Electric-field-induced isotropic-nematic phase transition

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We measure optically the quadrupolar order S induced by a stabilizing electric field E in the isotropic phase of the nematogenic 4′-*n*-pentyl-4-cyanobiphenyl, with large positive dielectric anisotropy $\epsilon_a \sim 10$. For high enough field and low enough temperaure, a paranematic-nematic first-order transition is induced, with a critical point at $E_c = 1.41 \times 10^5$ V/cm, $T_c = T_{NI} + 0.65$ K, and $S_c = 0.15$, where T_{NI} is the nematic-isotropic phase-transition temperature.

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Nematic liquid crystals (NLC's) can be constituted by rodlike, anisotropic molecules. Molecular interactions are strong enough to create long-range orientational order with molecules aligned, on the average, parallel to the director $\mathbf{n}$ ($\mathbf{n}^2=1$). This quadrupolar nematic ordering is described by the traceless tensor [1,2] $\mathbf{Q}_{\alpha\beta}=S(3\mathbf{n}_\alpha\mathbf{n}_\beta-\delta_{\alpha\beta})/2$. Here, S $(0\le S\le 1)$ is the modulus of the order parameter. All anisotropic rank-2 tensorial properties of the bulk material, like the dielectric permitivity or the diamagnetic susceptibility, are proportional to $\mathbf{Q}$. At lowest order, electric $\mathbf{E}$ or magnetic H fields couple quadratically with $\mathbf{Q}$. For materials with positive dielectric or diamagnetic anisotropy, a stabilizing field ($\mathbf{E}$ or $\mathbf{H}\|\mathbf{n}$) should increase S for fixed $\mathbf{n}$. In the absence of field a NLC undergoes a nematic-isotropic (N-I) phase transition at a temperature T_{NI}. In the isotropic phase orientational order is lost ($S=0$). When applying an external field, a small quadrupolar order $S\sim E^2$ is induced (Kerr effect). The I phase becomes paranematic (pN) with large pretransitional effects, since the N-I transition is weakly first order. If the field intensity is high enough and the temperature close enough to T_{NI}, a pN-N transition should be induced [3]. The pN-N transition is expected to be first order, since it relates two phases of the same symmetry. As for the liquid-gas transition there should be a critical point. This field-induced pN-N transition has been predicted in the molecular theory of Maier-Saupe [3,4] and in the phenomenological Landau–de Gennes formulation (LG) [5,6]. Experimentally, only qualititative information about the pN-N transition has been obtained [7]. In this paper we present a quantitative determination of the pN-N phase diagram.

According to the LG model the free-energy density f of a NLC in the presence of a stabilizing electric field $\mathbf{E}\|\mathbf{n}$ is [2]

$$f=f_0+\tfrac{1}{2}a(T-T^*)S^2-\tfrac{1}{3}bS^3+\tfrac{1}{4}cS^4-\delta E^2S\ , \qquad (1)$$

where $\delta=\epsilon_{a0}/12\pi$, $\epsilon_{a0}=\epsilon_a/S$ is the dielectric anisotropy for $S=1$, T is the absolute temperature, T^* is the lowest temperature at which the isotropic phase is metastable, f_0 is the free-energy density of the isotropic phase for $E=0$, a, b, c are supposed constants, and $S=S_0+S(E)$ is the sum of the field-induced order $S(E)$ and $S_0=S(0)$. The equilibrium condition $(\partial f/\partial S)=f'=0$ gives

$$a(T-T^*)S-bS^2+cS^3-\delta E^2=0\ , \qquad (2)$$

which defines $S(T,E)$. A critical point should exist for $f''=f'''=0$. The critical order S_c, field E_c, and temperature T_c are

