fluctuations.

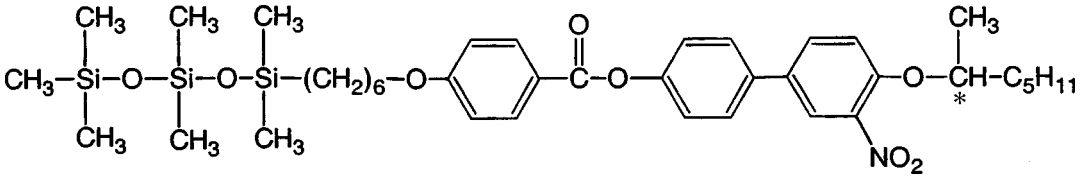
Strictly speaking, the molecules in the conventional Sm*A* phase are not perfectly perpendicular to the smectic layer either due to the nonideal molecular shape or the thermal fluctuations. Nevertheless, the average molecular director is perpendicular to the layers plane. In the de Vries phase, however, the local director of a sufficient volume (within the coherence length, ξ) makes a nonzero angle θ with the smectic layer normal.

In this paper, we present the results of the electro-optic and the polarized Fourier transform infrared investigations of three different liquid crystal samples possessing the de Vries type of Sm*A** phases. The experimental results for these materials are compared in order to understand the nature and the structural arrangement of these phases. We conclude that both types of molecular structures suggested by de Vries [2–4] are possible and both of them are observed in the present work.

EXPERIMENT

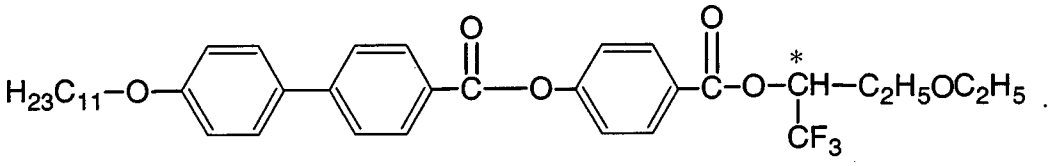
We have investigated three different materials TSiKN65, MC513, and C7.

The first sample under investigation is TSiKN65 [8,19]. The molecular structure and the phase sequence are presented below:



Sm*C**-25 °C–Sm*A**-56 °C–Is.

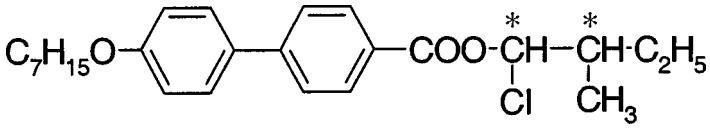
The second sample under investigation is MC513, the second component of the ''Tokyo mixture'' exhibiting a ''V-shape'' switching. The molecular structure of this compound is



From the phase diagram, presented in Ref. [20], the phase sequence of this compound was as follows:

Cr-35 °C–SmC_A^*-73 °C–Sm*C**-81.7 °C–Sm*A**-84.5 °C–Is.

The last material is C7, which is well known due to the papers of Bahr and Heppke [5,10,11];



Sm*G*-45 °C–Sm*C**-52 °C–Sm*A**-62 °C–Is.

The properties of C7 and MC513 are found to be almost identical to each other. In the manuscript, we present data only for MC513 because (i) this is a new material and (ii) the properties of MC513 and C7 are qualitatively the same. Therefore, the entire discussion about MC513 is valid for C7 too. Strictly speaking, there are no x-ray data on MC513. On the other hand, C7 is known as a material with (almost) unshrinkable smectic layers [5,10,11] at the Sm*C**-Sm*A** transition.

