

Electrically Induced Isotropic–Nematic–Smectic-A Phase Transitions in Thermotropic Liquid Crystals

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We measure optically the order induced by a stabilizing electric field E in the isotropic phase of a liquid crystal mixture of 4'-*n*-octyl-cyanobiphenyl and 4'-*n*-decyl-cyanobiphenyl which shows spontaneously an isotropic–smectic-A transition. Close to the transition, a paranematic to a nonspontaneous nematic (NSN) first-order transition is induced by the field with a critical point. At higher field another first-order transition is induced from the NSN to a likely smectic-A phase with a tricritical point. A phenomenological Landau–de Gennes model is developed to describe the transitions.

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The tricritical (TC) behavior of phase transition, where a line of phase transitions goes over from first to second order, has been studied extensively in various systems as metamagnets [1], He³-He⁴ mixtures [1,2], and superconductors [3]. Smectic liquid crystals (LC) are also expected to present a TC behavior. So far, in these systems, the tricritical point (TCP) of the nematic to smectic-A (N - S_A) phase transition has been observed by changing the length of the alkyl end chains [4], varying the concentration in binary mixtures [5], and increasing the pressure [6]. The effects of magnetic field on the N - S_A phase transition were investigated in the framework of McMillan's molecular field theory [7] or by solving a lattice model [8,9]. Converted into electric field, the TCP is estimated to appear for a field of ~ 50 – 60 V/ μ m. For LC materials which spontaneously transit from the I phase to the S_A phase (I - S_A), a field induced nonspontaneous nematic (NSN) phase was predicted [9] to arise at a higher field (~ 90 V/ μ m) than the TCP one. So far, no experiment has confirmed any of these two predictions.

In a recent paper [10] we demonstrated experimentally the existence of a paranematic to nematic (pN - N) phase transition, with a critical point above which the transition disappears. We investigated the phase diagram, using a new experimental method based on short bursts of high voltage ac fields and a digital accumulation technique. Physically, the paranematic phase describes the nematic-like ordering induced in the isotropic phase by the external field. This effect is well known for all isotropic liquids, which show, for instance, the Kerr effect under electric field. Its amplitude is enhanced close to an I - N transition. When the ordering is large enough, the internal nematic molecular field adds its effect to the external one, and one observes a pN - N transition. The smectic positional ordering implies the existence of a nematic orientational ordering [11]. The spontaneous I - S_A transition can be considered as an I - N transition, which forces immediately, because of a strong coupling, the onset of an S_A order. If one would be able to create a nematic phase with a lower ordering, one could eventually observe, when applying a field on the isotropic phase, a sequence of separated pN - N -

S_A phases. The intermediate nematic phase, in that case, is called [9] "nonspontaneous." In this Letter, using the same experimental technique as the one of Ref. [10], we present the first experimental evidence of a field induced NSN phase, and of an electric field induced TCP of the NSN- S_A phase transition.

To analyze our data, we first briefly present the main aspects of a model in the phenomenological Landau–de Gennes (LG) formulation which describes the above mentioned phase transitions in a unified way. Nematic liquid crystals present orientational order with the mean molecule parallel to the director \mathbf{n} ($\mathbf{n}^2 = 1$). The quadrupolar nematic ordering is described by the traceless tensor [11] $\mathbf{Q}_{\alpha\beta} = S(3\mathbf{n}_\alpha\mathbf{n}_\beta - \delta_{\alpha\beta})/2$, where $0 \leq S \leq 1$ is the order modulus. At lowest order, electric \mathbf{E} or magnetic \mathbf{H} fields couple quadratically with \mathbf{Q} through the susceptibility anisotropy. Applying a stabilizing electric field ($\mathbf{E} \parallel \mathbf{n}$) on a material with positive dielectric anisotropy, S should increase quadratically in $|\mathbf{E}|$. In the S_A phase the molecules form layers perpendicular to \mathbf{n} . An additional one-dimensional translational order exists. A density wave appears along \mathbf{n} as [11] $\rho \sim \rho_0[1 + (1/\sqrt{2})|\Psi|\cos(\mathbf{q}_S \cdot \mathbf{n} - \Phi)]$, where ρ_0 is the average density, $2\pi/q_S$ is the layer spacing, and $|\Psi|$ is the strength of the smectic order. Φ tells where the layers are. S and $|\Psi|$ are coupled [12,13]. The electric field couples directly to S , and indirectly to $|\Psi|$, through the (S, Ψ) coupling. The electric field can then influence the N - S_A phase transition [7,8]. In fact, there is also a direct coupling between $|\Psi|^2$, the density variation, and an electric field via electrostriction. As the relative density jump at the N - S_A phase transition is in the range $\delta\rho/\rho \sim 10^{-3}$, one expects electrostriction to be $\sim 10^{-3}$ lower than the dielectric anisotropy coupling, i.e., negligible.