$$S_c=b/(3c)=S_{NI}/2\ , \qquad (3a)$$

$$E_c^2=bS_c^2/(3\delta)\ , \qquad (3b)$$

$$T_c=T^*+b^2/(3ac)=T^*+3(T_{NI}-T^*)/2\ , \qquad (3c)$$

where S_{NI} is the order parameter of the nematic phase at T_{NI}. For the NLC 4′-*n*-pentyl-4-cyanobiphenyl (5CB) the f parameters are known from the literature [8]: $a=(0.13\pm0.01)10^7$ ergs/K cm^3, $b=(1.6\pm0.2)10^7$ ergs/cm^3, $c=(3.9\pm0.3)10^7$ ergs/cm^3, and $T_{NI}-T^*=1.1\pm0.25$ K. We estimate $T_c=T_{NI}+0.6$ K, $S_c=0.14$, and $E_c=1.3\times10^5$ V/cm. This electric-field intensity is accessible with our present technique. The equivalent critical magnetic field would be $H_c\sim1.3\times10^6$ G, which is more difficult to achieve. Figure 1 shows the predicted curves $S[E,T_r=(T-T^*)/(T_{NI}-T^*)]$. For $T<T_c$ the $S(E,T_r)$ curves show a discontinuous pN-N transition, which becomes second order for T_c. For $T>T_c$ the $S(E)$

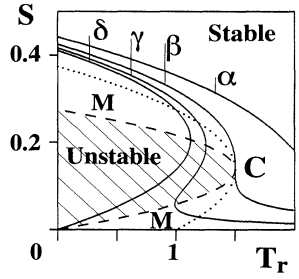

FIG. 1. Phase diagram of the field-induced isotropic-nematic transition for the nematic liquid crystal 5CB. $T_r=(T-T^*)/(T_{NI}-T^*)$. The dashed line is the spinodal and the dotted line is the coexistence line. Full lines correspond to different electric fields E: α, $E>E_c$, where E_c is the critical field; β, $E=E_c$; γ, $E<E_c$; and δ, $E=0$. M: metastable; C: critical point.

curves relate continuously the pN and N phases. The transition temperature $T_{NI}(E)$ is the solution of $f(S_1)=f(S_2)$ and $f'(S_1)=f'(S_2)=0$. Along the coexistence line $T_{NI}(E)$ (Fig. 1), S is given by

$$S_{1,2}=S_c\pm[3S_c^2-a(T_{NI}(E)-T^*)/c]^{1/2} . \quad (4)$$

The spinodal line (Fig. 1), is given by $f''=0$, i.e.,

$$E^2=[bS^2-2cS^3]/\delta . \quad (5)$$

There should exist a metastable (M) region between the coexistence line and the spinodal line (Fig. 1). The aim of our work is to investigate the predicted phase diagram and locate its critical point.

Observations of the critical point were previously tried [7] without much success. This was due to a heating effect [9] of ~ 1 K for the used dc field $\sim 10^5$ V/cm. To prevent heating we use a pulsed electric field. The consequent reduction of the measuring time leads to an increase of noise, which is compensated by a digital accumulation technique. To observe $S(E)$ we measure the optical path difference $\Delta l(E)$ of a uniform nematic cell with **n** perpendicular to the surface (the electrodes) and **E**$\|$**n**. The cell is shined at oblique incidence with a linearly polarized light at 45° of the incidence plane. The ordinary and extraordinary waves interfere behind an analyzer. From this interference we obtain the change $\Delta l(E)$ due to the field. From $\Delta l(E)$ we deduce [10] the birefringence change and finally $S(E)$.

The cell is made by two transparent glass electrodes separated by Mylar spacers with thickness $d\sim 10$ μm. The electrodes are silane coated to induced homeotropic alignment. We use the NLC 5CB (4′-*n*-pentyl-4-cyanobiphenyl) chosen for its good chemical stability and its high dielectric anisotropy. Our experimental method is described in detail elsewhere [10]. The experiments are carried out using a polarizing microscope with a tilted and rotating stage. The temperature is adjusted with an oven of accuracy ~ 25 mK and a stability ~ 10 mK. The electric field is a burst pulsed ac signal with a few positive and negative half-period square waves [Fig. 2(a)] produced by a digital signal generator. The pulse frequency is ~ 30 kHz. The duration of a burst of pulses is $\tau\sim 100$ μs with a time interval of $T\sim 10$ s. Heating phenomena are expected to be negligible for our small $\tau/T\sim 10^{-5}$. The pulsed driving field is amplified by a wideband amplifier of 1-μs response time, of maximum output ± 200 V. The optical signal is measured by the photocurrent i of a photomultiplier. Applying the field E we observe a transient signal $\Delta i(t,E)$ which stabilizes within $\tau_S\sim 5$ μs to a value $\Delta i(E)$. $\Delta i(E)$ does not change with the polarity of E. We measure only the stabilized value $\Delta i(E)$ during the pulse. From $\Delta i(E)$ we can calculate the birefringence induced by E. More information about the d calibration and the birefringence calculations are given elsewhere [10].