The sample cells consisted of two optically polished CaF_2 windows or glass plates for the infrared and electro-optic measurements, respectively, coated with thin conducting layers of indium tin oxide. We have made investigations on homogeneously aligned cells of thicknesses 5 μm and 15

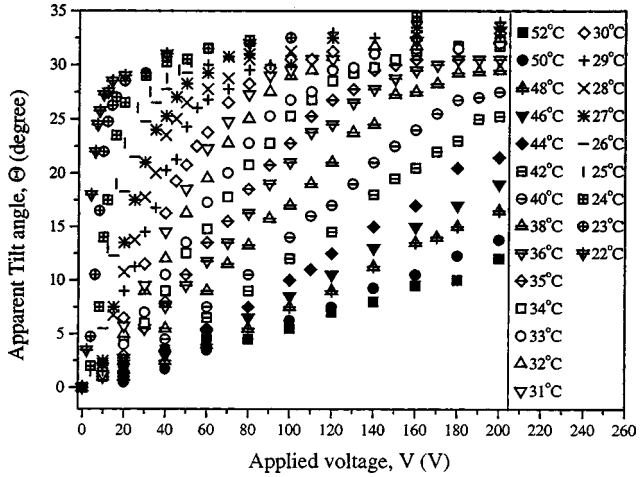


FIG. 1. Induced tilt angle versus applied voltage for a 5 μm cell of TSiKN65 for various temperatures.

μm: mylar films were used as a spacer. The orientant RN1266 (Nissan Chemicals Ltd.) was used as an alignment agent. The cells were filled with the liquid crystal in its isotropic phase by the capillary effect, and the samples were trained in order to produce a uniform structure. A Bio-Rad spectrometer FTS-60A with a 2 cm^{-1} resolution and averaging over 32 scans was used to record the spectra. Infrared spectra were measured as a function of the polarizer rotation angle under the application of bias voltage. We employed the (Perkin Elmer Grams Research) PEGR package to process the infrared spectra.

We focus only on the in-plane C-C phenyl ring stretching vibration positioned at about 1600 cm^{-1} due to the reason that the transitional dipole moment for this vibration is nearly parallel to the long molecular axis.

According to earlier papers [19,20] both materials, used in our study, show a Sm*A** phase on cooling. A thorough analysis of the properties of these Sm*A** phases reveals that they not only behave differently to a conventional orthogonal Sm*A* phase but also behave differently to each other. In our previous reports [9,12], we demonstrated that the Sm*A** phase seen for MC513 is not the conventional Sm*A** phase but is de Vries. In this paper, we compare the previously reported results with additional spectroscopic and electro-optic investigations in order to get a clearer view of the nature of these phases under investigation.

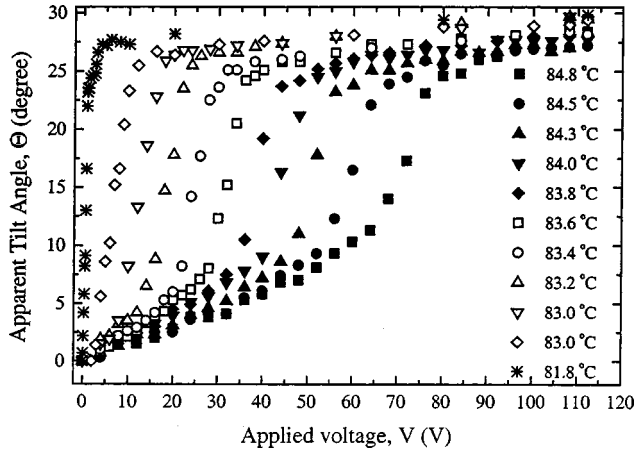


FIG. 2. Induced tilt angle versus an applied voltage for a 5 μm cell of MC513 for various temperatures.

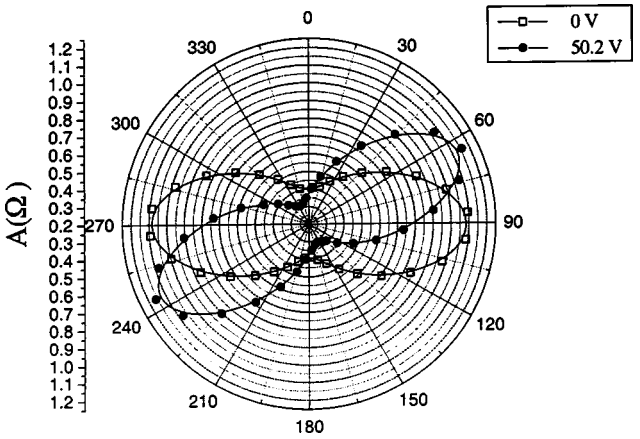


FIG. 3. Absorbance profiles $A(\Omega)$ of phenyl ring C-C stretching vibrations as a function of polarizer rotation angle for zero and saturated voltage of a 5 μm cell of TSiKN65 at a temperature of 27 °C (electric field is perpendicular to the page plane).