The total free energy density f of an S_A in the presence of a stabilizing electric field $\mathbf{E} \parallel \mathbf{n}$ is

$$f = f_0 + f_N + f_A + f_{NA} + f_{\text{diel}}, \quad (1)$$

where f_0 is the free energy density of the I phase ($S = |\Psi| = 0$ for $E = 0$), f_N is that of the N ordering, f_A is the free energy density corresponding to the translational

ordering, f_{NA} is the coupling between S and $|\Psi|$, and f_{diel} represents the lowering of f due to the dielectric coupling of E with S . In the frame of the LG formulation each term of f is expanded in powers of S and $|\Psi|$ as follows:

$$f_N = \frac{1}{2} A_N S^2 + \frac{1}{3} b_N S^3 + \frac{1}{4} c_N S^4, \quad (2a)$$

$$f_A = \frac{1}{2} A_A |\Psi|^2 + \frac{1}{4} c_A |\Psi|^4, \quad (2b)$$

$$f_{NA} = \gamma S |\Psi|^2 + \frac{1}{2} \lambda S^2 |\Psi|^2, \quad (2c)$$

$$f_{\text{diel}} = \delta E^2 S, \quad (2d)$$

with $A_N = a_N(T - T_{NI}^*)$, $A_A = a_A(T - T_{NA}^*)$, $\delta = -\varepsilon_{a0}/12\pi$, and $\varepsilon_{a0} = \varepsilon_a/S$ is the dielectric anisotropy for $S = 1$ ($\delta < 0$ for $\mathbf{E} \parallel \mathbf{n}$). T is the absolute temperature. T_{NI}^* is the lowest temperature at which the I phase is metastable and T_{NA}^* is the lowest temperature of the uncoupled system at which the N phase is metastable. a_N , b_N , c_N , a_A , c_A , γ , and λ are supposed constants. γ is chosen negative to favor the S_A phase [11]. The second coupling term represents a saturation, and is chosen positive. The equilibrium condition $\partial f / \partial \Psi = f'_{\Psi} = 0$ gives

$$|\Psi|^2 = -(\gamma S + \lambda S^2 + A_A) / c_A \geq 0, \quad (3)$$

which for $|\Psi| = 0$ defines the limits of existence of the S_A . In this Letter we restrict ourselves to the case of a LC which spontaneously (for $E = 0$) exhibits the I - S_A phase transition at T_{AI} . The detailed model will be presented elsewhere. If the coupling between S and $|\Psi|$ is weak enough and T is close enough to T_{AI} , a NSN phase should be induced for high enough values of E before the S_A phase is induced for higher fields. As long as the S_A phase is forbidden ($|\Psi|^2 < 0$), the analysis of the NSN phase does not differ from that of a LC which spontaneously presents the I - N transition discussed previously [10]. A critical point should exist. The critical order S_{CP} , field E_{CP} , and temperature T_{CP} are [10]

$$S_{CP} = -b_N / (3c_N), \quad (4a)$$

$$E_{CP}^2 = b_N S_{CP}^2 / (3\delta), \quad (4b)$$

$$T_{CP} = T_{NI}^* + b_N^2 / (3a_N c_N). \quad (4c)$$

In (3), $|\Psi|^2$ is negative for small $S(E)$. Increasing E above the NSN induction field, $S(E)$ should continue to increase. If E becomes strong enough S should attain a value $S_{\Psi=0}$ for which (3) has a solution $|\Psi| = 0$ and the S_A should appear. The equilibrium condition $\partial f(S) / \partial S = f' = 0$ gives