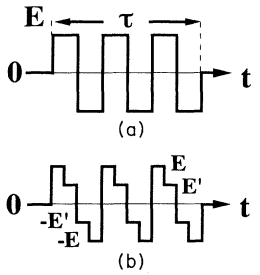

FIG. 2. The burst pulsed ac electric field used in the experiment. (a) far from the spinodal and (b) close to the spinodal.

In NLC there exists a temperature region around T_{NI} where both nematic and isotropic phases coexist. To prevent a spontaneous transition, coming from the I phase, we have measured the isotherms $S(E,T)$ at $T>T_{NI}$, where the I phase remains stable (in practice at $T>T^{**}\cong T_{NI}+0.2$ K). Coming from the N phase, we have measured the isotherms at $T<T_{NI}$, where the N phase remains stable. In practice, since $T_{NI}-T^*\sim 1$ K, we have been able to work in the stable temperature range $T^*<T<T_{NI}$.

We first measure the isotherm α at $T=T_{NI}+1.55$ K, coming from the I phase. $S(E)$ shows (Fig. 3) a quadratic dependence $\sim E^2$ and a saturation for the high-field $E\geq 2\times 10^5$ V/cm. This field induces a large $S\sim 0.2$ but this ordering is continuously built from zero. No phase change is observed. We reduce the temperature to $T=T_{NI}+0.25$ K just above T^{**} and below the expected $T_C=T_{NI}+0.6$ K. The material is stable in the isotropic phase ($S=0$) in the absence of field. Applying the field we obtain the isotherm γ (Fig. 3). For the low field $E<9\times 10^4$ V/cm, $S(E)$ keeps increasing $\sim E^2$ from zero. At $E\sim 9.5\times 10^4$ V/cm, $\Delta i(t,E)$ appears suddenly with a long characteristic time $\tau_S>\tau$. To observe a stationary $\Delta i(E)$, we try to increase the pulse duration, up to 1 ms. At 1 ms, $\Delta i(t,E)$ is not yet stabilized, but we already observe a shift of the optical signal just after the pulse, when $E=0$, i.e., a heating effect. For this reason we have kept $\tau\sim 100$ μs and extrapolated $\Delta i(t,E)$ to determine finally an approximated value for $S(E)$. This results in $S(E)$ values with large error bars in Fig. 3. Anyway, for $E\sim 9.5\times 10^4$ V/cm the NLC undergoes a discontinuous increase of order from $S\sim 0.06$ up to $S\sim 0.28$. For the

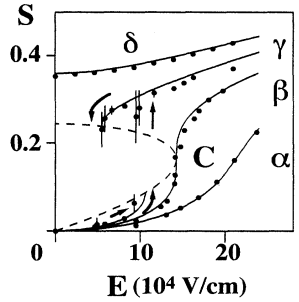

FIG. 3. Order increase $S(E)$ induced by a stabilizing electric field **E**$\|$**n** in the nematic liquid crystal 5CB at various temperatures near the critical point C. α, $T=T_{NI}+1.55$ K; β, at $T_c=T_{NI}+0.65$ K; γ, $T=T_{NI}+0.25$ K; and δ, $T=T_{NI}-0.15$ K. The solid lines are a fit of the experimental data using the Landau–de Gennes model. The dashed line is the spinodal.

