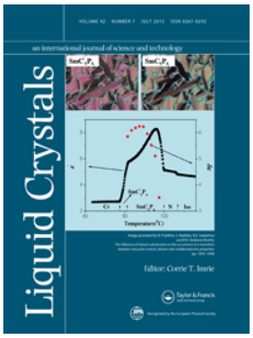

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Magnetically induced shift of the isotropic–nematic phase transition temperature in a mixture of bent-core and calamitic liquid crystals doped with magnetic particles

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We have investigated the influence of doping with spherical magnetic nanoparticles on the mixture of a bent-core and a calamitic liquid crystal. Results showed a reduction of the critical field of the magnetic Fréedericksz transition by more than a factor of two after the doping. Moreover, we give for the first time experimental evidence of the theoretically predicted magnetically induced negative shift of the isotropic to nematic phase transition temperature.

Keywords: nematic; nanocomposite; phase transition; magnetic properties; capacitance

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The possibility to alter the isotropic–nematic (I–N) transition temperature T_{I-N} in liquid crystals (LCs) with an external field has been known for long time. [1] However, the effect has not been produced via magnetic field until recently.[2,3] The first experimental observation of the predicted magnetic field dependence of the I–N phase transition temperature $T_{I-N}(B)$ has been carried out with a powerful electromagnet using a bent-core nematic LC.[2] An increase of the phase transition temperature by 0.7°C has been achieved with application of a magnetic induction of $B = 30$ T. The authors discussed their results within the context of both the Maier–Saupe and the Landau–de Gennes mean field models for the I–N transition and attributed the findings to the very high magnetic field strength on the one hand and to the 'unconventional' physical properties of the bent-core nematogens on the other hand. In a more recent study,[3] an even larger increase of the I–N phase transition temperature (4°C) has been reported in another bent-core nematic by an application of only $B = 1$ T. This extraordinary sensitivity to the magnetic field has been assigned to the peculiar biaxial-cluster structure of the cybotactic nematic phase N_{cyb} formed by the bent-core molecules.

Nowadays, ferronematics, i.e., suspensions of magnetic nanoparticles (MNPs) in nematic LCs, became a promising target for experimental and theoretical studies in many aspects.[4–6] As a representative example, the presence of the magnetic admixture enhances the magnetic susceptibility of ferronematics in comparison to that of the undoped nematic LCs and allows to control their orientation with much lower magnetic fields.[7] It has recently been demonstrated [8–10] that even very low magnetic fields ($B < 0.1$ T) may induce a significant magnetic response in ferronematics.

Doping with various magnetic particles may also affect the temperature of the I–N phase transition. In our previous work,[11] we have proven that ferronematics composed of calamitic LCs and rod-like MNPs can be just as effective in demonstrating the magnetic-field-induced I–N phase transition as bent-core nematics.[2] These observations altogether imply that doping bent-core nematics with MNPs may be even more effective regarding the response to the magnetic field. We note here, however, that doping of a calamitic LC with spherical MNPs did not result in a measurable magnetic-field-induced phase transition temperature change.[11]

In addition to the experimental findings, recently, a consistent molecular mean field theoretical model has been developed by Raikher et al. for the field-induced shift of the temperature of the equilibrium I–N phase transition (clearing point) in ferronematics.[12] It has been shown that depending on the anchoring conditions at the rod-like particle surface, the particles might either increase or decrease the clearing temperature of the suspension and that the expected magnitude of the effect depends on the material parameters of the ferronematic. To our knowledge, the predicted magnetic-field-induced decrease of the clearing temperature has not yet been demonstrated experimentally, as in all previous

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studies [2,3,11] the magnetic field has contributed to a linear increase of the I–N phase transition temperature with B^2. The above described experimental results and theoretical consideration have triggered our investigations.

In this article, we study the influence of an external magnetic field on the I–N transition temperature in the 50–50 wt% mixture of the bent-core 4,6-dichloro-1,3-phenylene bis (4′-(10-undecenyloxy) biphenyl-4-carboxylate) (11DClPBBC) and the calamitic 4-n-octyloxyphenyl 4-n-hexyloxybenzoate (6OO8) LC. The synthesis and physical properties of the bent-core 11DClPBBC (as well as its single unit shorter alkyl-end-chain homologue 10DClPBBC) and the calamitic 6OO8 LCs were described in Refs. [13] and [14], respectively. Differential scanning calorimetry and polarising microscopy observations have shown complete miscibility of 6OO8 with 10DClPBBC and a considerable expansion of the mesophase temperature range around their eutectic mixture (≈50–50 wt%).[15] Moreover, 11DClPBBC possess considerably wider temperature range of the nematic phase (extending to a lower temperature) than that of the 10DClPBBC.[13] Our intention to investigate systems possessing as wide and as low mesophase temperature range as possible led us thus to prepare the 11DClPBBC/6OO8 LC mixture. The ferronematic sample was prepared by doping this LC mixture with spherical magnetic particles at the volume concentration of $\phi = 2 \times 10^{-4}$. The diameter of the magnetic particles was 10 nm and oleic acid was used as a surfactant to avoid their aggregation.