$$(\delta E^2 - A_A \gamma / c_A) + [A_N - (\gamma A_A + 2\gamma^2) / c_A] S + (b_N - 3\lambda \gamma / c_A) S^2 + (c_N - \lambda^2 / c_A) S^3 = 0, \quad (5)$$

which defines $S(T, E)$ for $|\Psi| \geq 0$. The spinodal line of the coupled system is given from the condition

$$\partial^2 f(S \neq 0, |\Psi| \neq 0) / \partial S^2 = f'' = 0. \quad (6)$$

The conjugate of the line $|\Psi| = 0$ is given from the condition

$$f(S \neq 0, |\Psi| \neq 0) = f(S \neq 0, |\Psi| = 0). \quad (7)$$

To draw a typical phase diagram we chose the model parameters as follows: For the N parameters we use values near those of Ref. [10]: $a_N = 0.2 \times 10^7$ erg/K cm³, $b_N = -1.85 \times 10^7$ erg/cm³, $c_N = 2.5 \times 10^7$ erg/cm³, and $T_{NI}^* = T_{AN} - 1.7$ K. The parameters corresponding to the S_A phase and to the coupling between the two order parameters are chosen to get a NSN phase as $a_A = 0.13 \times 10^7$ erg/K cm³, $c_A = 0.25 \times 10^7$ erg/cm³, $\gamma = -0.5 \times 10^7$ erg/cm³, $\lambda = 0.65 \times 10^7$ erg/cm³, and $T_{NA}^* = T_{AN} - 2.2$ K. The S - T phase diagram is shown in Fig. 1. The ordinate scale represents the reduced temperature $t = (T - T_{AN}) / (T_{CP} - T_{AN})$. The dashed line represents the limit $|\Psi| = 0$. Below this line the S_A is not permitted. At the lower part of the diagram the solid line is the spinodal of the field induced NSN phase with its dotted coexistence line. In the upper part the dashed line is the conjugate of the $|\Psi| = 0$ line. The line $|\Psi| = 0$ and its conjugate coincide at the TCP where the spinodal (full) line of the coupled system comes also. The coordinates of the TCP are the tricritical order S_{TCP} , the tricritical temperature T_{TCP} (or t_{TCP} in reduced temperature), and the tricritical field E_{TCP} . The spinodal line of the field induced NSN phase intersects the $|\Psi| = 0$ line at t_s . For $t < t_s$ the system undergoes a first-order transition from the pN phase directly to the S_A phase. The NSN phase is induced only for $t > t_s$. If the system crosses the line $|\Psi| = 0$ at $t < t_{TCP}$ it enters an unstable region ($f'' < 0$) and transits with a discontinuous increase of S towards a state in the S_A phase. As t approaches t_{TCP} the discontinuous increase of order becomes smaller, and at t_{TCP} the system should go continuously from the

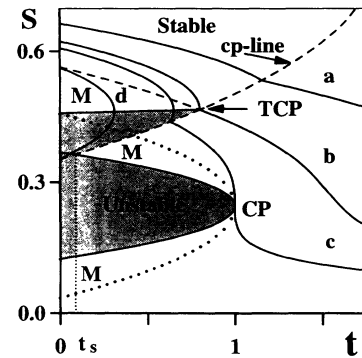


FIG. 1. Phase diagram of the field induced paranematic-nonspontaneous nematic-smectic-A (pN -NSN- S_A) phase transitions. The liquid crystal shows a spontaneous isotropic-smectic-A transition $t = (T - T_{AI}) / (T_{CP} - T_{AI})$. The lower branch of the dashed line is the $|\Psi| = 0$ line, while the upper branch is its conjugate. At the lower part the solid line is the NSN spinodal with its dotted coexistence line. The horizontal solid line is the S_A spinodal. The full lines a , b , c , and d are isofields. TCP: tricritical point; CP: critical point; M: metastable.

