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HOW TO CHANGE THE SENSITIVITY OF LIQUID CRYSTAL IN EXTERNAL MAGNETIC FIELD

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The influence of an external electric and magnetic field on the structural transitions in ferronematics based on thermotropic nematic 4-trans-4'-n-hexyl-cyclohexyl-isothiocyanatobenzene (6CHBT) is studied. Droplets of the nematic phase in the isotropic phase were observed in the solutions of nematogenic 6CHBT dissolved in phenyl isocyanate and 6CHBT dissolved in phenyl isocyanate and doped with the magnetic particles of different shape (nano-rods and chain-like particles). The magneto-dielectric measurements of structural transitions showed the magnetic field induced shift of the phase transition temperature from isotropic to droplet state in a magnetic field up to 12 T. The linear dependence of the temperature of isotropic-droplet state phase transition on the external magnetic field was observed.

Introduction. Complex materials are of fundamental research interest due to their novel properties, which are absent in the substances composing these materials. One of such materials is the suspension of magnetic particles in the nematic liquid crystal called ferronematic. Liquid crystals possess the anisotropy of the physical properties that allows to change the orientation of the liquid crystal optical axis (named the director **n**) under the influence of external electric or magnetic fields. However, due to small anisotropy of the liquid crystal diamagnetic susceptibility, the threshold magnetic field is large. Ferronematics are a manifestation of the idea of Brochard and de Gennes, who suggested that doping liquid crystals with fine magnetic particles may enhance their sensitivity to magnetic fields [1]. There are many reports showing that doping of a nematic liquid crystal with a small amount of nanoparticles affects the important properties of the nematic materials resulting in a decrease of the structural transition threshold [2–9]. In the last two decades the 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. The influence of the magnetic field on ferronematics depends on coupling energy and mutual orientation of magnetic particles and liquid crystal molecules. The theory of Brochard and de Gennes [1] predicts a rigid anchoring with $\mathbf{m} \parallel \mathbf{n}$, where the unit vector **n** (director) denotes the preferential direction of the nematic molecules and the unit vector **m** denotes the orientation of the magnetic moment of magnetic particles. Later, experiments with thermotropic ferronematics excluded the presence of parallel orientation of **m** and **n**. So, Burylov and Raikher's theory has been constructed [10–13]. This theory considers the finite value of the surface density of the anchoring energy W at the nematic–magnetic particle boundary. The finite value of W, as well as the parameter ω defined as the ratio of the anchoring energy to

the elastic energy of a liquid crystal ($\omega = Wd/K$), where d is the size of magnetic particles and K is the orientational-elastic Frank modulus), characterizes the type of anchoring of nematic molecules on the magnetic particle surface. The parameter $\omega >> 1$ characterizes the rigid anchoring. The soft anchoring is characterized by the parameter $\omega \leq 1$ and, unlike the rigid anchoring, permits both types of boundary conditions ($\mathbf{m} \parallel \mathbf{n}$ and $\mathbf{m} \perp \mathbf{n}$). Thus the theory of Burylov and Raikher could be applied for thermotropic ferronematics. It has long been known that the possibility exists in liquid crystals for an external field to substantially alter the nematic–isotropic transition temperature [14–16]. However, the effect could not have been induced by a magnetic field H [17] until recently [18]. The principal reason is that the estimated critical fields are well over 100 T for traditional liquid crystal materials [17]. The first experimental observation of the predicted magnetic field dependence of the nematic–isotropic phase transition temperature has been recently carried out [18] with 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 with considerably different from "traditional" calamitic nematics physical properties is also necessary. These properties, combined with the high magnetic field, have contributed to the observation of the phase transition temperature shift, which was $\sim$ 0.8°C at a magnetic field of 30 T. According to our previous magnetodielectric studies, the size and the shape of magnetic nanoparticles influence the critical magnetic field of liquid crystals doped with magnetic particles (ferronematics) [8]. The magnetic field induced isotropic-to-nematic phase transition in a "traditional" calamitic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) doped with rod-like magnetic particles was demonstrated in our previous work [21]. In the work of Kedziora et al. [19], the co-existence of nematic and isotropic phases was observed in the 6CHBT liquid crystal dissolved in a non-polar medium (benzene) close to the temperature of the isotropic-to-nematic transition. Due to the existence of a short-range orientational order of the mesogenic molecules 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT), pseudonematic domains (droplets of 500-1000 nm in size determined by the temperature) were formed in the isotropic phase. The size of these droplets increased, as the temperature of the liquid decreased. These results have inspired us to perform similar experiments with the nematogenic liquid crystal 6CHBT dissolved in phenyl isocyanate (more stable than benzene) doped with spherical magnetic nanoparticles [20]. In our previous work [22], the structural transitions in the liquid crystal 6CHBT dissolved in phenyl isocyanate and doped with nano-rods or chain-like magnetic nanoparticles in an external magnetic field were investigated. In this work, the structural transitions in the liquid crystal 6CHBT dissolved in phenyl isothiocyanate and doped with nano-rods or chain-like magnetic nanoparticles, exposed to a combined electric and magnetic field, were investigated.

