PREPARATION AND PROPERTIES OF A FERROMAGNETIC NEMATIC SUSPENSION

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A stable ferromagnetic suspension based on a nematic liquid crystal (LC) doped with nano-particles of ferric oxide is obtained for the first time. In the outward appearance, the suspension does not differ from a pure LC. Using AFM spectroscopy, the size of nano-particles is determined, and their concentration in the matrix is estimated. The basic characteristics of the suspension such as the phase transition temperature (nematic-isotrope), LC director pretilt angle on the orienting surface, and azimuthal anchoring energy are determined. A high sensitivity of the suspension to a magnetic field makes it promising for applications in the devices for information storage and display.

Introduction

Composite liquid crystals (LCs) attract a great attention due to their unique electro- and magneto-optical properties. Typical composite LC systems are aerosil suspensions, suspensions of ferroelectric nano-particles in a nematic matrix, and nematic suspensions of magnetic particles [1—8]. In the 1970s, ferromagnetic liquid crystal suspensions were suggested by Brochard and de Gennes for increasing the LC sensitivity to magnetic fields [4]. In 1983, Chen and Amer produced the first ferromagnetic suspension based on ferro-particles of ferric oxide in a LC matrix MBBA. It was demonstrated that this system was sensitive even to the magnetic field of the Earth [5]. Unfortunately, the strong aggregation of ferro-particles in magnetic fields $H > 10$ G was an essential drawback of this system.

The problem of ferro-nematic LC suspension instability was partially solved for lyotropic LCs only in the 1990s [9]. A stable ferromagnetic suspension based on thermotropic nematics never was developed. The aim of our work was producing and investigating a stable optically homogeneous ferromagnetic suspension based on nematic LC. Unlike other works, where a high volume concentration ($f \approx 10^{-2} \div 10^{-3}$) of micro-particles [4] or a small volume concentration ($f < 10^{-4}$) of submicron (≈ 0.5 μm) particles [5—6] was applied, we used the low-concentrated ($f < 10^{-5}$) dispersion of nano-particles in a liquid crystal matrix. The use of low-concentrated nano-scale particles allowed strongly decreasing the orientational elastic interaction and the magnetic dipole-dipole interaction between particles that led to the particles' aggregation. Due to a small size of nano-particles, they do not disturb the director field, and such a system looks like pure LC. At the same time, the doping of nano-scale particles results in the enhancement of the LC sensitivity to magnetic fields.

1. Materials and Experiment

The ferro-nematic suspension consisted of the dispersion of ferromagnetic particles Fe_3O_4 covered with a surfactant in liquid crystal 5CB (Merk). Ferromagnetic material Fe_3O_4 is an oxide of ferrous iron and ferric iron that forms crystals with the spinel structure. Under normal conditions, the Fe_3O_4 magnetization is 450—500 G, and the magnetic moment $\mu \approx 4.1\ \mu_B$. 5CB is a classic nematic LC, whose phase transition temperature to the isotropic phase $T_c = 36.6$ °C. 5CB possesses small diamagnetic anisotropy $\Delta\chi = 10^{-7}$ esu. As a surfactant, we used oxyethyl-propylene glycol which consists of polymer chains (a molecular weight of 1000—3000) with central hydrophilic fragments and side hydrophobic fragments.

Ferric oxide particles having size ≈ 1 μm were mechanically milled with the surfactant in ratio 1:2. The milling time was hundreds of hours, at least 120 h. During the milling, the particles were covered with a thin layer of the surfactant that decreased their coagulation. To separate the particles by size, the mixture was placed after the milling in a segregation column. After keeping in the column during 3 days, the upper part of the mixture was taken out for the suspension preparation and added to LC at T=50 °C $> T_c$. Then the suspension was additionally segregated in a centrifuge with a rotation speed of 1500 rpm. The final suspension did not differ from pure LC by site.