NSN to the S_A phase with increasing E . The part of the $|\Psi| = 0$ line above the TCP is a critical point line which terminates at the TCP. The full lines a , b , c , and d correspond to different isofields: a , $E > E_{\text{TCP}}$; b , $E = E_{\text{TCP}}$; c , $E = E_{\text{CP}} < E_{\text{TCP}}$; and d , $E = 0$. When the isofield lines cross the $|\Psi| = 0$ line, they either show a first-order transition at the left of the TCP or a simple discontinuous change of slope at the right of the TCP. Just at the TCP the field induced NSN phase arrives with finite slope while the S_A approaches from the upper side with infinite slope.

To observe the I - N - S_A phase transitions under field, we use the same experimental setup as in Refs. [10,14]. We improve the sample preparation to use higher fields. On the indium tin oxide transparent glass electrodes we evaporate a SiO_2 thin film (200 nm) to prevent short circuits. We make the corresponding capacitance corrections for E . The glass plates are silane coated to induce homeotropic orientation (\mathbf{n} perpendicular to the surface electrodes). The cell thickness is fixed around $\sim 3 \mu\text{m}$ by Mylar spacers. We use mixtures of 4'- n -octyl-cyanobiphenyl (8CB) and 4'- n -decyl-cyanobiphenyl (10CB) of known phase diagram [15]. We adjust the molecular concentration of the mixture at 25% in 8CB to obtain a material that spontaneously exhibits the I - S_A phase transition but not too far from the concentration where the N phase appears spontaneously. The cell is filled with LC in the I phase. We can produce homogeneous homeotropic samples by cooling slowly in the presence of a high frequency ac electric field with $\mathbf{E} \parallel \mathbf{n}$. The experiments are carried out using a polarizing microscope with a tilted rotating stage. T is adjusted with an oven of resolution ~ 25 mK. To prevent heating we use a pulsed ac signal to induce ordered phases above T_{A1} . We decrease the noise by a digital accumulation technique [14]. The field frequency is ~ 30 kHz. The duration of the pulses is $\tau \sim 0.1$ – 1 ms with a dead time interval of $T \sim 10$ s. The optical signal, from the induced birefringence, is measured by the photocurrent i of a photomultiplier. Applying the field E we observe a transient signal $\Delta i(t, E)$ which stabilizes after a relaxation time τ_s at $\Delta i(E)$. We measure $\Delta i(E)$ and τ_s . The cell thickness calibration and the birefringence calculations have been previously described [14].

All our measurements have been performed outside the I - S_A coexistence region. To prevent a spontaneous I - S_A transition, we have measured the isotherms $S(T, E)$ at $T > T_{A1} + 0.25$ K. We first measure the isotherm a at $T = T_{A1} + 1.4$ K, coming from the I phase. $S(E)$ shows (Fig. 2) a linear dependence on E until $S \sim 0.1$ and a quadratic $\sim E^2$ for higher field intensity. No discontinuity is observed and a saturation appears at $E \geq 50$ V/ μm . The inflexion of S indicates that the system should be near a critical or multicritical point. We decrease the temperature at $T = T_{A1} + 0.35$ K, and we measure the isotherm c . $S(E)$ shows a quadratic dependence on E , while $\tau_s \sim 10 \mu\text{s} \ll \tau \sim 0.1$ ms. For $E > 20$ V/ μm τ_s

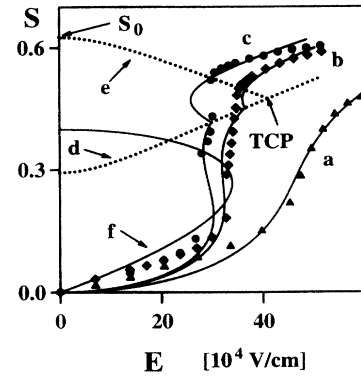


FIG. 2. Order $S(E, T)$ induced by the electric field E in a 8CB-10CB mixture. Measurements at various temperatures: a , $T = T_{A1} + 1.4$ K; b , $T = T_{A1} + 0.55$ K; and c , $T = T_{A1} + 0.35$ K. Solid lines are calculated using the Landau-de Gennes model. f is the nonspontaneous nematic spinodal line; d , the $|\Psi| = 0$ line; and e , the conjugate of the $|\Psi| = 0$ line. TCP: tricritical point.

