

INCREASE OF THE SENSITIVITY OF LIQUID CRYSTALS TO MAGNETIC FIELD DUE TO DOPING WITH MAGNETIC NANOPARTICLES

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Abstract: The contribution is an overview of the observations regarding the structural transitions in ferronematics based on thermotropic nematics doped with magnetic nanoparticles of different shape, and the magnetic field induced shift of the isotropic to nematic phase transition temperature. Due to presence of magnetic particles an increase of the isotropic-nematic phase transition temperature was observed as a function of applied magnetic field. The response of ferronematics to very low magnetic fields is also presented which is important for the construction of various magneto-optical devices.

1. Introduction

Liquid crystals can be oriented by electric or magnetic fields due to the anisotropy of the dielectric permittivity or the diamagnetic susceptibility [1]. As the former is in the order of unity, in conventional devices the driving voltages are in the order of a few volts. However, because of the small value of the anisotropy of the diamagnetic susceptibility ($\sim 10^{-7}$), the magnetic field necessary to realign liquid crystals have to reach rather large values ($B \sim 10$ T depending on the thickness of the liquid crystal layer). In an effort to enhance the magnetic susceptibility of liquid crystals, the idea of doping them with small amount of tiny magnetic particles was theoretically introduced by Brochard and de Gennes [2]. They have developed the continuum theory of magnetic suspensions in nematic liquid crystals (ferronematics). In their theoretical work rod-like magnetic particles with the length $L \gg a$ (where a is the molecular size of the nematic liquid crystal) and with a diameter of $d \sim L/10$ were considered. The volume concentration of magnetic particles was supposed to be sufficiently small ($\phi \sim 10^{-4}$) in order to be able to ignore the inter-particle magnetic dipole-dipole interaction. They predicted that a rigid anchoring with $\mathbf{m} \parallel \mathbf{n}$ would result in the ferromagnetic behaviour of the mixture. Here the unit vector $\mathbf{n}$ (the director) describes the preferential direction of the nematic molecules and the unit vector $\mathbf{m}$ denotes the orientation of the magnetic moment of the magnetic particles. In the first experimental paper, Rault et al. [3] reported about the basic magnetic properties of a suspension of rod-like $\gamma\text{-Fe}_2\text{O}_3$ particles in the liquid crystal MBBA. In order to stabilize the suspension, the particles were first coated with a surfactant and then mixed with the nematic liquid crystal. The obtained results confirmed the existence of a ferromagnetic state in such suspension. Additionally they have found that the temperature of the nematic-isotropic transition decreases with increasing volume concentration of particles. Later, based on the estimations given in [2], first lyotropic [4,5] and then thermotropic [6] ferronematics have been prepared and studied. These experiments confirmed the existence of considerable orientational and concentrational effects in liquid crystals doped with magnetic particles, but raised a lot of questions as well.

One of the most important questions solved in the theory of ferronematics is the problem of the equilibrium orientation of magnetic particle, i.e. the direction of its magnetic moment $\mathbf{m}$,

in the nematic matrix. The Brochard and de Gennes theory [2] considers the rigid anchoring with $\mathbf{m}$ parallel with $\mathbf{n}$. Based on later experiments, which excluded the co-alignment of $\mathbf{m}$ and $\mathbf{n}$ in some thermotropic ferronematics, the Burylov and Raikher's theory was constructed [7-9]. This theory considers the finite value of the surface density of the anchoring energy W at the magnetic particle - nematic boundary. The finite value of W , as well as the parameter $\omega = Wd/K \leq 1$, characterize the soft anchoring of nematic molecules on the surfaces of magnetic particles (d - typical size of magnetic particle, K - corresponding Frank orientation-elastic modulus of liquid crystal). The soft anchoring, unlike the rigid one, permits both types of boundary conditions ($\mathbf{m} \perp \mathbf{n}$ and $\mathbf{m} \parallel \mathbf{n}$), thus the Burylov and Raikher's theory could explain the experimental findings. In the frame of this theory the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric field (Fréedericksz transitions) were analysed and the expressions for their critical fields in different geometries were derived.

2. Results

The studied ferronematic samples were based on the thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT is an enantiotropic liquid crystal with high chemical stability [10]. The temperature of the nematic-to-isotropic transition (the clearing point) of the studied nematic is $T_{NI} = 42.8^\circ\text{C}$. The nematic samples were doped with different kind of magnetic particles in volume concentration of 2×10^{-4} . The synthesis of magnetic particles of various shape was described in [11]. The size of spherical particles was 11.6nm; the diameter and the length of rod-like particles were 25nm and 1200nm, respectively. The length of chain-like particles was approximately 400nm; the size of a single particle in the chain was 34nm.