The magnetic properties of the prepared LC mixture and the LC mixture doped with magnetic particles were measured by a SQUID magnetometer (Quantum Design MPMS 5XL). The samples were filled into cylindrical capsules, which were hermetically closed. The diameter of the capsules was 2.5 mm; their length was 6.5 mm. The orientation of the magnetic field was parallel with the axis of the capsule.

Figure 1 shows the magnetisation curves of the undoped LC mixture and the ferronematic sample, recorded at 80°C. While the undoped LC mixture is diamagnetic, the ferronematic behaves as a paramagnetic material in the low magnetic field range due to the doping. At high fields, however, the diamagnetic contribution of the host LC mixture becomes dominant.

Structural transitions in the samples were monitored by capacitance measurements in a capacitor made of indium-tin-oxide-coated glass electrodes covered with rubbed polyimide layer that assured the planar initial alignment (nematic director $\boldsymbol{n}$ parallel with the bounding plates). The capacitor with the

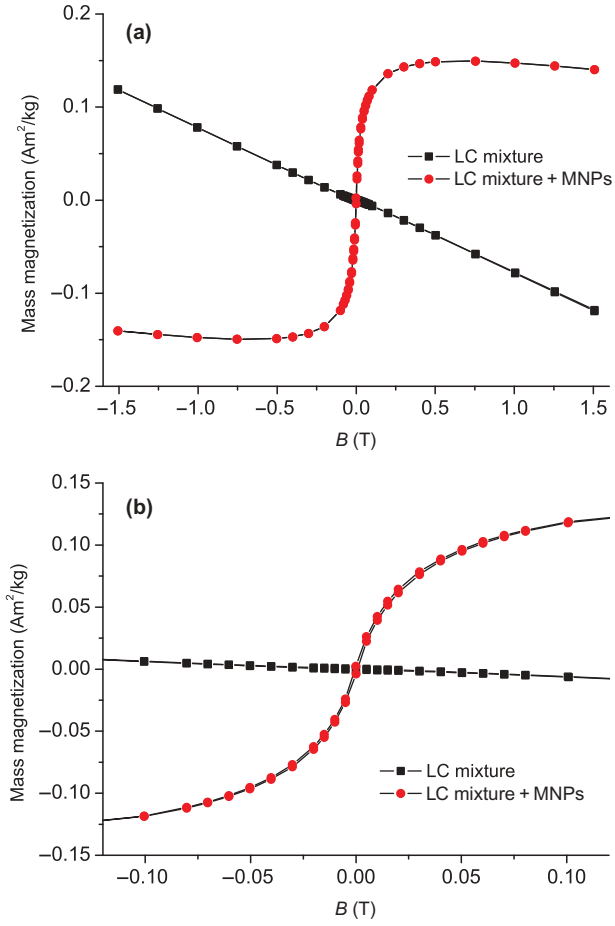

Figure 1. (colour online) (a) Magnetisation curves of the LC mixture and the LC mixture doped with magnetic particles (MNPs), measured at T = 80°C. (b) A blow-up of the magnetisation curves around zero magnetic field.

electrode area approximately 1 cm × 1 cm was placed into a regulated thermostatic system. The distance between the electrodes (sample thickness) was D = 50 μm. The capacitance was measured at the frequency of 1 kHz by a high precision capacitance bridge Andeen Hagerling with the accuracy of 0.8 aF. The samples were heated above the clearing point (to approximately 110°C). A constant magnetic field was applied perpendicular to the surface of the electrodes and then the samples were cooled at a rate of 2°C min^{-1}. The actual temperature of the sample was measured by a calibrated Pt thermometer. Monitoring the variation of the capacitance on the external field and/or on the temperature reflects the appearance of the orientational order as well as the reorientation of the nematic molecules by the field.