becomes longer than ~ 1 ms. This increase means that the system has entered a metastable region. Increasing the field at $E = E_{a1} \sim 27$ V/ μm we see a discontinuous increase of order from $S \sim 0.15$ up to $S \sim 0.35$. Further increase of E begins to saturate S . Increasing more E at ~ 30 V/ μm the induced order again starts to increase rapidly while τ_s again becomes longer than $\tau \sim 1$ ms. At $E_{a2} \sim 30$ V/ μm the order jumps again from $S \sim 0.42$ up to $S \sim 0.53$, while $\tau \sim 0.2$ ms. This time is 2 orders of magnitude larger than the one of a pure nematic, and seems to indicate the presence of a new kind of ordering. For $E > E_{a2}$ the order saturates quickly with E . The first of the two $S(E)$ discontinuities brings the LC at a value of $S \sim 0.35$, which is in the range of S for NLC near T_{N1} and far from the S_A measured value of $S(E = 0) \sim 0.68$ of the present mixture near T_{A1} , in the S_A phase. For these reasons we interpret this first discontinuity as a first-order transition from the pN phase (weakly ordered by the field) to a N phase where the larger S is produced by the nematic self-ordering field. $E_{a1} \sim 27$ V/ μm is the threshold field for the pN - N phase transition. This phase did not show spontaneously and is the predicted NSN phase. The second $S(E)$ discontinuity increases the order of the LC up to $S \sim 0.6$ near the S_A value of 0.68. We interpret this second $S(E)$ discontinuity as a first-order transition from the NSN phase to the S_A phase. The larger S is produced this time by the onset of the one-dimensional translational order $|\Psi|$. We now look for the tricritical isotherm. We increase the temperature at $T = T_{A1} + 0.55$ K and we measure the isotherm b . Increasing E we observe a linear increase of S until $S = 0.11$ for $E \sim 27$ V/ μm . For higher E a quadratic increase of S appears which diverges quickly, producing a discontinuous increase of S from 0.19 at $E_{b1} \sim 33$ V/ μm up to 0.29. For higher fields S increases rapidly, while at $S \sim 0.45$ appears either a small

jump or a divergence of S . Within our present accuracy we are not able to distinguish between them. This behavior of S indicates that the system should be close to its TCP. The TCP coordinates can be estimated as $E_{\text{TCP}} = 35 \pm 3 \text{ V}/\mu\text{m}$, $T_{\text{TCP}} = T_{AI} + 0.5 \pm 0.1 \text{ K}$, and $S_{\text{TCP}} = 0.47 \pm 0.03$. From the data, we can estimate the CP of the NSN phase at $E_{\text{CP}} = 34 \pm 3 \text{ V}/\mu\text{m}$, $T_{\text{CP}} = T_{AI} + 0.6 \pm 0.1 \text{ K}$, and $S_{\text{CP}} = 0.24 \pm 0.03$.

The linear part of the isotherms at low field could be attributed to surface effects. In fact, approaching T_{AI} , one knows that smectic layers can grow at the surface [16]. An external field could enhance these effects. We have made surface birefringence measurements on our samples which confirm this appearance of smectic ordering at surfaces. From our measurements we find that this surface effect is important for $S < 0.15$, i.e., far from the TCP. These results will be presented in a forthcoming work.

