Magnetic-Field Induced Isotropic to Nematic Phase Transition in Ferronematics

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In this work the thermotropic liquid crystal 4-(trans-4′-n-hexylcyclohexyl)-isothiocyanato-benzene (6CHBT) was doped with differently shaped magnetic nanoparticles with the aim to increase the sensitivity of the liquid crystal on the external magnetic field. The volume concentration of the magnetic particles was 2×10^{-4}. The phase transition temperature from isotropic to nematic phase in external magnetic fields up to 12 T was monitored by precise capacitance measurements in capacitance cells filled with the prepared ferronematic samples. The shift in the temperature from isotropic to nematic phase was observed in the liquid crystal doped with rodlike particles. To our knowledge, this is the first observation of such a magnetic-field induced transition in ferronematics based on a calamitic liquid crystal.

Index Terms—**Ferronematics, liquid crystals, magnetic nanoparticles, structural transitions.**

I. Introduction

LIQUID crystals are anisotropic fluids with long-range orientational order, which combine the fluidity of ordinary liquids with the interesting electrical and optical properties of crystalline solids. The majority of liquid crystals are formed by rodlike organic molecules with a length of approximately 2.5 nm. Their ordering is a function of temperature. In nematic phase the molecules have no positional order, but tend to point in the same direction (along the director $\boldsymbol{n}$).

The major technical application of liquid crystals is their use in the nowadays widespread liquid crystal displays. In these devices the most characteristic feature of liquid-crystalline systems is exploited—a strong response of their molecular and supermolecular organization to a small external perturbation. Due to the anisotropy of the dielectric permittivity of liquid crystals their molecular orientation can be easily controlled by relatively weak electric fields. As for the use of magnetic fields, their values have to be rather large $(B \sim 1\ \mathrm{T})$ because of the small value of the anisotropy of diamagnetic susceptibility $(\chi_a \sim 10^{-7})$.

In an effort to enhance the magnetic susceptibility of liquid crystals, the idea of doping them with fine magnetic particles was introduced by Brochard and de Gennes [1], theoretically. They constructed a continuum theory of magnetic suspensions in nematic liquid crystals (ferronematics) in their fundamental paper prior to the chemical synthesis of these systems. In the first experimental paper Rault *et al.* [2] reported the basic magnetic properties of a suspension of rodlike $\gamma - \mathrm{Fe_2O_3}$ particles in the 4-methoxy-benzylidene-4′-n-butyl-aniline (MBBA) liquid crystal. Later, lyotropic and then thermotropic ferronematics were prepared and studied [3], [4].

In the last two decades interest in these materials has grown substantially; not only because of the interesting physical problems, but also for the promise to provide an optical device technology based on magnetic switching.

It has long been known that the possibility exists in liquid crystals for an external field to substantially alter the nematic-isotropic transition temperature [5]–[7]. However, the effect could not been induced by magnetic-field H [8] until recently [9]. The principal reason is that the estimated critical fields are well over 100 T for traditional liquid crystal materials [8]. The first experimental observation of the predicted magnetic-field dependence of the nematic-isotropic phase transition temperature has been recently carried out [9] on a powerful electromagnet (H up to 30 T). To demonstrate the effect, besides the powerful electromagnet, the proper choice of a "non-traditional" (bent-core) nematic liquid crystal material was also necessary. The "non-traditional" nematic material chosen in [9], has considerably different physical properties from "traditional" calamitic nematics; the first-order character of the nematic-isotropic transition at the "clearing point" is substantially weaker than for "traditional" nematics. These properties, combined with the high magnetic field have contributed to the observation of the phase transition temperature shift that was $\sim 0.8°\mathrm{C}$ at the magnetic field of 30 T. According to our previous magneto—dielectric studies, the size and shape of magnetic nanoparticles influence the critical magnetic field of liquid crystals doped with magnetic particles (ferronematics) [10]. The effect of the magnetic field on the orientation of

