Orientational Order-Magnetization Coupling in Mixtures of Magnetic Nanoparticles and the Ferroelectric Liquid Crystal

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We have studied the ferroelectric SmC* phase of SCE9 ferroelectric liquid crystal (LC) mixtures with magnetic nanoparticles (NPs). The impact of the NPs on the Goldstone and soft mode dielectric response has been determined by the dielectric spectroscopy measurements. The possible indirect coupling between the magnetic moments and the electrical polarization has been verified by measuring the impact of the electrical field on the magnetic susceptibility via SQUID susceptibility measurements. The disordering effects on the ferroelectric phase transition have been studied by the high resolution calorimetry. Similar disordering effects have been found as in the case of the aerosil particles [1, 2].

Keywords Liquid crystal; nanoparticles; mixtures; structural ordering; magnetoelectric

Introduction

Magnetic NPs are of great interest for researchers. In recent years they have tried to produce new NPs exhibiting extraordinary properties. In addition it is known that mixtures of NPs and other conventional materials could exhibit special behaviours not found in either of the individual components [3]. Not long ago it has been shown experimentally [4–6] that the spontaneous onset of LC ordering could be a way to obtain very well aligned NPs [7]. Liquid crystals (LCs) exhibit a long-range orientational order and they extremely response to various perturbations e.g., from external electric or magnetic fields. LCs consist of anisotropic molecules that become ordered, over a given temperature interval in case of thermotropic LC or for appropriate concentrations of LC molecules in case of lyotropic LCs. We will focus on thermotropic LCs formed by rod-like molecules. As we mentioned above, thermotropic LCs exhibit a variety of phases with changing temperature. At high enough temperatures LCs exists in the isotropic liquid phase. By decreasing the temperature \( T \) the sequence of LC phases is as follows. At \( T = T_{IN} \), the nematic phase is found in which
molecules tend to be aligned along a director \( \vec{n} \). Further at \( T = T_{NA} < T_{IN} \), a smectic A (SmA) phase is established, where molecules are arranged in equidistant and parallel layers. The average orientation of the molecules is along the normal \( \vec{\nu} \) of layer. At \( T = T_{AC} < T_{NA} \), a smectic C phase is reached. Here molecules are become tilted with respect to \( \vec{\nu} \). In the case of chiral molecules the structural ordering exhibits a helical structure and for symmetry reasons the electrical polarization appears. This ferroelectric phase is denoted as SmC*.

We experimentally analyse mixture of weakly anisotropic ferromagnetic NPs and ferroelectric liquid crystal (LC) across the SmA-SmC* phase transition. Such mixture could potencially form new magnetoelectric materials. Magnetoelectrics are very interesting for application in memories because they show simultaneously ferromagnetic and ferroelectric properties. In such materials it would be possible to control the magnetic properties via electrical ones, and vice versa.

**Experiments and Discussion**

The mixtures of a ferroelectric LC and ferromagnetic NPs have been investigated. Measurements were performed on a SCE9 ferroelectric LC mixed with weakly anisotropic NPs. A SCE9 LC [8] contains the ferroelectric SmC* phase and the phase sequences with decreasing temperature from the isotropic phase (I) are as follows: I-N at \( T_{IN} \approx 392 \text{K} \), N-SmA at \( T_{NA} \approx 360 \text{K} \), and SmA-SmC* at \( T_{AC} \approx 334 \text{K} \). For the magnetic NPs we used maghemite (\( \gamma - \text{Fe}_2\text{O}_3 \)) particles of 20 nm diameter that were covered with oleic acid and dispersed in toluene. A transmission electron microscopy (TEM) image of these NPs is shown on Fig. 1 and the preparation of them was as follows. Oleic acid coated, hydrophobic particles were synthesized by coprecipitation of Fe(II) and Fe(III) cations by ammonia. The synthesized nanoparticles were, on average, 11nm in size. In order to promote NPs growth, synthesized suspensions of NPs were treated hydrothermally at 200°C for 3 hours. The hydrophobic nanoparticles were precipitated by adding HNO3. The particles were soaked in oleic acid and the excess oleic acid was removed by washing the NPs with acetone. At the end the