To compare with our model we did not perform a least squares fit because of the large number of parameters. We have chosen instead reasonable values which seemed to reproduce fairly well our measurements. The full line isotherms presented in Fig. 2 are calculated from the model using $a_N = 0.14 \times 10^7 \text{ erg/K cm}^3$, $b_N = -1.44 \times 10^7 \text{ erg/cm}^3$, $c_N = 1.8 \times 10^7 \text{ erg/cm}^3$, $T_{NI}^* = T_{AI} - 2.1 \text{ K}$, $T_{NI} = T_{AI} - 0.3 \text{ K}$, $a_A = 0.115 \times 10^7 \text{ erg/K cm}^3$, $c_A = 0.35 \times 10^7 \text{ erg/cm}^3$, $\gamma = -0.5 \times 10^7 \text{ erg/cm}^3$, $\lambda = 0.625 \times 10^7 \text{ erg/cm}^3$, and $T_{NA}^* = T_{AI} - 2.3 \text{ K}$. As one sees, the overall agreement is acceptable. The nematic order coefficients are in the usual range for nematic materials [10]. From (3) and the value of $S_0 = S(E = 0) = 0.62$ (Fig. 2), one calculates the translational order $|\Psi| = 0.58$. One can estimate a_A from latent heat measurements. For the I - S_A phase transition of 10 CB the latent heat (ΔH) is 2.83 kJ/mol [17] or $a_A = 2\Delta H/(T_{AI} |\Psi|^2)$, and, using the value of $|\Psi|$ calculated from our experimental data, one finds $a_A = 0.17 \times 10^7 \text{ erg/K cm}^3$, in the same range. For the other coefficients of the smectic free energy density there are no data in literature to compare.

Our experimental technique does not allow a direct measure of $|\Psi|$. In fact, one should perform scattering measurements with neutrons or x rays to prove that the second S jump really brings the system into the S_A phase. These scattering experiments are delicate, from the small volume of the sample and the short pulse duration, but they will be tried in the future.

In conclusion, we have investigated the influence of an electric field on the phase transitions of a liquid crystal which spontaneously shows a first-order isotropic

to smectic- A transition. With the LC in the isotropic phase and close enough to the spontaneous transition temperature, we have observed a field induced first-order phase transition from a paranematic phase to a nonspontaneous nematic phase. This first-order transition disappears above a critical point analogous to the one recently observed at an isotropic nematic transition [10]. The observation of this NSN phase confirms an old prediction [9]. For higher values of the applied field appears another first-order phase transition from the NSN to a phase with the same S as the smectic- A phase. This last first-order transition changes to second order at a tricritical point. These two transitions have been described by a phenomenological Landau-de Gennes model in a unified way. We continue our work on the field induced surface effects and on the dynamical behavior of the order parameters.

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- [1] L. Reatto, Phys. Rev. B **5**, 204 (1972).
 - [2] R. B. Griffiths, Phys. Rev. Lett. **24**, 715 (1970).
 - [3] P. G. de Gennes, Solid State Commun. **10**, 753 (1972); B. I. Halperin and T. C. Lubensky, Solid State Commun. **14**, 997 (1974).
 - [4] J. W. Doane, R. S. Parker, B. Cvikel, D. L. Johnson, and D. L. Fishel, Phys. Rev. Lett. **28**, 1694 (1972).
 - [5] D. L. Johnson, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. Lett. **34**, 1143 (1975).
 - [6] T. J. McKee and J. R. McColl, Phys. Rev. Lett. **34**, 1076 (1975).
 - [7] H. Hama, J. Phys. Soc. Jpn. **54**, 2204 (1985).
 - [8] C. Rosenblatt, J. Phys. (Paris), Lett. **42**, L9 (1981).
 - [9] C. Rosenblatt, Phys. Lett. **83A**, 221 (1981).
 - [10] I. Lelidis and G. Durand, in *Proceedings of the 14th International Liquid Crystal Conference, Pisa, 1992*, [Phys. Rev. E **48**, 3822 (1993)].
 - [11] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1973).
 - [12] W. L. McMillan, Phys. Rev. A **4**, 1238 (1972).
 - [13] K. Kobayashi, Mol. Cryst. Liq. Cryst. **13**, 137 (1971).
 - [14] I. Lelidis, M. Nobili, and G. Durand, Phys. Rev. E **48**, 3818 (1993).
 - [15] H. Marynissen, J. Thoen, and W. Van Dael, Mol. Cryst. Liq. Cryst. **124**, 195 (1985).
 - [16] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen, and M. Deutsch, Phys. Rev. Lett. **57**, 94 (1986).
 - [17] H. Marynissen, J. Thoen, and W. Van Dael, Mol. Cryst. Liq. Cryst. **97**, 149 (1983).