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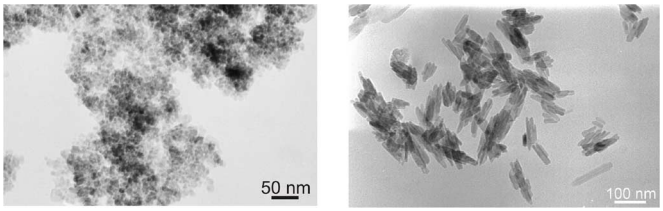

Fig. 1. TEM images of spherical (left) and rodlike (right) magnetic particles.

the liquid crystal molecules in a "traditional" calamitic nematic 4-(trans-4′-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) doped with different kind of magnetic nanoparticles (spherical, rodlike, chainlike) was demonstrated.

The present work is devoted to studying magnetic field induced isotropic-nematic phase transition in the "traditional" calamitic liquid crystal 6CHBT doped with spherical magnetic particles and rodlike magnetic particles.

II. Materials and Methods

Spherical magnetic particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} salts by NH_4OH at 60°C. To obtain Fe_3O_4 precipitate, $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved in deionized water by vigorous stirring (the molar ratio Fe^{3+}/Fe^{2+} was 2:1). The solution was heated to 80°C and 25% NH_4OH was added. After precipitation, the iron oxide nanoparticles were isolated from the solution by magnetic decantation, then filtered with distilled water and, finally, with isopropanol before drying at 40°C under vacuum.

Magnetic rodlike particles were synthesized through hydrolysis of $FeCl_3$ and $FeSO_4$ solutions (Fe^{3+}/Fe^{2+} molar ratio was 2:1) containing urea. In a typical experiment oleic acid was ultrasonically dispersed in water to form homogenous micelles. Then, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ and $(NH_2)_2CO$ were dissolved in the above solution. This mixture was added to a flask with reflux condenser and was heated in water bath for 12 hours at 90–95°C. The dark precipitate has been formed. The sample was cleaned several times by purified and deoxygenated water, and then it was dried under low pressure at 50°C for 3 hours.

Magnetic properties of the prepared particles were estimated by magnetization measurements with a SQUID magnetometer (Quantum Design MPMS 5XL) and the size and morphology of the particles were determined by transmission electron microscopy (TEM, Tesla BS 500). Fig. 1 shows the TEM image of prepared spherical and rodlike particles. The mean diameter and length of the obtained nearly spherical and rodlike magnetic particles were determined by fitting a Gaussian to the histograms of the size distribution.

The studied ferronematic samples were based on the thermotropic nematic 6CHBT. The 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [11]. The temperature of the nematic-to-isotropic transition (clearing point) of this nematic is $T_{N-I} = 42.8$°C. The nematic samples were doped with a magnetic suspension consisting of spherical or rodlike particles coated with oleic acid as a surfactant. The doping was simply done by adding this suspension, under continuous stirring, to the liquid crystal in the isotropic phase. Due to the small volume concentrations of the magnetic particles

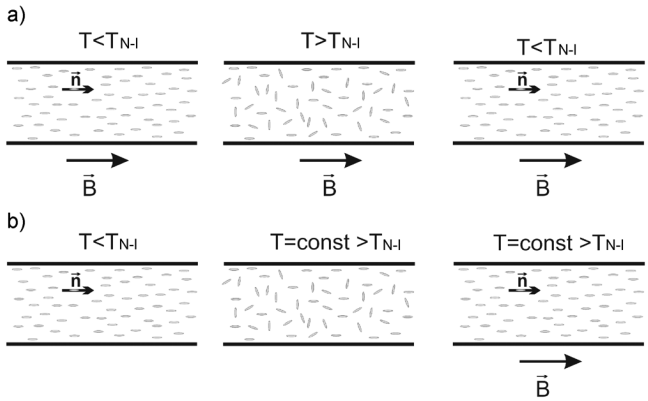

Fig. 2. Cross section of the cell in the initial state and after application of the magnetic field; (a) the magnetic field is held constant, (b) temperature is held constant.

