7th International pamir Conference on

Fundamental and Applied MHD

Presqu'Île de Giens, France - 2008
Volume 2

pamir

Proceedings of the

7th International pamir Conference

Fundamental and Applied MHD

And

COST P17 Annual Workshop 2008

Presqu'Île de Giens, France
September 8-12, 2008

pamir

cost

Chairman :	A. Alemany	SIMAP/EPM/pamir, France
Co-chaimen:	J.P. Chopart	DTI, Univ. de Reims, France
	J. Freibergs	IPUL, Latvia
Secretary:	B. Collovati	Grenoble INP, France

SIMaP

Dynamique des Transferts aux Interfaces

University of Latvia
Institute of Physics

Grenoble INP

THE ROLE OF SHAPE OF FINE MAGNETIC PARTICLES ON STRUCTURAL TRANSITIONS IN FERRONEMATICS

KOPCANSKY P., TOMASOVICOVA N., KONERACKA M., ZAVISOVA V., TIMKO M., DZAROVA A., SPRINCOVA A.
Institute of Experimental Physics, SAS, Watsonova 47, 040 01 Kosice, Slovakia
e-mail: kopcan@saske.sk
TOMCO L.
Faculty of Aeronautics, Technical University, Rampova 7, 041 21 Kosice, Slovakia
EBER N., FODOR-CSORBA K., TOTH-KATONA T., VAJDA A.
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1525 Budapest, Hungary
JADZYN J.
Institute of Molecular Physics, Polish Academy of Sciences, Smoluchovskiego 17, 60179 Poznan, Poland

Abstract: The 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene liquid crystal was doped by differently shaped magnetite nanoparticles. The critical magnetic field was established for pure liquid crystal for liquid crystal doped with spherical, chain-like and rod-like magnetic particles (volume concentration $\Phi = 2\times10^{-4}$). The experimental results indicated soft anchoring in the case of spherical magnetic particles and rigid anchoring in the case of rod-like and chain-like magnetic particles, with parallel initial orientation between the magnetic moment of the magnetic particles and director.

1. Introduction

Liquid crystals can be orientated under magnetic or electric fields due to their anisotropic properties but the response of liquid crystals to an external magnetic field is weak due to small value of the anisotropy of diamagnetic susceptibility. Brochard and de Genes [1] proposed doping liquid crystals with fine magnetic particles to increase this sensitivity, i.e. they created so called ferronematics. Ferronematics are stable colloidal suspensions of fine magnetic particles in nematic liquid crystals. They attract considerable interest of investigation because their response to the external magnetic field exceeds sufficiently that of pure nematics. The most essential feature of these systems is an orientational coupling between the magnetic particles and the liquid crystal matrix. The influence of the magnetic field depends on the type of anchoring that is characterized by value of density of anchoring energy and initial orientation between liquid crystals molecules (characterized by unit vector $\boldsymbol{n}$ - director) and magnetic moment of magnetic particles ($\boldsymbol{m}$). The aim of this study was to change the shape of magnetic particles dissolved in the liquid crystal and studied their influence on the properties of obtained ferronematic samples.

2. Experimental

The synthesis of the spherical magnetic nanoparticles was based on co-precipitation of Fe^{2+} and Fe^{3+} salts in NH_4OH at 60°C. Magnetite nano-rods were synthesized through hydrolysis of $FeCl_3$ and $FeSO_4$ solutions containing urea. The chain-like particles have been obtained from the magnetotactic bacteria *Magnetotacticum Magnetospirillum* (AMB-1). For the cultivation of AMB-1 a medium consisting of Wolfe's vitamin solution, Wolfe's mineral solution, KH_2PO_4, sodium succinate hexahydrate, sodium tartrate dihydrate, sodium acetate trihydrate, resazurin (aqueous), $NaNO_3$, ascorbic acid, ferric quinate was used. Isolation of magnetosomes: *Magnetotacticum Magnetospirillum* cells suspended in 4-(2-hydroxyethyl)piperazine-1-etha (HEPES) and chelaton 2 (EDTA), pH 7.4, were disrupted by sonification. The unbroken cells and the cell debris were removed from the sample by centrifugation. The cell extract was placed on the NdFeB magnets for 1 hr. The black magnetosomes sedimented at the bottom of the tube and the residual contaminating cellular material was retained in upper part of the tube. The residual contaminating cellular material was decantated. The magnetosome suspension (the black sedimentation) was centrifugated. After centrifugation the cell extract was placed on the magnet for 30 minutes. The magnetic particles were sedimentated at the bottom of the tube, whereas residual contaminating cellular material was retained in upper part of the tube. The last procedure was repeated 10-times to obtain well purified chains of magnetosomes.