Figure 2 shows the magnetic Fréedericksz transition at the temperature of 80°C in the undoped LC mixture as well as that in the ferronematic doped with spherical MNPs. The dependence of the relative

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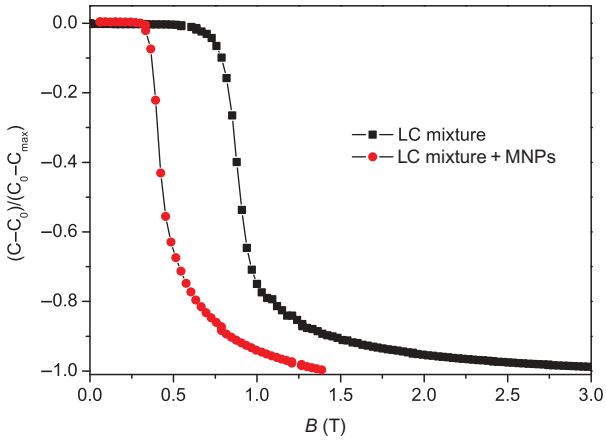

Figure 2. (colour online) Relative capacitance versus magnetic induction for the liquid crystal mixture and for the liquid crystal mixture doped with spherical Fe_3O_4 MNPs at $T = 80°C$.

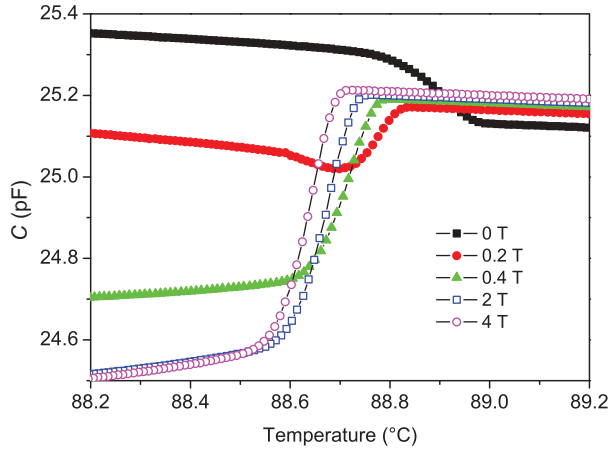

Figure 4. (colour online) Capacitance versus temperature for the liquid crystal mixture doped with spherical Fe_3O_4 MNPs for different values of the magnetic induction.

capacitance variation $(C - C_0)/(C_0 - C_{max})$ on B demonstrates that the critical magnetic induction B_c of the Fréedericksz transition, i.e., the magnetic induction that initiates the reorientation of the director towards its direction, is shifted to much lower values by doping with MNPs (from linear extrapolations applied on the curves in Figure 2, $B_c = 1.0$ T and $B_c = 0.38$ T for the undoped LC mixture and for the ferronematic, respectively). Here, C, C_0 and C_{max} are the capacitances at a given magnetic field, at $B = 0$, and at the maximum value of B, respectively.

Figures 3 and 4 show the temperature dependence of the capacitance of the undoped LC and the LC doped with spherical MNPs, respectively. The dependence of the measured capacitance on the external magnetic field reflects the reorientation of the nematic molecules in the presence of the magnetic field. Comparing these figures, it is obvious that the presence of the magnetic particles in our mixture of bent-core and calamitic LCs shifts considerably the temperature of the transition from the isotropic to the nematic phase to a lower value in the absence of the magnetic field. This is in accordance with the theoretical model [12] considering that the LC molecule/particle volume ratio $\eta = V/V_p$ in our case is relatively small ($\eta = 0.0135$) – compare Figure 3 of Ref. [12].

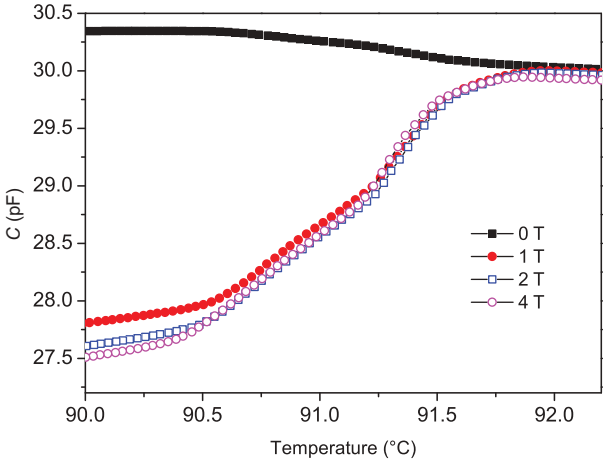

Figure 3. (colour online) Capacitance versus temperature for the undoped liquid crystal mixture for different values of the magnetic induction.