1. Experiment. The rod-like magnetic particles were synthesized through the hydrolisis of $FeCl_3$ and $FeSO_4$ solutions [22]. The chain-like particles were produced from magnetotactic bacteria Magnetotacticum Magnetospirillum (AMB-1) [23]. The studied ferronematic samples were based on the thermotropic nematic 6CHBT [22]. The doping was done by adding nanoparticles, under continuous stirring, to the liquid crystal in the isotropic phase. The nematic droplets of 6CHBT in the isotropic phase were created in 6CHBT liquid crystal dissolved in phenyl isocyanate (molar fraction of the liquid crystal was $X = 0.906$) and in 6CHBT liquid crystal dissolved in phenyl isocyanate and mixed with a small volume concentration of magnetic particles $\phi = 5 \times 10^{-4}$, close to the isotropic-to-

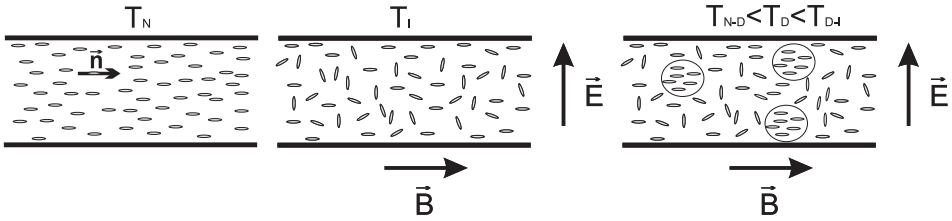

Fig. 1. Cross-section of the cell in the initial state (nematic phase), after heating to the isotropic phase and after cooling to the droplet state. The electric field is applied perpendicular to the electrode surfaces and the magnetic field is applied parallel to the electrode surfaces.

nematic transition temperature. The magnetic particles used for doping were of two different shapes: rod-like and chain-like. The samples were deposited between two glass slides and heated above the nematic-to-isotropic transition point (to approximately 35°C). Then a constant electric and a magnetic field were applied, and the samples were then slowly cooled at a rate of 2°C min^{-1} in the external electric and magnetic fields.

The structural transitions in the prepared samples were indicated by capacitance measurements by a capacitor composed of ITO-coated glass electrodes (LINCAM Co.). The capacitor with the electrode area of approximately 1 cmx1 cm was connected to a regulated thermostat system; 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 1 kHz frequency by the high precision capacitance bridge Andeen Hagerling. The dependence of the measured capacitance on the external field shows the re-orientation of the nematic molecules.

In the experiment, the liquid crystal had a planar initial alignment, i.e. the director was parallel to the capacitor electrodes (see Fig. 1). It should be pointed out for the following consideration that the minimum value of capacitance is observed for the planar alignment, while the maximum value for the homeotropic alignment, i.e. when the director **n** is perpendicular to the capacitor electrodes.