The magnetic properties of prepared Fe_3O_4 nanoparticles were estimated by magnetization measurements using a vibrating sample magnetometer (VSM) and the size and morphology of the particles were determined by transmission electron microscopy (TEM). The TEM images of spherical, rod-like and chain-like particles are shown in the Figure 1. The mean diameter of obtained spherical magnetic nanoparticles was 11.6 nm, the average diameter of rod-like particles was 25 nm and the mean length determined from the histogram of size distribution was 1200 nm. In the case of chain-like magnetic particles the mean size of a single magnetic particle coated with surfactant, i.e. the magnetosome was 34 nm, so the mean length of the chain-like particle as a whole was 446 nm.

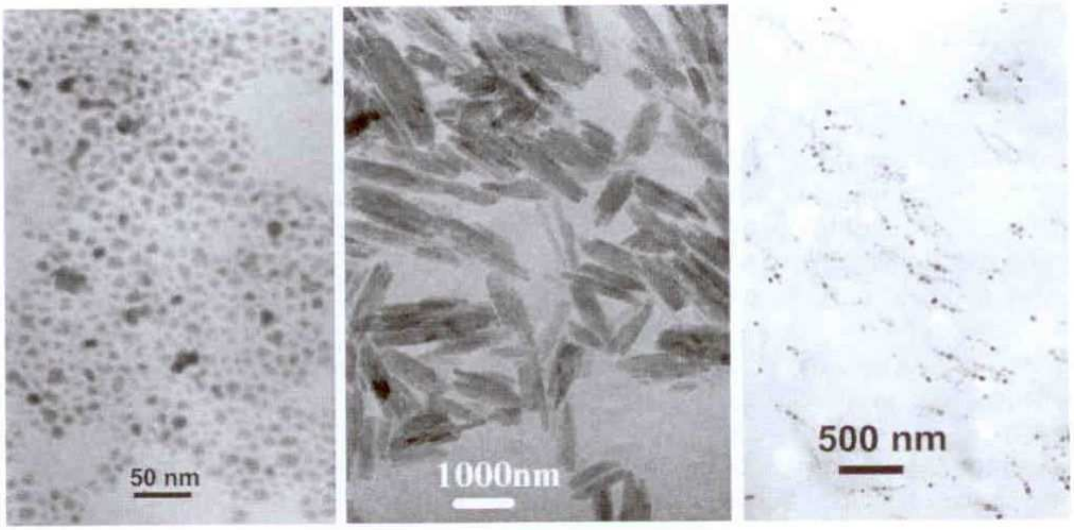

Figure 2. TEM image of spherical (left picture), rod-like (central picture) and chain-like (right picture) magnetic particles.

The studied ferronematic samples were based on the thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). The 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [2]. The nematic samples were doped with a magnetic suspension consisting of Fe_3O_4 particles coated with oleic acid as a surfactant in the case of spherical and rod-like particles. 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 $2x10^{-4}$ and surfactant in the prepared ferronematic samples the interparticle dipole-dipole interactions are avoided. The calorimetric scans were performed by using a DSC instrument Mettler FP80HT at a scan rate 4°C min^{-1} in the temperature range from 20°C up to 90°C. No influence of the admixture of magnetic particles on the temperature of the nematic-to-isotropic transition have been observed. The structural transitions in ferronematic samples were indicated by capacitance measurements in a capacitor made of ITO-coated glass electrodes (LINCAM Co.). The capacitor with the electrode area approximately 1cmx1cm 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 $D = 5\mu m$. The capacitance was measured at the frequency of 1 kHz by the 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.