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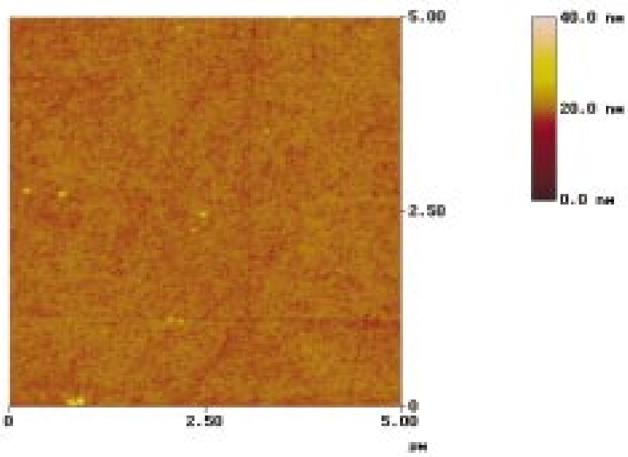

Fig. 1. Substrate surface with deposited particles in AFM

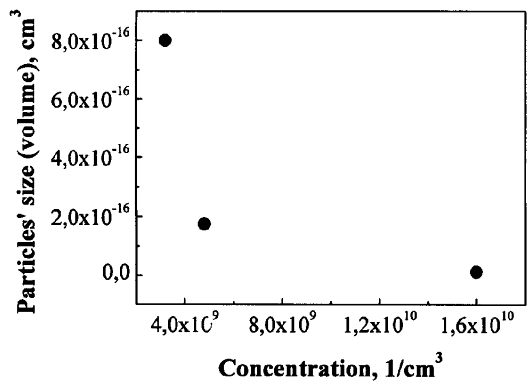

Fig. 2. Dependence of particles' size on the concentration of particles in the LC matrix

To estimate the size and concentration of particles, we used AFM microscopy. The studied cell consisted of two glass substrates with deposited polymer layers of 4F-PVCN. A drop of the suspension being in the isotropic phase was placed on one of the substrates and squeezed with the other one. The cells' thickness was set with calibrated cylindrical polymer spacers of 50 μm. After that, the cell was put onto a magnet pole for 60 min at $T > T_c$. The magnetic field attracted the particles from the LC bulk, and particles were deposited onto the 4F-PVCN-surface. After that, the cell was dismantled, and LC was washed with ethyl alcohol. Then substrate was dried at 50 °C during 2 h, and the 4F-PVCN-surface with ferro-particles was investigated with AFM. The image of the 4F-PVCN-surface with deposited particles is presented on Fig. 1. Nano-particles have almost elliptical form with a typical size of $10 \times 15 \times 50$ nm. The average distance between particles was about 1 μm. The distribution of particles over their size is shown in Fig. 2.

The experimental data point to the distance between particles being rather big, so the particles interaction can be neglected, and their orientation in the LC matrix occurs due to the LC elastic energy action, surface energy of the interaction between particles and LC, and dipole-dipole interaction. [10—11]. Owing to the shape anisotropy and surface anchoring with LC, the long axes of ferro-particles oriented in parallel to the LC director.

We found that the produced ferro-nematic suspension remained stable during at least six months. We also found that the system kept homogeneous after heating it to the isotropic phase and the following cooling to room temperature.

We measured basic mesogenic properties of the suspension. The investigation with a polarizing microscope showed that the phase transition temperature to the isotropic state $T_c = 35.4$ °C was slightly shifted from the value $T_c = 36.6$ °C of pure LC. We measured the pretilt angle in the suspension and pure LC with crystal rotation methods [12] and found that pure LC and the suspension had practically the same pretilt angle $\theta = (2.4 \pm 0.2)°$. The azimuthal anchoring energies of the suspension and pure LC were estimated with the twist angle measurement method in a twist-cell [13]. It was found that the anchoring energy of suspension was more than two orders weaker than that of pure LC. This amazing result needs further detailed investigations. The table shows the basic characteristics of pure LC and ferromagnetic nematic suspension.

