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INCREASING THE MAGNETIC SENSITIVITY OF LIQUID CRYSTALS BY ROD-LIKE MAGNETIC NANOPARTICLES

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Magnetic Fréedericksz transition was studied in ferronematics based on the nematic liquid crystal 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT was doped with rod-like magnetic particles of different size and volume concentration. The volume concentrations of magnetic particles in the prepared ferronematics were ϕ_1=10^{-4} and ϕ_2=10^{-3}. Structural changes were observed by capacitance measurements, which evidenced of a significant influence of the concentration, shape anisotropy and/or the size of the magnetic particles on the magnetic response of these ferronematics.

1. Introduction. Liquid crystalline phases occur as additional, thermodynamically stable states of matter between the liquid state and the crystal state in some materials. They can be characterized by a long-range orientational order of the molecules and, as a consequence, by an anisotropy in their physical properties. Liquid crystals can be oriented under electric or magnetic fields due to the anisotropy of dielectric permittivity or diamagnetic susceptibility [1].

One of the most important findings related to the control of liquid crystals by external fields was the threshold behaviour in the reorientational response of liquid crystals – an effect described by Fréedericksz [2] and named after him as the "Fréedericksz transition". The dielectric permittivity anisotropy of liquid crystals is, in general, relatively large; thus, driving voltages of the order of a few volts are sufficient to control the orientational response. Therefore, most of the liquid crystal devices are driven by the electric field. On the other hand, because of the small value of the anisotropy of diamagnetic susceptibility ($\chi_a \sim 10^{-7}$), the magnetic field H necessary to align liquid crystals has to reach rather large values ($B = \mu_0 H \sim 1\,\mathrm{T}$), and therefore, liquid crystal applications using magnetic fields are rather limited. Consequently, the increase of the magnetic sensitivity of liquid crystals is an important challenge, which can potentially broaden the area of applications and may offer an opportunity to develop new devices.

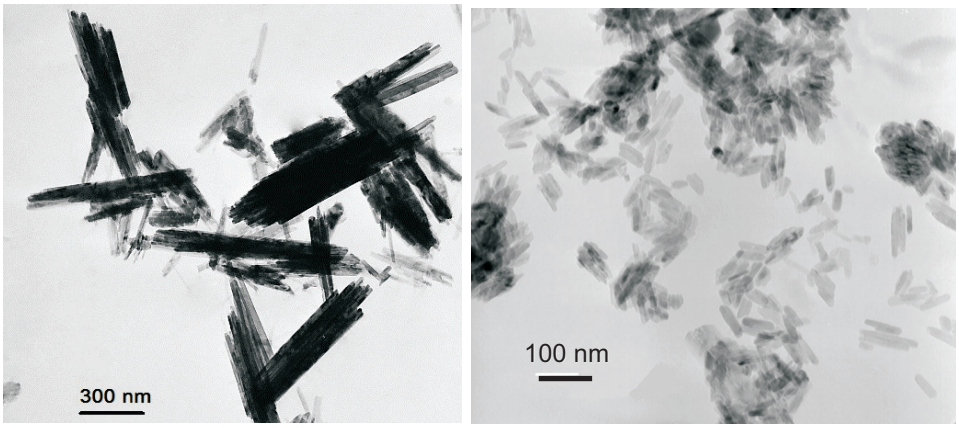
Brochard and de Gennes [3] first suggested theoretically the idea that could increase the magnetic sensitivity of liquid crystals. According to them, colloidal systems called "ferronematics", consisting of nematic liquid crystals doped with magnetic nanoparticles in small concentrations, should respond to low magnetic fields of the order of tens of Gauss. Such small magnetic fields cannot affect the

undoped nematics, however, they may be sufficiently strong to align or rotate the magnetic moments of the particles inside the ferronematic suspensions according to the predictions. This realignment or rotation effect could be then extended to the host nematic through the coupling between the nanoparticles and the liquid crystal molecules. One has to note here that the realignment of the host nematic was assumed to be entirely determined by the ferromagnetic properties of nanoparticles (not affected by the intrinsic diamagnetic properties of the nematic), since the theory [3] predicted a rigid anchoring with $\mathbf{n} \parallel \mathbf{m}$, where $\mathbf{n}$ is the unit vector of the preferred direction of the nematic molecules (director), and $\mathbf{m}$ is the unit vector of the magnetic moment of the magnetic particles.