RESULTS

The results of electro-optic measurements on a 5 μm cell of TSiKN65 are presented in Fig. 1. An induced optical tilt angle is measured as a function of the applied voltage for different temperatures. For temperatures close to the transition to the isotropic phase the dependence is linear, result typical of the electroclinic effect, but as the sample approaches closer to the transition to the Sm*C** phase, shapes of the curves change. With an increase in applied voltage, the dependence becomes nonlinear; the tilt angle saturates at a value of about 32°. The response of the tilt angle to the external electric field shows a Langevin-type dependence. A

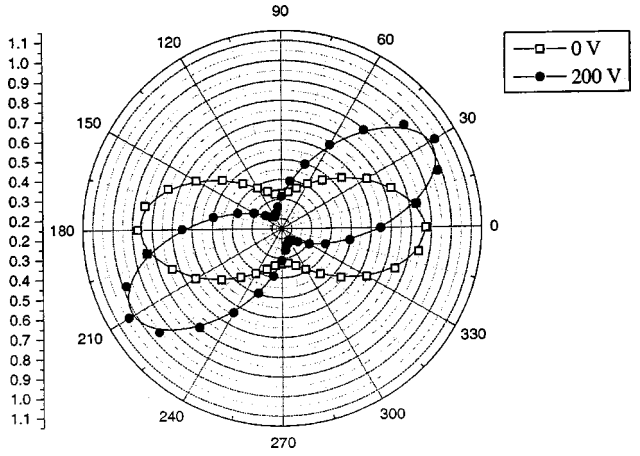


FIG. 4. Absorbance profiles $A(\Omega)$ of phenyl ring C-C stretching vibrations as a function of polarizer rotation angle for zero and saturated voltage of a 5 μm cell of MC513 at a temperature of 83.5 °C (electric field is perpendicular to the page plane).

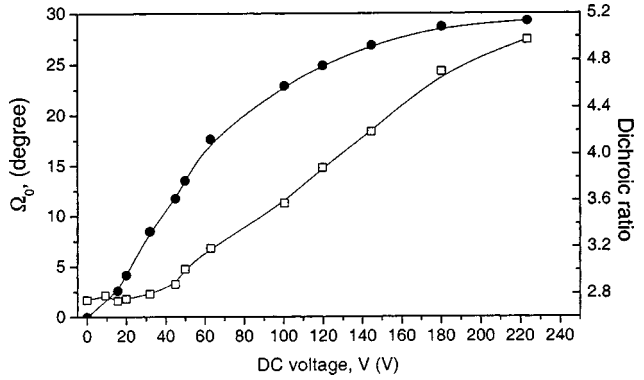


FIG. 5. Dichroic ratio (open squares) and angular shift (filled circles) versus applied dc voltage for a 5 μm cell of TSiKN65 at a temperature of 27 °C.

quite different behavior is found for the second sample. Figure 2 presents the induced tilt angle versus the applied electric field for a 5 μm cell of MC513. When the electric field is low, the electro-optic response is similar to that exhibited by the electroclinic effect in the Sm*A* phase. However, further increase in the applied voltage causes the electro-optic response to increase abruptly at some threshold voltage followed by saturation at about 27°. The threshold voltage decreases rapidly with temperature, while the saturation angle stays almost the same. For both materials, the saturated voltage is considerably large. We also performed electro-optic investigations for cells with a thickness of 15 μm in order to show that the results are independent of the cell thickness. The results indeed appeared to be identical to those for the cell of thickness 5 μm.