In addition, for the ferronematic a magnetic field dependent shift $\Delta T_{I-N}(B) = T_{I-N}(B) - T_{I-N}$ was observed in the temperature of the I–N transition (while such a magnetic field induced shift of T_{I-N} is absent in the undoped LC mixture). Most importantly, the observed shift in our case is negative, i.e., the magnetic field, reduces the phase transition temperature (i.e., helps to maintain the orientational disorder) as it is demonstrated in Figure 5. This is again in agreement with the predictions of the theoretical description in Ref. [12], which allows for the negative $\Delta T_{I-N}(B)$ in case of negative values of the orientation coupling parameter $\omega = \varepsilon_p/\varepsilon < 0$ (ε and ε_p is the strength of the LC molecule–LC molecule and the LC molecule–MNP orientational coupling, respectively) – compare Figure 4 of Ref. [12].

However, the dependence of the phase transition temperature $T_{I-N}(B)$ on the applied magnetic field in our system is non-linear, as seen in Figure 5. The experimental data can be fitted fairly well by a power law, having the form

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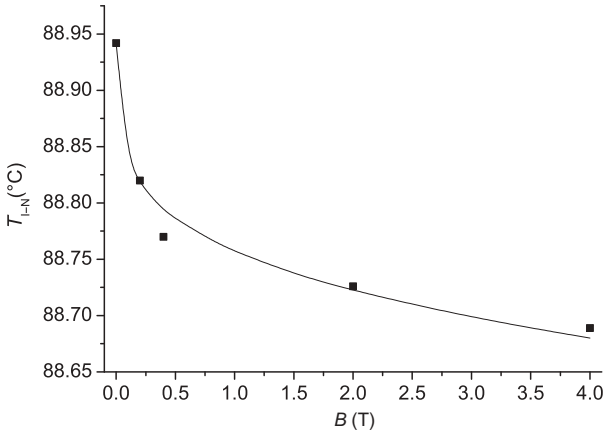

Figure 5. The isotropic–nematic phase transition temperature versus the applied magnetic induction, measured in the liquid crystal mixture doped with spherical magnetic nanoparticles. Size of the symbols corresponds to the uncertainty of the measurements. The solid curve corresponds to a fit to Equation (1).

$$T_{\mathrm{I-N}}(B) = T_{\mathrm{I-N}}\left[1 - C \cdot \eta \left(\frac{m_s B}{\mu_0 k_{\mathrm{B}} T_{\mathrm{I-N}}}\right)^{\frac{1}{4}} \phi\right]. \qquad (1)$$

Here $m_s = 0.219 \times 10^{-24}$ Tm^3 is the magnetic moment of the nanoparticle, μ_0 is the vacuum permeability and k_{B} is the Boltzmann constant. Therefore, constant C remains as the only fit parameter, and the solid curve in Figure 5 corresponds to a fit to this function with $C = 4.1$.

In summary, we have shown that the critical field of the magnetic Fréedericksz transition in a LC mixture can be drastically reduced by doping with spherical MNPs. We have also detected that doping results in a considerable reduction of the phase transition temperature $T_{\mathrm{I-N}}$ in the absence of a magnetic field, which is in agreement with the theoretical prediction due to the small volume ratio η.[12] Furthermore, the measured magnetic field induced negative shift of the phase transition temperature is proportional to η and ϕ as the theory predicts [12] for the negative coupling parameter ω. There is, however, a disagreement between the experimental results presented here and the previous experimental findings as well as the theoretical expectations regarding the $\Delta T_{\mathrm{I-N}}(B)$ dependence. Previous experiments on undoped bent-core LCs [2,3] and on a calamitic LC doped with rod-like MNPs [11] as well as the theoretical description considering calamitic LC doped with rod-like MNPs [12] have found that $\Delta T_{\mathrm{I-N}}$ changes with B^2 (in all experiments it increases, while the theory allows for both increase and decrease). In contrast to that, we have found a much weaker dependence on the magnetic induction $|\Delta T_{\mathrm{I-N}}| \propto B^{\frac{1}{4}}$ – see Equation (1). The background of this discrepancy may be related to the fact that the LC matrix in our case is a mixture of bent-core and calamitic LCs and represents a more complex system than those previously studied (one-component matrices of bent-core molecules [2,3] or ferronematics based on calamitic LCs [11,12]). Furthermore, the ferronematic investigated in this work has been obtained by doping the LC mixture with spherical MNPs, and not by rod-like ones as considered in Refs. [11] and [12]. We emphasise again that doping a calamitic LC with the same spherical MNPs as studied here did not result in a magnetic-field-induced phase transition temperature shift.[11] Therefore, the clarification of the functional form of the $\Delta T_{\mathrm{I-N}}(B)$ dependence in various ferronematics needs further experimental and theoretical efforts.

Disclosure statement

No potential conflict of interest was reported by the authors.

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