The first experimental realization of ferronematic materials was carried out by Chen and Amer [4]. Later experiments on some other ferronematics have indicated that besides the predicted $\mathbf{n} \parallel \mathbf{m}$ condition, the case of $\mathbf{n} \perp \mathbf{m}$ is also possible. To bridge this gap between theory and experiment, Burylov and Raikher modified the theoretical description by considering a finite value of the surface density of anchoring energy W at the nematic–magnetic particle boundary [5–8]. The finite value of W as well as the parameter $\omega = Wd/(2K)$ (d is the mean diameter of the magnetic particles and K is an orientational-elastic Frank modulus) characterizes the type of nematic molecules' anchoring on the magnetic particle's surface. For $\omega >> 1$, the anchoring is rigid, while the soft anchoring is characterized by $\omega \leq 1$, which (unlike the rigid anchoring) permits both types of boundary conditions, $\mathbf{n} \parallel \mathbf{m}$ and $\mathbf{n} \perp \mathbf{m}$.

So far the magnetic nanoparticles have established their wide range of applications. The properties of magnetic nanoparticles significantly depend on their size, shape and structure. Controlling the shape and the size of nanoparticles is one of the ultimate challenges in modern material research. These magnetic particles can be made so small that each particle becomes a single magnetic domain exhibiting abnormal magnetic properties known as superparamagnetism. Doping liquid crystals with low volume concentration of nanoparticles has been shown to be a promising method to modify the properties of liquid crystals. At such a low amount, nanosized particles do not disturb significantly the liquid crystalline order, hence, producing a macroscopically homogeneous structure. However, the particles can share their properties with the host liquid crystal enhancing the existing properties or introducing some new properties for the composite mixtures.

2. Experiment. Two types of magnetic rod-like particles were prepared through the hydrolysis of $FeCl_3$ and $FeSO_4$ solutions (the molar ratio 2 : 1) containing urea. To prepare larger rod-like particles (sample A), 0.6756 g of $FeCl_3 \cdot 6H_2O$, 0.3426 g of $FeSO_4 \cdot 7H_2O$ and 0.60 g of $(NH_2)_2CO$ were dissolved in 10 ml of purified deoxygenated water. The product was added to a flask with a reflux condenser, which was kept at 90–95°C for 12 h and then cooled to room temperature [9]. After the synthesis, the particles were coated with oleic acid as a stabilizer. During the synthesis of smaller rod-like particles (sample B), at first, the stabilizer (oleic acid) was ultrasonically dispersed in water to form homogenous micelles. Then, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ were dissolved in the above solution. This mixture was added to a flask with a reflux condenser and heated in a water bath for 12 h at 90-95 °C, during which a dark precipitate was formed [10]. The prepared particles were a mixture of magnetite and hematite. We suppose the core was magnetite with a hematite shell. Fig. 1 shows transmission electron microscopic images of the prepared magnetic particles. The diameter of the larger rod-like particles (sample A) was $d_A = (18 \pm 3)$ nm and their mean length $L_A = (400 \pm 52)$ nm. The mean diameter and the length of the smaller rod-like particles (sample B) were



(*a*) (*b*)

Fig. 1. TEM image of (*a*) larger rod-like particles with a mean diameter of 18 nm and mean length of 400 nm; (*b*) smaller rod-like particles with a mean diameter of 10 nm and mean length of 50 nm.

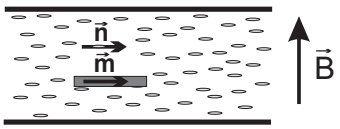


Fig. 2. The cross-section of a planar cell with initially parallel **n** and **m**.

$d_{\mathrm{B}} = (10 \pm 1)$ nm and $L_{\mathrm{B}} = (50 \pm 9)$ nm, respectively. Hence, the mean shape anisotropies of the nanoparticles were approximately $L_{\mathrm{A}}/d_{\mathrm{A}} \approx 22$ and $L_{\mathrm{B}}/d_{\mathrm{B}} \approx 5$ for the two types of samples.