($\Phi = 2 \times 10^{-4}$) and surfactant in the prepared ferronematic samples the interparticle dipole-dipole interactions are avoided.

Structural transitions in the samples were monitored by capacitance measurements in a capacitor made of indium-tin-oxide (ITO) coated glass electrodes (LINCAM Co.). The capacitor with the electrode area of approximately 0.5 cm × 0.5 cm was placed into a thermostated system, where the temperature was stabilized with an accuracy of ±0.05°C. The distance between the electrodes (sample thickness) was $D = 5$ μm. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling. In the experiments the liquid crystal had a planar initial alignment; i.e. the director $\boldsymbol{n}$ was parallel to the capacitor electrodes. It should be pointed out for the next consideration that the minimal value of capacitance is observed for the planar alignment while, the maximal value for the homeotropic alignment, i.e. when the director $\boldsymbol{n}$ is perpendicular to the capacitor electrodes. The experimental geometry is shown in Fig. 2. There were two, complementary, measurement protocols. First, the constant magnetic field was held, while the temperature was increased above the temperature of the transition from nematic to isotropic phase T_{N-I} and then slowly decreased. The second protocol was to hold the temperature constant and the magnetic field was ramped up to 12 T, and then decreased back to zero.

III. Results and Discussion

The influence of the magnetic particles on the magnetic field induced isotropic-nematic phase transition in "traditional" calamitic liquid crystal in 6CHBT was studied by capacitance measurements. The used magnetic particles were spherical and rodlike. In both cases the size of 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 to the capacitor electrodes (see Fig. 2). The dependence of the measured capacitance on the external magnetic field reflects the re-orientation of the nematic molecules in the presence of the magnetic field. Fig. 3 and Fig. 4 show the dependence of the capacitance of pure 6CHBT liquid crystal and 6CHBT liquid

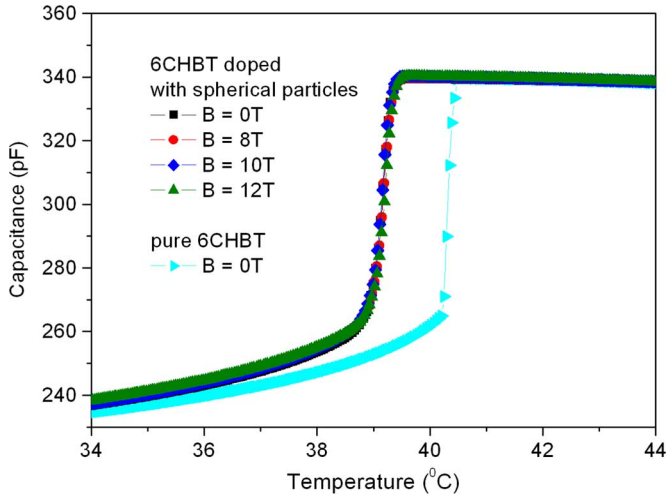

Fig. 3. Capacitance vs. temperature for pure 6CHBT and 6CHBT doped with spherical magnetic particles measured at different magnetic fields.

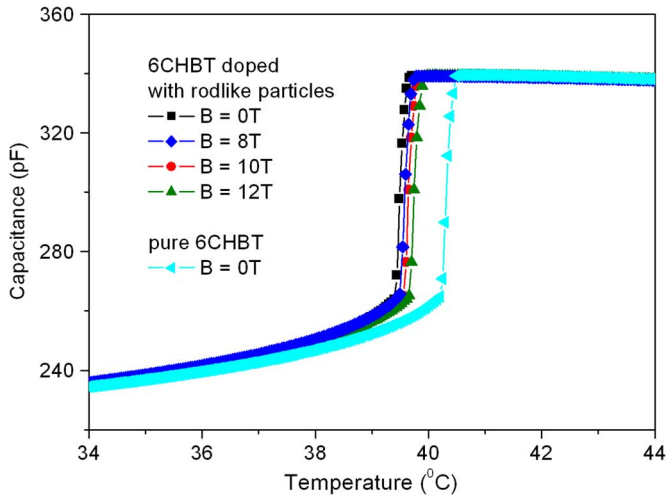

Fig. 4. Capacitance vs. temperature for pure 6CHBT and 6CHBT doped with rodlike magnetic particles measured at different magnetic fields.