Figures 3 and 4 present the absorbance profiles $A(\Omega)$ as a function of the polarizer rotation angle for zero and saturated voltages in the Sm*A** phase of TSiKN65 and MC513, respectively. Application of a dc voltage results in the rotation of the absorbance profiles by an angle Ω_0; at sufficiently large voltages, Ω_0 reaches saturated value of $\Omega_{\max}$. The absorbance versus polarizer rotation angle for different values of the dc voltage was fitted to Eq. (1) [21,22]:

$$A(\Omega) = -\log_{10}[10^{-A_{\parallel}} + (10^{-A_{\perp}} - 10^{-A_{\parallel}})\sin^2(\Omega - \Omega_0)], \tag{1}$$

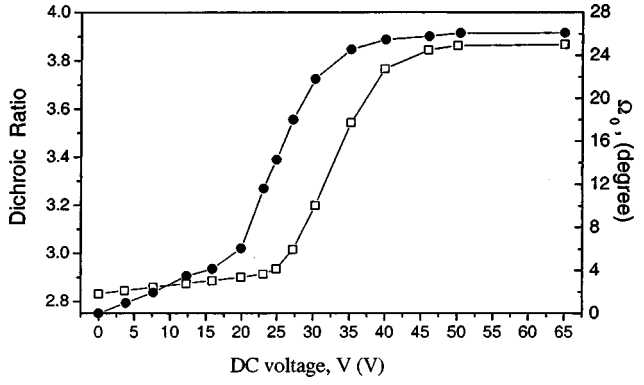


FIG. 6. Dichroic ratio (open squares) and angular shift (filled circles) versus applied dc voltage for of 5 μm cell of MC513 at a temperature of 83.5 °C.

where $A_{\parallel}$ and $A_{\perp}$ are the maximum and minimum values of the absorbance, Ω is the polarizer angle, and Ω_0 is the angle of maximal absorbance. Figures 5 and 6 show the dichroic ratio ($=A_{\parallel}/A_{\perp}$) and the angular shift Ω_0 versus the applied voltage for both materials. The behavior of the dichroic ratio is unusual. It is found to be strongly dependent on the applied electric field; furthermore, it reaches a saturated value at higher voltages. There is a difference in the voltage dependencies of the dichroic ratio between the two materials: it follows a smooth Langevin-type dependence for TSiKN65, whereas a steep jump to saturation occurs for MC513.

The angular shift exhibits very much the same voltage dependence as the optical tilt angle (see Figs. 1 and 2) for both samples.

Previously, the results of x-ray study of TSiKN65 were reported [8]. Layer spacing was determined as a function of temperature and electric field. It was found that the transition from the Sm*A** to the Sm*C** phase at zero field is not accompanied with a decrease in the layer spacing as normally seen for the transition from the orthogonal Sm*A* to the Sm*C** phase. In general, due to the tilting of the molecules in the Sm*C** phase, layer contraction by $\approx$10–20 %, depending on molecular conformation, is expected, but the experiment shows that the shrinkage in the layer spacing is less than 1%. An application of the electric field also does not result in any considerable layer shrinkage. This suggests that the molecules in Sm*A** phases are already tilted, but random azimuthal distribution leads to a uniaxial overall symmetry of the Sm*A** phase; further cooling to the Sm*C** phase induces azimuthal order.

DISCUSSION

It is clearly seen from the experimental results that materials under investigation do not possess a conventional Sm*A* phase, except the de Vries type of Sm*A** phase but their behavior to the induced tilt angle (angular) shift and dichroic ratio in the Sm*A** phase is different. TSiKN65 reveals the Langevin-like dependence, however, MC513 and C7 show a slow increase and then an abrupt jump to saturated values. The dielectric spectroscopy of these materials [9,23] shows that TSiKN65 possesses a second-order Sm*A**-Sm*C** transition [23], while MC513 exhibits a first-order transition [9]. This implies different mechanisms of the molecular reorientation under electric field and probably different molecular arrangements. Two possible molecular arrangements are suggested for the de Vries type of phases so far [3,4]. In the limit of zero field, both structures are indistinguishable from each other with $\langle \cos\varphi \rangle = 0$ and $\langle \cos^2\varphi \rangle = 0.5$. In this way, the only possibility to attribute structural arrangement to the observed behavior is to model the response of both structures to the external electric field. This can be done by a comparison of the experimental data (Langevin-type for TSiKN65 and an abrupt jump for MC513 and C7) with the relevant theoretical models. There are several theoretical models for both structures, and some of them [13,16,24] predict the electro-optic response for the de Vries structure with a short-range correlation in between the smectic layers.