The ferronematic samples were based on thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT), which was synthetized and purified at the Institute of Chemistry, Military Technical University, Warsaw, Poland. The 6CHBT is a low-temperature-melting enantiotropic liquid crystal with high chemical stability [11]. The phase transition temperature from the isotropic liquid to the nematic phase was found at 42.6°C. Doping was done by adding nanoparticles to the liquid crystal in the isotropic phase under continuous stirring.

The structural transitions in the prepared samples were monitored by capacitance measurements in a capacitor composed of ITO-coated glass electrodes. The capacitor with an electrode area of approximately 1 cm × 1 cm was placed into a regulated thermostat system, the temperature of which was stabilized at 35°C. The distance between the electrodes (sample thickness) was $D = 5\,\mu$m. The capacitance was measured at a frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling.

In the experiment, the liquid crystal had a planar initial alignment, i.e. the director was parallel to the capacitor electrodes and the magnetic field was applied perpendicular to them (see Fig. 2). The dependence of the measured capacitance on the external field illustrates the reorientation of the nematic molecules.

3. Results. The results presented in [12] show that the doping with magnetic particles shaped similarly to the molecules of the host liquid crystal is more effective and thus offers better perspectives for ferronematics applications, where a magnetic field is necessary to control the orientation of the liquid crystal. With the aim to study the influence of the size of particles on the magnetic response,

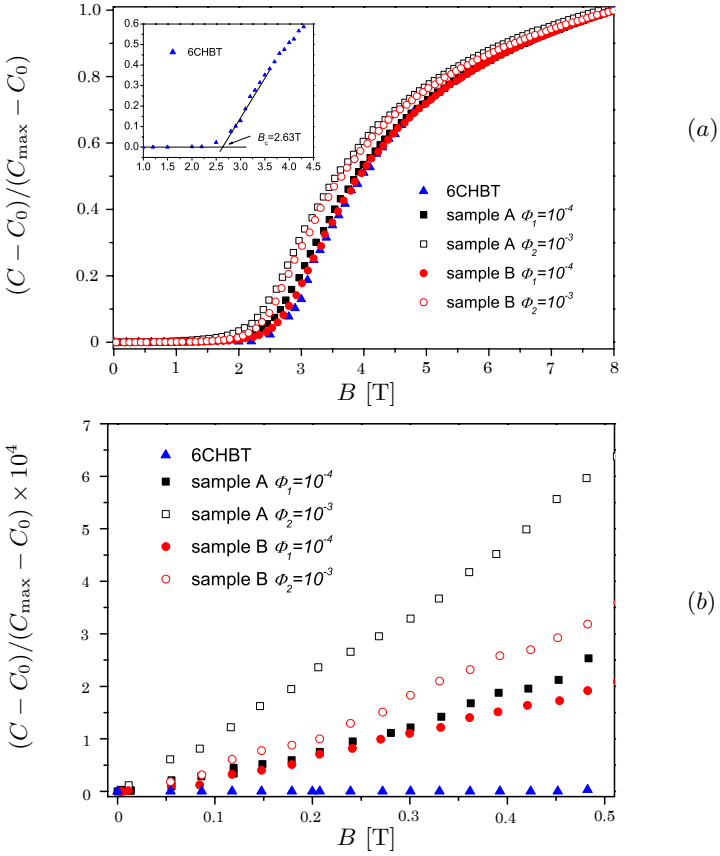


Fig. 3. Reduced capacitance versus magnetic field (*a*) for pure 6CHBT and for 6CHBT doped with different rod-like particles and with different volume concentrations of magnetic particles; the inset demonstrates the linear extrapolation procedure for the determination of B_c; (*b*) blowup of the low magnetic field region for the same data.

two kinds of rod-like magnetic particles (sample A and sample B) were prepared as described above. Both ferronematics A and B were based on the nematic 6CHBT and doped in two different volume concentrations $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$.