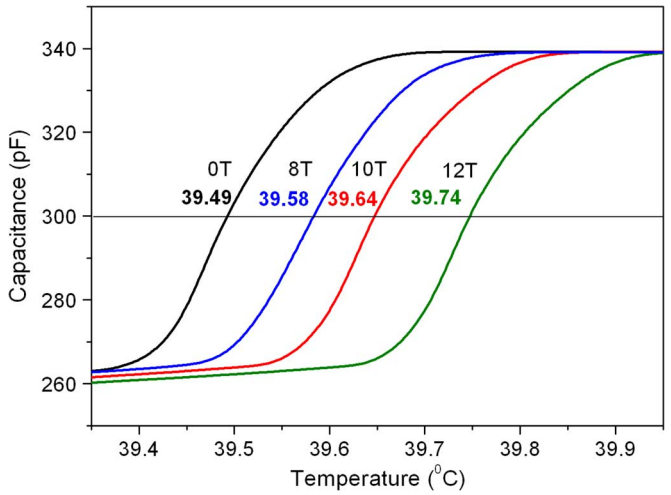

Fig. 5. Capacitance vs. temperature for 6CHBT doped with rodlike magnetic particles measured at different magnetic fields.

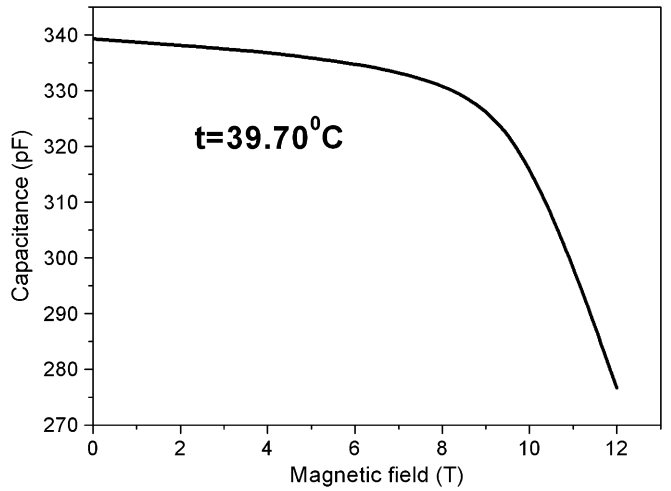

Fig. 6. Capacitance vs. magnetic field for 6CHBT doped with rodlike magnetic particles measured at constant temperature.

crystal doped with spherical and rodlike magnetic particles on the temperature, respectively. From these figures it is seen that the presence of magnetic particles in the liquid crystal shifts the temperature of the transition from isotropic to nematic phase to lower values. This shift seems to be more significant in the case of doping with spherical magnetic particles.

On the other hand, in the case of doping with rodlike magnetic particles, an additional, magnetic field dependent shift was observed in the temperature of the transition from isotropic to nematic phase by application of external magnetic fields up to 12 T. Such a shift was not observable in ferronematics doped with spherical particles. Fig. 5 shows details of the measured structural transition from isotropic to nematic phase for 6CHBT liquid crystal doped with rodlike magnetic particles. There is an observed shift of about 0.25°C in the transition temperature when a magnetic field of 12 T is applied. This is the same value what was obtained in the case of a bent-core nematic liquid crystal at the same magnetic field of 12 T [9].

In the next experiment, the temperature was held constant at the value 39.70°C, at which the sample doped with rodlike magnetic particles is in the isotropic state. Then the external magnetic field was ramped up to 12 T. The dependence of the capacitance on the applied magnetic field is shown in Fig. 6. A decrease in the capacitance was observed with increasing magnetic field in accordance with results obtained from measurements of the temperature dependence of the capacitance at constant magnetic field.