Recently, Clark *et al.* [13] reported two samples with the

de Vries phase, exhibiting properties similar to MC513 and C7. They treated electro-optic results (similar to Fig. 2) assuming a simple model for the de Vries SmA^* phase structure with a short-range correlation in smectic layers. The local correlated regions are assumed to be uniaxial with a principal axis in the tilt plane, which is tilted by the angle θ_A. Coupling of the local polarization **P** with electric field **E** is expressed in terms of the molecular orientation correlation volume $\xi^3(T)$ with a coupling energy $U_p = -\xi^3(T)\mathbf{P}\cdot\mathbf{E} = -pE\cos\varphi$, where p is local dipole moment. The induced optical angle (angular shift) is related to $\langle\cos\varphi\rangle$ and $\langle\cos^2\varphi\rangle$ as follows:

$$\frac{\tan 2\theta(E)}{\tan 2\theta_A} = \langle\cos\varphi\rangle \frac{\tan^2\theta_A - 1}{\langle\cos^2\varphi\rangle\tan^2\theta_A - 1}. \qquad (2)$$

$\langle\cos\varphi\rangle$ and $\langle\cos^2\varphi\rangle$ are evaluated using the Langevin equation. However, they found that for the samples they studied, the model does not predict correct $\theta(E)$ shape for all electric field values; only the low field behavior can be predicted. From the model based on the Langevin equation, a smooth dependence without any inflection points, $d^2\theta(E)/dE^2 < 0$ for all E, is expected, instead of that, just before the saturation is achieved, curves experience discontinuities in $\theta(E)$. It seems that the suggested structure is not appropriate for their sample as well as for MC513 and C7. Nevertheless, this model seems to reproduce well the results for TSiKN65. Therefore, one may conclude that the de Vries structure (without long-range order in smectic layers) discussed in Ref. [13] is more appropriate to TSiKN65 than for MC513 and C7.

The second argument for such an assignment is also supported by the Monte Carlo simulations [16], which give the Langevin-like dependence of tilt and polarization on the electric field. These simulations predict that the slope of the induced tilt angle depends on the temperature, the higher the temperature the lower is the slope. Precisely, we observed the same type of electro-optic response to that exhibited by TSiKN65 (see Figs. 1, 3, and 5).

The third argument is supported by the theoretical model recently developed by Meyer *et al.* [24]. They considered the de Vries structure with a short-range order in smectic layers and showed that for such a phase the induced polarization and/or tilt angle changes continuously with the electric field (Langevin-like), similar to TSiKN65 (Fig. 1).

All three theoretical approaches for the de Vries phase with a short-range order of azimuthal angle in smectic layers discussed above predict the Langevin-like dependence of tilt and polarization on the electric field, similar to the experimental data for TSiKN65.

A strong argument for the existence of such a structure was given by Collings *et al.* [14] They reported an unusually low order parameter (0.35–0.4) in TSiKN65, which is considerably lower than the order parameter of conventional smectic phases (~0.7). This fact could explain the absence of long-range correlation in this material.

On the other hand, the microscopic observation of MC513 [Fig. 7(b)] detects the coexistence of two types of domains at a voltage around the threshold. The shape of the domains is strongly elongated in the direction of the smectic layer plane, similar to dechiralization lines in the helical SmC^* phase. Normally, a growth of the domains accounts for sharp changes or abrupt jumps in physical properties of the LC under the electric field. Such a scenario is more appropriate for the de Vries structure with a long-range correlation in smectic layers (sliding phase [15] or disordered phase [18]). Nevertheless, we cannot compare the shape of the curves for MC513 (and C7) (Figs. 2 and 6) since the electroclinic response is not developed in these models [15,18].