The structural transitions in ferronematic samples were monitored by capacitance measurements in a capacitor made of ITO-coated glass electrodes (LINCAM Co.). The capacitor with an electrode area of approximately $1\text{cm} \times 1\text{cm}$ was connected to a regulated thermostat system; the temperature was stabilized with the accuracy of 0.05°C . The distance between the electrodes (sample thickness) was $D = 5\mu\text{m}$. The capacitance was measured at the frequency of 1kHz by a high precision capacitance bridge Andeen Hagerling. The stability of the samples in the strong magnetic fields was verified by repeating the capacitance measurements after 5 months on the same samples, with reproducible results.

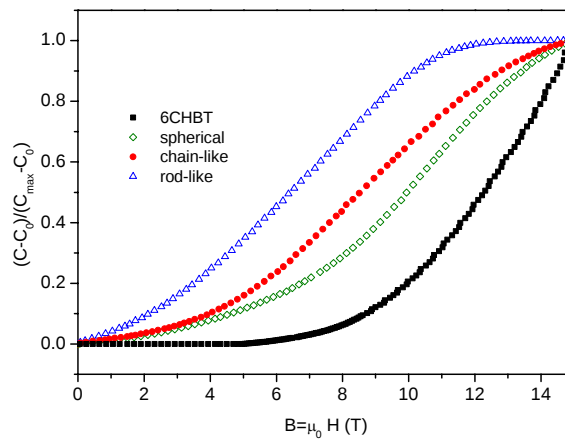


Figure 1: Reduced capacitance dependence of undoped 6CHBT and 6CHBT doped with spherical particles, chain-like particles and rod-like particles on external magnetic field measured at $U_B = 10\text{V}$ (C_0 and C_{max} are the capacitance at $B=0$ and at B which restores the planar alignment, respectively).

The ferronematics based on the magnetic particles of various shape [11] were subjected to the combined action of electric and magnetic fields at the temperature of 35 °C. The magnetic field was applied perpendicular to E . Fig. 1 exhibits the dependence of the dimensionless reduced capacitance on the magnetic field at a bias voltage of 10V for undoped 6CHBT as well as for 6CHBT doped with magnetite particles of different shape. Doping with magnetic nanoparticles evidently reduces the critical field, confirming that the coupling between the director and the magnetic moment favours $\mathbf{m} \parallel \mathbf{n}$. The reduction is the smallest for spherical particles and the largest for rod-like particles. It has been concluded [11] that the larger shape anisotropy of the particles changes the character of the anchoring at the liquid crystal – particle interface from soft to rigid. The presented results show that doping with magnetic particles shaped similarly to the molecules of the host liquid crystal is more effective and thus offer better perspectives for ferronematics in applications where the magnetic field is necessary to control the orientation of the liquid crystal.

Another interesting phenomenon in liquid crystals is the possibility to alter the isotropic to nematic phase transition with external field [12-14]. However, the effect could not be induced by magnetic-field [15] until recently [16]. The principal reason is that the estimated critical fields are well over 100 T for traditional liquid crystal materials [15]. The first experimental observation of the predicted magnetic-field dependence of the nematic-isotropic phase transition temperature has been recently carried out [16] on a powerful electromagnet (B up to 30T). To demonstrate the effect, besides the powerful electromagnet, the proper choice of a „non-conventional” (bent-core) nematic liquid crystal material was also necessary. The „non-conventional” nematic material chosen in Ref. [16], has considerably different physical properties compared to „conventional” calamitic nematics; the first-order character of the nematic-isotropic transition at the „clearing point” is substantially weaker than that for „conventional” nematics. These properties, combined with the high magnetic field have contributed to the observation of the phase transition temperature shift of $\sim 0.8^\circ\text{C}$ at the magnetic field of 30T.

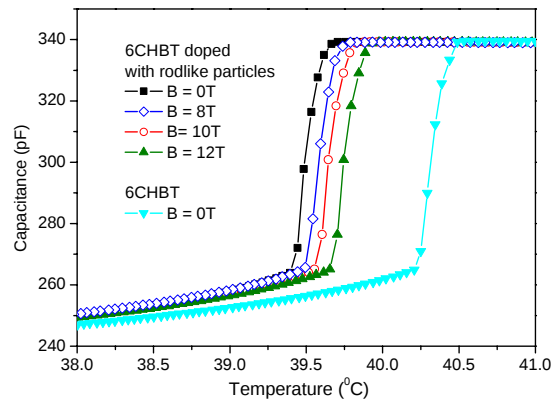


Figure 2: Capacitance vs. temperature for undoped 6CHBT and 6CHBT doped with rodlike magnetic particles measured at different magnetic fields.