Freedericksz transition in combined electric and magnetic fields were studied in the assumed experimental geometry shown in Fig. 1. at temperature 35°C. Our previous measurements on 6CHBT-based ferronematics (doped with spherical particles) showed the soft anchoring of nematic molecules on the surface magnetic nanoparticles and the boundary condition between ***m*** and ***n*** was found to be parallel [3]. In the experiments an initial alignment of the magnetic moments was achieved by applying a strong magnetic field temporarily before starting the measurement. Then the external magnetic field was switched off and the initially planar nematic layer was realigned by a strong electric field applying a bias voltage $U_B > U_F$ at $B = 0$, where U_F is critical voltage of electric Freedericksz transition. Then the magnetic field was applied perpendicular to $\boldsymbol{E}$, along the initial surface aligment. The magnetic field increased the electric Freedericksz threshold $U_c(B)$, reducing therefore the distortion angle in the cell. At a critical magnetic field B_c, where $U_c(B_c) = U_B$, the distortion of the director disappeared and the initial planar texture was restored.

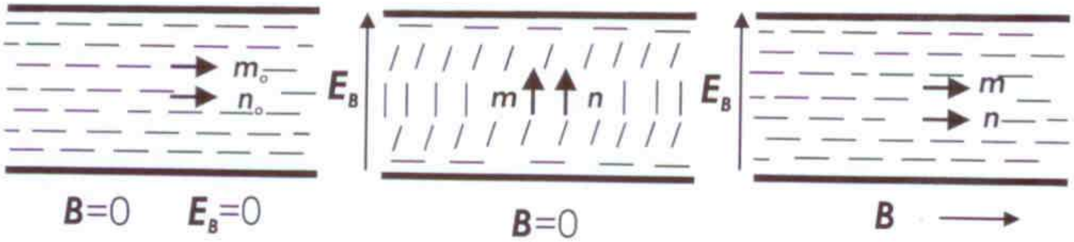

Figure 2. Cross section of the cell in the initial state, after application of the electric field $E_B > E_C$ and after application of the external magnetic field $B > B_C$.

3. Results and disscussion

The observations of the structural transitions in ferronematics in external field can be used for determination of the type of anchoring of nematic molecules on magnetic particle surfaces as well as the surface density of the anchoring energy W at the nematic - magnetic particle boundary. During measurements the bias electric field was applied perpendicular to the capacitor electrodes and the external magnetic field was applied perpendicular to the bias electric field. The dependence of the measured capacitance on the external magnetic field reflects the re-orientation of the nematic molecules in the strong magnetic field. The obtained values of the critical magnetic fields for different values of bias voltage are summarized in

Figure 2, that shows dependence of critical magnetic field on the applied bias voltage for pure 6CHBT and 6CHBT doped with spherical, chain-like and rod-like magnetic particles. The surface density of anchoring energy W at the nematic - magnetic particle boundary for different magnetic particles was determined from the measurements of the critical magnetic fields for pure 6CHBT and for 6CHBT doped with different shaped magnetic particles at the temperature $T = 35°\mathrm{C}$.

The Burylov and Raikher's teory was used to evaluate the obtained result [4]. This theory considers the finite value of the surface density of anchoring energy W at the nematic - magnetic particle boundary. The finite value of W, as well as the parameter ω that is defined as a ratio of anchoring energy to elastic energy of liquid crystal $\omega = Wd/K$, where d is size of the magnetic particles and K is orientational-elastic Frank modulus), characterize the type of anchoring of nematic molecules on magnetic particle surface. The parameter $\omega >> 1$ characterizes the rigid anchoring. The soft anchoring is characterized by parameter $\omega \leq 1$ and unlike the rigid anchoring, permits both types of boundary conditions $\boldsymbol{m}$ parallel $\boldsymbol{n}$ and $\boldsymbol{m}$ perpendicular $\boldsymbol{n}$. Thus the Burylov and Raikher's theory could be applied for thermotropic ferronematics. In its frame the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric field (Fredericksz transitions) could be studied. The calculated values of surface density of anchoring energy and parameter ω are summarized in the table 1.