2. Results. In our previous work [6], from the measurements of the 6CHBT-based ferronematics, we have obtained the parameter $\omega = 10^{-2}$, which characterizes the soft anchoring, and the boundary condition between **m** and **n** is found to be parallel. This result is in good agreement with the theory of Burylov and Raikher [10–13]. However, our previous experiments on the droplets have shown that the orientation of the nematic molecules in the droplets could be more complicated than in the case of pure nematic [20, 22]. As shown in [3, 8, 24], the particles' size, shape and the functionalisation of the particles play an important role in the coupling between the magnetic moment of the magnetic particles and the director of the liquid crystal. The uniform alignment of the liquid crystal matrix is distorted by inclusion of particles due to the local constrains imposed by the anchoring of the liquid crystal molecules at the surfaces of magnetic nanoparticles. These constrains can impose conflicting orientations on the liquid crystal, which result in the formation of local defects. These are determined by the shape and size of the particles and lead to a different behaviour of ferronematic samples [24].

In pure liquid crystals in the nematic phase, the preferred orientation of the liquid crystal molecules is parallel to the surface of electrodes due to the surface treatment (the capacitance decreases with the decreasing temperature), if the electric field is not strong enough to turn the molecules away. For $U >> U_c$, the

electric field rotates the director to its direction, i.e. the liquid crystal molecules are oriented perpendicular to the electrodes (the capacitance increases with the decreasing T). The magnetic field, being applied parallel to the electrode surfaces, stabilizes the parallel orientation of the crystal molecules, and the electric field has to be higher to rotate the director to its direction. As the temperature decreases, the orientation of the liquid crystal molecules depends on the value of applied voltage and magnetic field.

In ferronematics, the liquid crystal is doped with magnetic particles, as the sample is heated to a temperature higher than the temperature $T > T_{\mathrm{N-I}}$; the sample is in the isotropic phase and the molecules as well as the magnetic moments are disordered. The magnetic field applied parallel to the electrode surfaces stabilizes the parallel orientation of the magnetic particles and also, via magnetic particles, the liquid crystal molecules due to the coupling between them. As the temperature decreases, the orientation of the liquid crystal molecules depends on the value of applied voltage and magnetic field. If a small amount of phenyl isocyanate is added to the sample, the transition from nematic to isotropic state goes via the droplet state [19, 20].

The temperature dependencies of the capacitances of the prepared samples – 6CHBT dissolved in phenyl isocyanate and 6CHBT dissolved in phenyl isocyanate doped with rod-like or chain-like magnetic particles – were measured without the magnetic field and with magnetic fields ($B = \mu_0 H$) of 4, 8 and 12 T and at different voltage values $U = 2$ V and 10 V.

Fig. 2 shows the temperature dependencies of the capacitance in pure 6CHBT dissolved in phenyl isocyanate measured at the constant voltages 2 V and 10 V without the external magnetic field and in the external magnetic fields 4 T, 8 and 12 T. As seen from Fig. 2, as the temperature reaches a value, at which the droplets of the nematic phase in the isotropic phase occur, the capacitance of the samples decreases or increases with a decreasing temperature, depending on the applied electric field values. In the case of a sample without particles, there is no observable shift in the temperature of transition from the isotropic phase to the droplet state.