Fig. 3*a* shows the magnetic Fréedericksz transition in a pure 6CHBT and in ferronematics doped with larger (A) and smaller (B) rod-like particles for both volume concentrations. It demonstrates that the critical magnetic field B_c of the Fréedericksz transition, i.e. the magnetic field that initiates the reorientation of the director toward its direction, is shifted to the lower values with increasing the volume concentration, and that B_c is lower for larger particles than for smaller ones at a given ϕ. For all samples the critical magnetic field was determined from the dependence of $(C-C_0)/(C_{max}-C_0)$ versus B, where 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. B_c was determined by linear extrapolation of the data in Fig. 3*a* as demonstrated in the inset for 6CHBT. The obtained critical value of the magnetic field for pure 6CHBT is 2.63 T. In ferronematics, B_c is lower, and the values obtained for various samples are listed in Table 1. The reduction of B_c becomes larger if the concentration is increased (in case of the same nanoparticle) as well as if the nanoparticle is larger (at the same concentration).

Table 1. Critical magnetic fields measured in the ferronematics and the calculated values of the surface density of the anchoring energy W and parameter ω.

sample	B_{cFN} [T]	W [Nm^{-1}]	ω
sample A ϕ_1	2.39	4.14×10^{-5}	0.055
sample A ϕ_2	2.12	8.34×10^{-6}	0.011
sample B ϕ_1	2.52	1.08×10^{-5}	0.008
sample B ϕ_2	2.25	3.54×10^{-6}	0.003

Observations of the structural transitions in ferronematics in an external field can be used to determine the type of anchoring of nematic molecules on the surfaces of magnetic particles as well as the surface density of the anchoring energy W at the nematic–magnetic particle boundary. By means of the Burylov and Raikher's expression for the free energy of ferronematic [7] the formula for the critical magnetic field is

$$B_{\mathrm{c}}^2 - B_{\mathrm{cFN}}^2 = \frac{2\mu_0 W \phi}{\chi_{\mathrm{a}} d}, \tag{1}$$

where B_{c} and B_{cFN} are the critical fields for the magnetic Fréedericksz transition of the pure liquid crystal and ferronematic, respectively, d is the "characteristic size" of the particles (the mean diameter), ϕ is the volume concentration of magnetic particles in the liquid crystal, μ_0 is the permeability of vacuum, and χ_a is the anisotropy of the diamagnetic susceptibility of the liquid crystal (for 6CHBT $\chi_{\mathrm{a}} = 4.805 \times 10^{-7}$ at 35°C).

The calculated values of W and the values of parameter ω are summarized in Table 1. ω was calculated using the same $K_1 = 6.71$ pN elastic constant for all ferronematics as for the pure 6CHBT. In all cases, $\omega < 1$ that characterizes the soft anchoring of the nematic molecules on the surface of magnetic particles.

In recent works by Podoliak *et al.* [13] and Buluy *et al.* [14] both experimental and theoretical investigations on the optical response of suspensions of ferromagnetic nanoparticles in nematic liquid crystals to the imposed magnetic field are reported. The authors measured the linear optical response in ferronematics at very low magnetic fields (far below the threshold of the Fréedericksz transition).

A similar effect was also observed in our dielectric measurements in samples doped with rod-like particles, as it is illustrated in Fig. 3*b*. The figure provides a clear evidence for a nearly linear magnetic field dependence of the capacitance in the low magnetic field region.

4. Conclusion. We have demonstrated that both the threshold of the magnetic Fréedericksz transition and the dielectric response to low magnetic fields (far below the Fréedericksz transition) depend not only on the volume concentration of the magnetic particles, but also on the size of the particles. According to the results, the larger is the particle, the bigger are the effects (a larger decrease of the threshold of the Fréedericksz transition and a more pronounced linear response to low magnetic fields). Since in our experiments the larger particles have also a larger aspect ratio L/d, further experiments are needed to clarify whether the volume size, the linear size or the shape anisotropy (i.e. L/d) influence primarily the magnitude of the effects.

The other challenging task is to explain the linear dielectric response to low magnetic fields. To our present understanding, within the framework of the Burylov and Raikher's continuum theory [5–8], both the magnetic moment of a magnetic particle **m** and the presence of an initial out-of-plane pretilt angle of

the nematic director **n** are necessary for the linear $C(B)$ dependence in the low B limit. A more detailed theoretical analysis is, however, needed to justify this assumption.

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