Fig. 7 shows H^2 dependence of critical point shift of temperature. On the base of simple thermodynamical arguments [8] the expression for this shift in pure liquid crystal is given by

$$\delta T = T_{NI}(H) - T_{NI}(0) = \frac{T_{NI}(0)}{Q}\frac{\chi_a}{3}H^2 \qquad (1)$$

where $T_{NI}(0)$ and $T_{NI}(H)$ is the transition temperature from isotropic to nematic phase in zero field and in field H, respectively, Q is the latent heat of the transition and χ_a is the anisotropy of diamagnetic susceptibility in the nematic phase.

The coupling of magnetic particles, which are added to the liquid crystal, to external magnetic field is strong, therefore we assume that the partial equilibrium of magnetic particles

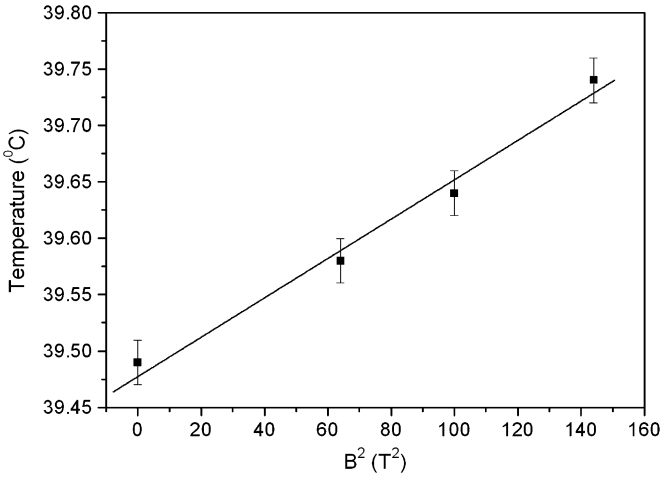

Fig. 7. Nematic-isotropic transition temperature vs. applied magnetic field (line represents the best linear fit).

is reached prior to the equilibrium in the whole system. This brings about an effective magnetic field which is the external field enhanced by the magnetic moments of magnetic particles. This effective field replaces the external magnetic field in the coupling to the diamagnetic liquid crystal molecules and leads to a much larger shift of the nematic-isotropic transition temperature than the magnetic field in pure liquid crystal. The effective magnetic field is obtained by the substitution

$$H \rightarrow (1+\chi)H \tag{2}$$

where χ is the magnetic susceptibility of the system of magnetic particles. Due to low concentration of the magnetic particles, the susceptibility may be calculated as that of the ideal gas

$$\chi = \frac{C}{k_B T} \tag{3}$$

and obeys Curie's law. Curie's constant in the ideal gas is

$$C = \frac{N}{V}\mu_0 \mu^2 \tag{4}$$

where μ is the magnetic moment of the magnetic particle, V the volume of the ferronematic. In terms of the volume of the magnetic particle ΔV we obtain

$$\frac{N}{V}\mu_0\mu^2 = \frac{1}{\Delta V}\mu_0(m\Delta V)^2 = \mu_0 m^2 \phi V \tag{5}$$

where Φ is the volume concentration of the magnetic particles, and $m = \mu/\Delta V$ is the magnetization of the magnetic particles. In strong external fields this is the saturation magnetization of the magnetic particles. Thus, the temperature shift is

$$\delta T = \frac{T_{NI}(0)}{Q}\frac{\chi_a}{3}H^2\left(1+\frac{\mu_0 m^2 \phi \Delta V}{k_B T}\right)^2. \tag{6}$$

IV. Conclusion

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 12 T. 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 12 T. Therefore, our results have proven that ferronematics composed of calamitic liquid crystals and rodlike magnetic nanoparticles can be just as effective in demonstrating the magnetic field induced isotropic-nematic phase transition as bent-core nematics [9].

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