The situation changes if the samples are doped with magnetic nanoparticles. Fig. 3 and Fig. 4 illustrate the temperature dependencies for the capacitance in the 6CHBT liquid crystal dissolved in phenyl isocyanate and doped with magnetic

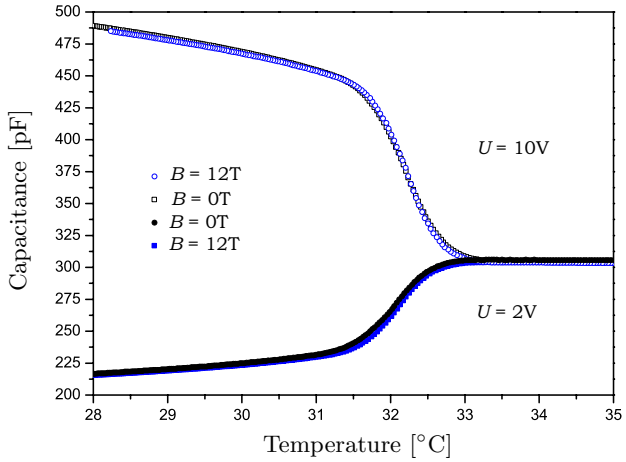

Fig. 2. Temperature dependence of the capacitance of 6CHBT dissolved in phenyl isothiocyanate under external electric and magnetic fields.

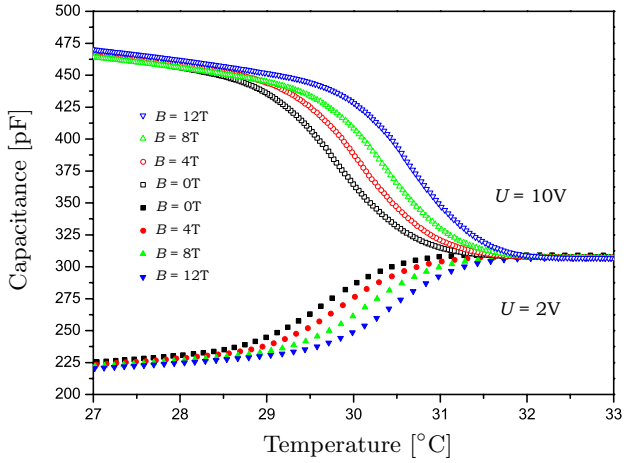

Fig. 3. Temperature dependence of the capacitance of 6CHBT dissolved in phenyl isothiocyanate and doped with rod-like particles in external electric and magnetic fields.

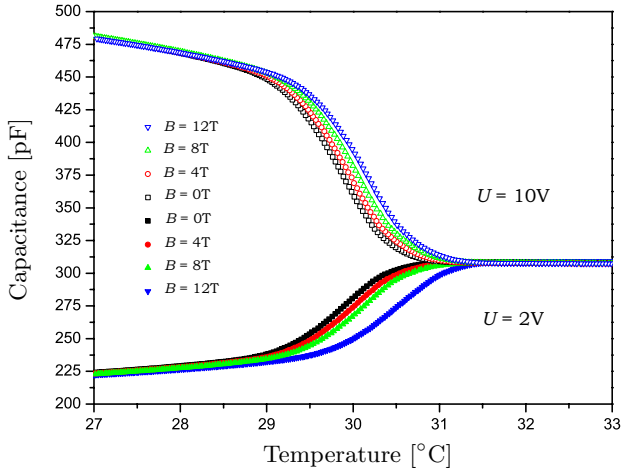

Fig. 4. Temperature dependence of the capacitance of 6CHBT dissolved in phenyl isothiocyanate and doped with chain-like particles in external electric and magnetic fields.

rod-like and chain-like magnetic particles, respectively, and measured without the magnetic field and with magnetic fields of 4, 8 and 12 , respectively, and for two values of the voltage 2 V and 10 V. As seen from these figures, with the increasing external magnetic field, the temperature of the phase transition increases.