It was ascertained that the magnetic nano-suspension had unique sensitivity to magnetic fields. To investigate this characteristic, we used a combined cell, which consisted of two glass substrates covered with a thin polymer layer: the reference surface was coated with rubbed polyimide that provided a strong anchoring energy for LC, and the command surface was covered with 4F-PVCN that gave a weak anchoring energy [13]. A drop of the suspension being in the isotropic phase was placed onto one of the substrates and pressed with the other one. Calibrated polymer spacers of 50 μm controlled the sample's thickness. As a result, due to the strong interaction energy on the reference surface,

Basic characteristics of pure LC and the ferromagnetic nematic suspension

Characeristic	Pure LC	Suspension
Phase transition temperature, °C	36.6	35.4
Director pretilt angle, degree	2.3±0.2	2.5± 0.2
Azimuthal anchoring energy, erg/cm^2	3.6×10^{-4}	1×10^{-5}
Cell's stability time, months	∞	6

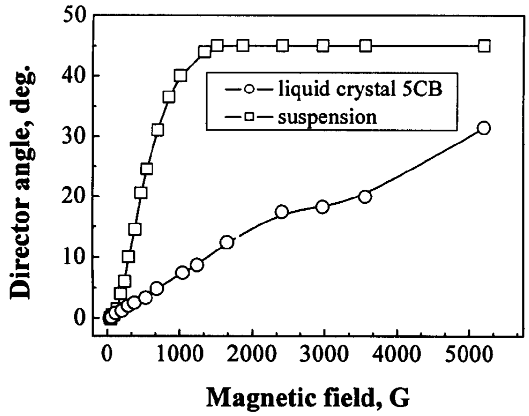

Fig. 3. Dependence of the LC director reorientation on the command-surface in a magnetic field

we got a homogeneous planar orientation in a cell. The cell was placed between two magnet poles in the way that the magnet field made an angle of 45° with the director of the suspension. The polarization of the probe beam from a He-Ne laser was parallel to the director direction on the command surface. The action of the magnetic field resulted in the reorientation of the director in the cell, mainly over the command surface. It led to the rotation of the polarization of the probe beam after passing the cell. The dependence of the director reorientation on the command surface on the magnetic field is presented in Fig. 3 both for the ferromagnetic nano-suspension and pure LC. One can see that the director reorientation in the ferro-nematic suspension occurred at the magnetic fields of tens of Gausses that was lower by one order in comparison with that for pure LC.

Conclusions

For the first time, a stable ferromagnetic nematic suspension was prepared. The suspension consists of nano-size particles of Fe_3O_4 covered with a surfactant in liquid crystal 5CB. The suspension does not differ from the pure liquid crystal by sight, has unique sensitivity to magnetic fields, and possesses the ultra weak anchoring energy with the aligning layer 4F-PVCN. The obtained results gave a possibility to consider the ferro-suspension as a highly perspective system for many different applications.

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ПРИГОТУВАННЯ ТА ВЛАСТИВОСТІ ФЕРОМАГНІТНОЇ НЕМАТИЧНОЇ СУСПЕНЗІЇ

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Р е з ю м е

Вперше отримано стабільну феромагнітну суспензію на основі нематичного рідкого кристала (РК) легованого наночастинками оксиду заліза. Суспензія зовнішньо не відрізняється від чистого РК та має унікальну чутливість до магнітного поля, яка на порядок вища ніж у чистого РК. За допомогою AFM-спектроскопії визначено розміри наночастинок та оцінено їх концентрацію в матриці. Визначено основні характеристики суспензії: температуру фазового переходу нематик—ізотропна рідина, кут переднахилу директора РК на орієнтуючій поверхні, азимутальну енергію зчеплення РК. Висока чутливість суспензії до магнітного поля робить її багатообіцяючою для застосування у пристроях збереження та відображення інформації.

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