higher field we reobserve $\tau_S \sim 5\ \mu s \ll \tau$, which allows us to measure accurately $S(E)$. $S(E)$ keeps increasing continuously. We interpret the observed $S(E)$ discontinuity as a first-order transition from the pN phase, only weakly ordered by the field, to the N phase where the larger S is produced by the nematic self-ordering field. $E_{th}(T) \sim 9.5 \times 10^4$ V/cm is the threshold field for the pN-N transition. We try now to induce the reverse N-pN transition. We need to lower E while keeping the NLC in the N phase. We use then a special pulse shape [(Fig. 2(b)]. Each pulse has a positive and a negative half-period. The positive half-period is composed of two square waves of different amplitudes. The first amplitude $E = 1.2 \times 10^5$ V/cm, larger than E_{th}, is supposed to induce the N phase. The second one $E' < E$ is varied to allow measurements along the isotherm. We observe now that Δi stabilizes with a time $\tau_S \sim 5\ \mu s$ toward two values $\Delta i(E)$ and $\Delta i(E')$ from which we calculate $S(E)$ and $S(E')$. We remeasure more accurately $S(E)$ above the threshold field $E_{th}(T)$. As E' decreases at values smaller than $E_{th}(T)$, $S(E')$ decreases continuously. A hysterisis loop begins to be formed. Decreasing E' below $\sim 6 \times 10^4$ V/cm, $S(E')$ falls discontinuously from 0.25 down to 0.015 in the pN phase. This point is on the first $S(E)$ curve. The hysterisis loop is closed. $E'_{th}(T) \sim 6 \times 10^4$ V/cm is the threshold field for the N-pN transition. For the isotherm γ we observe that, as E approaches from below $E_{th}(T)$ or from above $E'_{th}(T)$, the pN phase or the metastable N phase approach the limit of metastability. $S(E_{th})$ and $S(E'_{th})$ are then two points of the spinodal line.

We look now for the critical isotherm. We increase T in steps of $\Delta T = 0.1$ K and we measure $S(E,T)$ until we find the isotherm β at $T = T_{NI} + 0.65$ K. Within our experimental accuracy, β shows a vertical increase of S with the smallest amplitude and no measurable hysterisis. Increasing T again by 0.05 K, no more vertical increase of $S(E)$ is observed. We conclude that β is the critical isotherm. Within our present accuracy, the coordinates of the critical point are $E_c = (1.41 \pm 0.03) 10^5$ V/cm, $S_c = 0.15 \pm 0.02$, and $T_c = T_{NI} + 0.65 \pm 0.05$ K. The last isotherm δ is measured at $T = T_{NI} - 0.15$ K, starting from the nematic phase $S(0) = 0.35$. $S(E)$ varies continuously and follows a linear increase for low field and a quadratic law at higher field. This behavior has two origins: the linear effect is due to the quenching of macroscopic fluctuations [1] and the quadratic one is a superposition of the expected microscopic Kerr effect and of a saturation term from the macroscopic one. This analysis has been presented elsewhere [10].

We can fit the experimental phase diagram with the LG model. We measure $T_{NI} = 306.8 \pm 0.05$ K; $T_{NI} - T^* = 1.5 \pm 0.3$ K from the extrapolated inverse Kerr coefficient in the isotropic phase. The three other coefficients are defined by E_c, T_c, S_c, using (3). We find $a = (0.11 \pm 0.04) 10^7$ ergs/K cm^3, $b = (1.56 \pm 0.4) 10^7$ ergs/cm^3, and $c = (3.47 \pm 0.7) 10^7$ ergs/cm^3. Within our accuracy, we vary a, b, c, and T^* to obtain the best fitting of the total $S(E,T)$ data. The solid lines in Fig. 3 show the result of this $S(E,T)$ fitting. As one sees, the overall agreement is reasonable. The observed discrepancies could be attributed to the quenching of macroscopic fluctuation not taken into account in the LG model. It should be interesting, but probably complicated, to build a model which would take into account both effects. The obtained values of the coefficients are now $a = (0.105 \pm 0.01) 10^7$ ergs/K cm^3, $b = (1.37 \pm 0.1) 10^7$ ergs/cm^3, $c = (2.81 \pm 0.2) 10^7$ ergs/cm^3, $T_{NI} - T^* = 1.41 \pm 0.2$ K. The agreement appears acceptable with the data previously obtained indirectly from the Kerr effect, refractive indices, and dielectric and $S(T)$ measurements [8]. Note that these $S(T)$ data [11] have been later renormalized [12] by $\sim 25\%$, so that the accuracy of Ref. [8] data was strongly overestimated.

In conclusion, we have investigated the electric-field-induced isotropic-nematic transition in the nematogenic material 5CB. At low field, the isotropic phase becomes a weakly ordered paranematic material (Kerr effect). Increasing the field one observes a field-induced paranematic to nematic first-order transition and a critical point above which the transition is continuous. These measurements confirm a long ago predicted phase diagram. We continue our work with measurements of the dynamical behavior of the system in the homogeneous phases and at the spinodal decomposition.

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