The interaction between the magnetic particles and the liquid crystal molecules favours the parallel initial orientation of the magnetic moments of the magnetic particles and the director around them. If the sample is in the isotropic phase and no external magnetic field ($B = \mu_0 H = 0$) is imposed, the molecules as well as the magnetic moments are disordered. By switching on a strong external magnetic field the energy of thermal excitation may be overcome and the magnetic moments of the nanoparticles tend to align parallel to B turning along the molecules of the liquid crystal, too. Thus, the nematic order is induced by the magnetic field around the nanoparticles already above the temperature higher than the temperature of the isotropic–droplet state phase transition $T_{\mathrm{D-I}}$, i.e. the isotropic–droplet state phase transition is apparently shifted to higher temperatures. At low applied voltages ($U < U_c$), this induced order is presented in Fig. 3 and Fig. 4 as

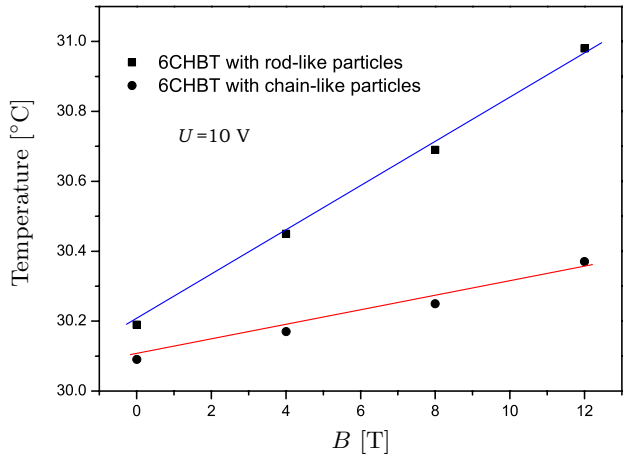

Fig. 5. Magnetic field dependence of the temperature of the structural transition from the isotropic phase to the droplet state at the constatnt voltage (10 V) of 6CHBT dissolved in phenyl isothiocyanate and doped with rod-like and chain-like particles, respectively. The lines represent the best linear field.

the capacitance decreasing with the decreasing temperature. The higher magnetic field, the higher the temperature at which the induced order appears. Once the induced order is established at a given temperature at high enough applied voltages ($U > U_c$), the electric field can re-orient the director (a Freedericksz transition can occur) just as in the regular nematic phase below $T_{\mathrm{N-I}}$. This is illustrated in Fig. 3 and Fig. 4 as an increasing capacitance, as the temperature decreases. As the electric field does not exert a direct torque on the magnetic moment of the nanoparticles, at $B > 0$ one expects that $\mathbf{m}$ is hold firmly by a strong external magnetic field. Therefore, at high voltages, the mutual orientation of the magnetic moment of the magnetic particles and the director of the bulk director of the liquid crystal changes. With $B > 0$ and $U >> U_c$, the liquid crystal molecules are still oriented along the external magnetic field near the surface of the magnetic particle of the nematic droplets, but the rest of the molecules change their orientation to parallel to E. Moreover, it is seen from Fig. 3 and Fig. 4 that the temperature dependence of the capacitance becomes weaker (the slope of the curves in Fig. 3 and in Fig. 4) in stronger magnetic fields. This suggests that the temperature interval, in which the isotropic-to-nematic phase transition occurs via the droplet state (i.e. the width of the two-phase region), increases as the external magnetic field increases.

Fig. 5 shows the magnetic field dependence of the temperature of the structural transition from the isotropic phase to the droplet state at the constatnt voltage (10 V) for the 6CHBT dissolved in phenyl isothiocyanate and doped with rod-like and chain-like particles. The temperature shift is higher in the case of doping with rod-like particles. For both samples, the dependence of the temperature of the isotropic–droplet state phase transition on the external magnetic field is linear.

Conclusion. Embedding the magnetic particles in the nematic liquid crystal causes an effective orientational coupling between the magnetic moment of the magnetic particle and the director of the nematic one. This coupling may come from the anisotropy of anchoring of the nematic molecules on the particle surface. The obtained results suggest that in the case of ferronematics based on the 6CHBT liquid crystal dissolved in phenyl isocyanate, the temperature of

the phase transition increases due to doping with magnetic particles due to the field-induced nematic order. The observed dependence of the temperature of the isotropic–droplet state phase transition on the external magnetic field is linear.

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