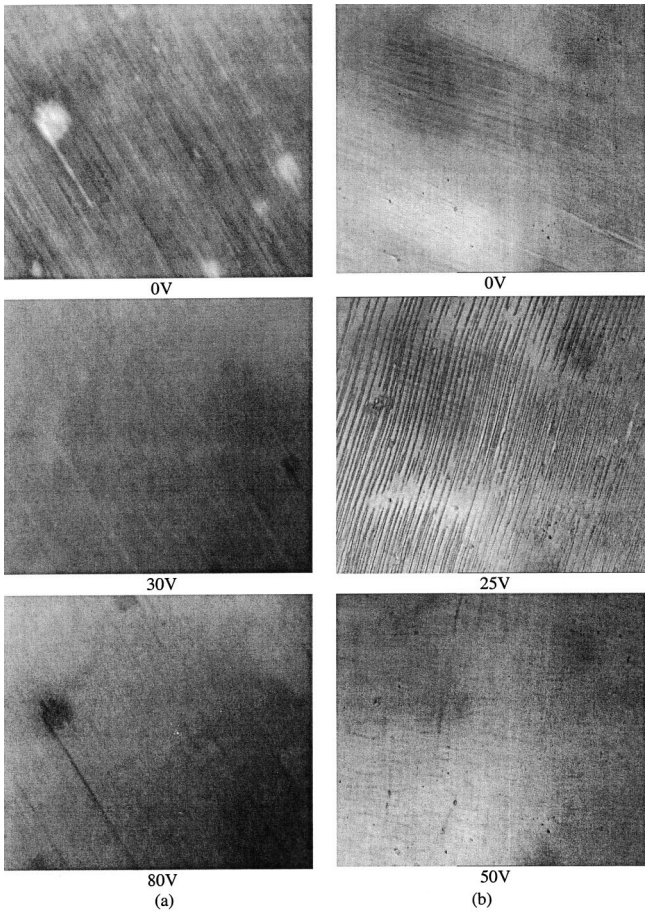


FIG. 7. Cell texture of both materials with and without a applied voltage: (a) TSiKN65 at a temperature of 27 °C and (b) MC513 at a temperature of 83.4 °C.

Finally, a strong argument for these structural assignments of de Vries phases was presented recently at ILCC'2002, Edinburgh. The critical behavior of the SmA^*-SmC^* transition of de Vries compounds as well as conventional SmA^* phases was investigated by the electro-optic technique [25]. The temperature dependence of the electro-optic V_{eo} response, which is proportional to the susceptibility, in the SmA^* phase was fitted to the power law equation [26]:

$$V_{eo} = A\left(\frac{T - T_{AC}}{T_{AC}}\right)^{-\gamma}.$$

The critical exponent value γ was found to be 0.67 for MC513 and C7, 1.72 for TSiKN65, and 1.34 for conven-

tional Sm*A* materials. In a conventional (orthogonal) Sm*A* material, the correlations are two dimensional and $\gamma = 2\nu = 1.33$, where $\nu = 0.67$ is a critical exponent for the correlation length. This result ($\gamma \approx 1.33$) is in a good agreement with theoretical values for the Sm*A*-Sm*C* phase transition developed by de Gennes and Prost [27].

In the case of MC513 and C7, $\gamma = \nu = 0.67$; this implies that the correlations are one dimensional, the result is consistent with the sliding phase structure.

For the de Vries structure with only a short-range order in the smectic layers, the correlations can be at least two dimensional ($\gamma = 1.33$) or even three dimensional ($\gamma = 2$). So the value $\gamma = 1.72$ for TSiKN65 lies within a possible range (1.33–2.0); the details of these results will be published elsewhere.

CONCLUSION

Three materials showing the de Vries type of Sm*A** phases are studied using the electro-optic and FTIR techniques. A comparison of the experimental results with Monte Carlo simulations [16] and some theoretical findings [13,24] leads us to suggest that one of the samples (TSiKN65) with a second-order Sm*A*-Sm*C** transition possesses a structure with no long-range correlation within the smectic layer suggested by de Vries [4]. On the other hand, two other de Vries materials (MC513 and C7) with a first-order Sm*A*-Sm*C** transition more likely possess a structure with long-range order of azimuthal angle in the smectic layers [3] (or the sliding phase [15]).

ACKNOWLEDGMENTS

We thank Professor A. Fukuda for supplying MC513 material and for fruitful discussions. Professor T. C. Lubensky is thanked for very useful discussions. O.E.P. thanks Enterprise Ireland for financial support.