These results show that the shape and size of the magnetic particle play an important role in ferronematics and significantly influence the structural transitions in these materials.

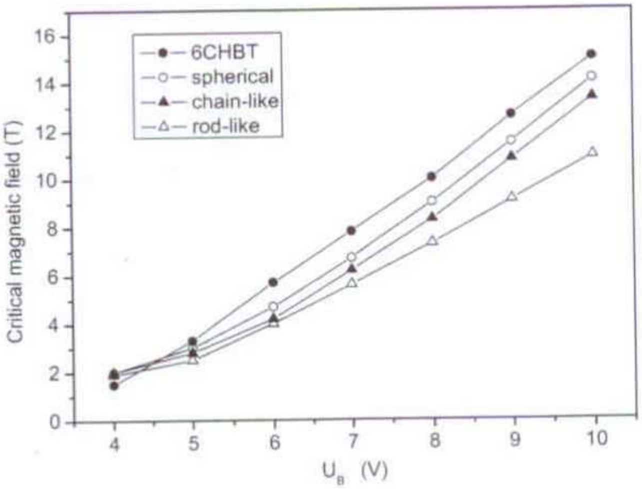

Figure 3. Dependence of critical magnetic field on the bias voltage for pure 6CHBT and 6CHBT doped with spherical, chain-like and rod-like particles.

Doping with magnetic particles reduced the critical magnetic field. Changing the shape of the particles from spherical to chain-like the reduction increased. The largest decrease of B_C was obtained for rod-like particles. From these results it can be seen that the shape and the size of the magnetic particles significantly influence the strength of anchoring of the nematic molecules on the surface of magnetic particles and the behaviour of ferronematics in the external magnetic field. The experimental results indicated soft anchoring in the case of spherical magnetic particles and rigid anchoring in the case of rod-like and chain-like magnetic particles, with parallel initial orientation between the magnetic moment of the magnetic particles and director.

	W (Nm^{-1})	ω
spherical	$\sim 10^{-5}$	$\sim 10^{-1}$
chain-like	$\sim 10^{-3}$	$\sim 10^{2}$
rod-like	$\sim 10^{-2}$	$\sim 10^{4}$

Table 1. Calculated values of the density of anchoring energy W and parameter ω for spherical, chain-like and rod-like particles.

It can be concluded that doping with magnetic particles shaped similarly to the liquid crystal molecules, gives better exploration of ferronematics in the applications where the magnetic field is necessary to control the orientation of the liquid crystal molecules.

Acknowledgments

We thank Ivo Vavra for assistance with TEM analysis.
This work was supported by the Slovak Academy of Sciences (grant No. 6166), Slovak Research and Development Agency under the contract APVV-SK-MAD-026-06, APVV-0509-07 and APVV-99-026505, the Grenoble High Magnetic Field Laboratory, with support of EC Program RITA-CT-2003-505474, by Hungarian Research Funds OTKA K61075, NKTH/KPI SK-19/2006 and the Slovak-Hungarian bilateral exchange.

4. References

[1] Brochard F., de Genes P.G.: J. Phys. (Paris) 31 (1970) 691
[2] Dabrowski R., Dziaduszek J., Szczucinski T.: Mol.Cryst.Liq.Cryst.Lett. 102 (1984) 155
[3] Kopcansky P., Koneracka M., Timko M., Potocova I, Tomco L, Tomasovicova N, Zavisova V, Jadzyn J.: J.Magn.Magn.Mater. 300 (2006) 75
[4] Burylov S.V., Raikher Y.L.: J.Magn.Magn.Mater. 122 (1993) 62