The influence of the magnetic particles on the magnetic field induced isotropic-nematic phase transition was also studied in a “conventional” calamitic liquid crystal 6CHBT by capacitance measurements [17]. The used magnetic particles were either spherical or rod-like. In both cases the size of the magnetic particles was much greater than the dimensions of the liquid crystal molecules, i.e. the magnetic particles can be regarded as macroscopic objects floating in the liquid crystal. The surface of the magnetic particles is able to orient the adjacent liquid

crystal molecules. During the measurements the magnetic field was applied parallel with the capacitor electrodes.

Our results have confirmed that the shape of the magnetic particles affects the phase transition from the isotropic phase. In the pure 6CHBT as well as in 6CHBT doped with spherical magnetic particles no measurable field induced shift of the isotropic-nematic phase transition temperature was observed in magnetic fields up to 12T. On the contrary, in 6CHBT doped with rodlike magnetic particles (diameter size 10 nm, length 50 nm and volume concentration 2×10^{-4}) a shift of 0.25°C was found in the phase transition temperature at 12T (Fig. 2). Therefore, our results have proven that ferronematics composed of calamitic liquid crystals and rod-like magnetic nanoparticles can be just as effective in demonstrating the magnetic field induced isotropic-nematic phase transition as bent-core nematics [16].

In recent works by Podoliak et al. [18], and Buluy et al. [19] both experimental and theoretical investigations have been reported about the optical response of suspensions of ferromagnetic nanoparticles in nematic liquid crystals on the imposed magnetic field. The authors have measured a linear optical response in ferronematics at very low magnetic fields (far below the threshold of the Fredericksz transition). A similar effect was also observed in our dielectric measurements in samples doped with spherical [20] or rod-like [21] magnetic particles as it is demonstrated in Fig.3. The figure provides a clear evidence for a nearly linear magnetic field dependence of the capacitance in the low magnetic field region.

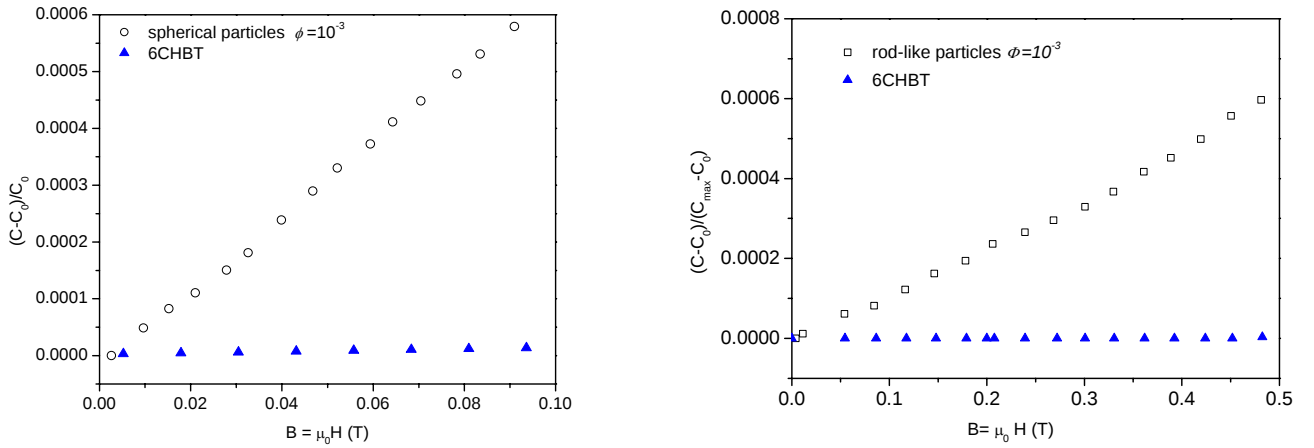


Figure 3: Reduced capacitance versus magnetic field for undoped 6CHBT and for 6CHBT doped with spherical particles and rod-like particles.

3. Conclusion

We have shown, that doping liquid crystals with magnetic nanoparticles increases the sensitivity to external magnetic field. The shape and the size of the magnetic nanoparticles play significant role in structural transitions. We have observed an increase of the isotropic-nematic phase transition temperature in ferronematics based on the calamitic liquid crystals doped with magnetic nanoparticles in magnetic field of $\sim 10\text{T}$. Moreover, the magnetic particles can influence the response of liquid crystals also in the low magnetic field region, far below Fréedericksz transition.

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