[1] S. Diele, P. Brand, and H. Sackman, Mol. Cryst. Liq. Cryst. **16**, 105 (1972).
[2] A. De Vries, in *Abstracts of the Fifth International Liquid Crystal Conference, Stockholm*, edited by G. H. Brown (ILC Society, Kent, OH, 1974), p. 150.
[3] A. De Vries, Mol. Cryst. Liq. Cryst. **41**, 27 (1977).
[4] A. De Vries, A. Ekachai, and N. Spielberg, Mol. Cryst. Liq. Cryst. Lett. **49**, 143 (1979).
[5] B. R. Ratna, R. Shashidhar, G. G. Nairi, S. K. Prasad, Ch. Bahr, and G. Heppke, Phys. Rev. A **37**, 1824 (1988).
[6] M. D. Radcliffe, M. L. Brostrom, K. A. Epstein, A. G. Rappaport, B. N. Thomas, R. Shao, and N. A. Clark, Liq. Cryst. **26**, 789 (1999).
[7] F. Giesselmann, P. Zugenmaier, I. Dierking, S. T. Lagerwall, B. Stebler, M. Kaspar, V. Hamplova, and M. Glogarova, Phys. Rev. E **60**, 598 (1999).
[8] M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt, and R. Shashidhar, Phys. Rev. E **61**, 1579 (2000).
[9] Yu. P. Panarin, V. Panov, O. E. Kalinovskaya, and J. K. Vij, J. Mater. Chem. **9**, 2967 (1999).
[10] Ch. Bahr and G. Heppke, Phys. Rev. A **41**, 4335 (1990).
[11] Ch. Bahr and G. Heppke, Ferroelectrics **114**, 311 (1991).
[12] O. E. Kalinovskaya, Yu. P. Panarin, and J. K. Vij, Europhys. Lett. **57**, 184 (2002).
[13] N. A. Clark, T. Bellini, R.-F. Shao, D. Coleman, S. Bardon, D. R. Link, J. E. Maclennan, X.-H. Chen, M. D. Wand, D. M. Walba, P. Rudquist, and S. T. Lagerwall, Appl. Phys. Lett. **80**, 4097 (2002).
[14] P. Collings, B. R. Ratna, and R. Shashidhar, Phys. Rev. E **67**, 021705 (2003).
[15] C. S. O'Hern, T. C. Lubensky, and J. Toner, Phys. Rev. Lett. **83**, 2745 (1999).
[16] J. Xu, R. L. B. Selinger, J. V. Selinger, B. R. Ratna, and R. Sashidhar, Phys. Rev. E **60**, 5584 (1999).
[17] F. Affouard, M. Kroger, and S. Hess, Phys. Rev. E **54**, 5178 (1996).
[18] M. Yamashita and S. Miyazima, Ferroelectrics **148**, 1 (1993).
[19] J. Naciri, J. Ruth, G. Crawford, R. Shashidhar, and B. R. Ratna, Chem. Mater. **7**, 1397 (1995).
[20] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, and A. Fukuda, J. Mater. Chem. **6**, 671 (1996).
[21] W. G. Jang, C. S. Park, J. E. Maclennan, K. H. Kim, and N. A. Clark, Ferroelectrics **180**, 213 (1996).
[22] A. Kocot, R. Wrzalik, and J. K. Vij, Liq. Cryst. **21**, 147 (1996).
[23] Yu. P. Panarin, O. E. Kalinovskaya, M.-S. Chang, and J. K. Vij, in *Abstract Book of the Eighth International Conference on Ferroelectric Liquid Crystals, Washington, D.C.*, edited by R. Shashidhar (FLC Society, Washington, D.C., 2001), Vol. P2-40.
[24] R. B. Meyer and R. A. Pelcovits, Phys. Rev. E **65**, 061704 (2002).
[25] Yu. P. Panarin, O. E. Kalinovskaya, M. S. Chang, and J. K. Vij, *19th International Liquid Crystal Conference 2002, Edinburgh, Abstracts Book* (Royal Society of Chemistry, Cambridge, 2002), p. 664.
[26] J. V. Selinger, P. J. Collings, and R. Shashidhar, Phys. Rev. E **64**, 061705 (2001).
[27] P. G. de Gennes, and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993), p. 529.