![Figure 1. TEM image of maghemite magnetic nanoparticles covered with the oleic acid dispersed in toluene.](image-url)
NPs were dispersed in toluene. SQUID susceptometry on NPs shows that the blocking temperature is well above 400 K. This means that NPs act as permanent magnets in the temperature range of interest. Concentrations of LC + NPs mixtures were $x = 0.10$ and 0.14, where $x = m_{\text{NP}}/(m_{\text{NP}} + m_{\text{LC}})$, and $m_{\text{NP}}$ and $m_{\text{LC}}$ are denotations of the masses of the NPs and the LC in the samples. The LC-NP mixtures were prepared by dissolving the LC in toluene and adding the magnetic NPs also dispersed in toluene. Such solutions were mixed for approximately 2 hours at 393 K to achieve relatively homogeneous dispersions, and to allow all the solvent to evaporate. Then the samples were, in case of dielectric experiments, kept between two glass plates covered with ITO electrodes. The cell thickness was $120\mu\text{m}$. In case of the magnetic susceptibility measurements, samples were inserted into thin glass tubes. For a calorimetry study a sample was placed in silver cell thermally linked to a temperature stabilized bath through supportive wires and air. Details about calorimetry method are described elsewhere [9–11]. Frequency dependent dielectric constant of SCE9 samples

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**Figure 2.** Temperature dependence of the real $\varepsilon'$ (a) and imaginary part $\varepsilon''$ (b) of the dielectric constant on SCE9 liquid crystal compound mixed with magnetic nanoparticles. A constant background value $\varepsilon_{\infty}$ was subtracted from $\varepsilon'$ data.
Figure 3. Excess magnetization $\Delta m = m - m_L$ (solid squares) and excess heat capacity $\Delta C_p$ (open circles) of SCE9 liquid crystal compound mixed with maghemite nanoparticles of 20 nm with $x = 0.14$. Here $m_L$ represents the linear temperature dependence of magnetization in SmA phase extrapolated to low temperatures. The SmA-SmC* transition temperature $T_{AC} = 330$ K.

was measured between 400 Hz and 300 kHz by using a HP4284A Precision LCR meter in temperature range from 360 to 300 K. Cooling rate was 400 mK/h and an excitation voltage of 1 V was used. The dielectric spectroscopy results are presented in Fig. 2. It is shown that the both soft mode and Goldstone mode anomalies are similary suppressed and smeared as in the case of aerosils mixtures [12]. The magnetic properties of these mixtures were measured with a commercial SQUID-based magnetometer with a 5 T magnet (Quantum Design MPMS XL-5). The measurements were performed in the temperature interval were bulk LC SCE9 has SmA-SmC* phase transition. The samples were first heated to about 320 K in a zero magnetic field. Then an external magnetic field $H = 100$ Oe was applied and the temperature dependence of the sample’s magnetization was measured from 320 K to 400 K with a heating rate 0.15 K/min. The anomaly in the excess magnetization $\Delta m$ (solid squares) observed at the SmA to SmC* phase transition shows the coupling between the LC director field and the magnetization of NPs (see Fig. 3). Heat capacity data (open circles) are also shown in Fig. 3. Calorimetry measurement has been made in temperature range from 325 K to 337 K. Scan rate was 300mK/h. Excess heat capacity data ($\Delta C_p$) demonstrates that $\Delta m$ anomaly appears below SmA-SmC* transition temperature at $\approx 330$ K. The anomaly in $\Delta m$ bellow $T_{AC}$ can be a consequence of the coupling between the magnetic moments and LC director field. It should be noted that the temperature dependence of $\Delta m$ is proportional to the director tilt temperature dependence. Therefore, our measurements confirm the finite coupling between weakly anisotropic magnetic NPs and LC.

Conclusions

To conclude, a dielectric spectroscopy, magnetic susceptibility, and high resolution calorimetry have been carried out in the vicinity of the ferroelectric smectic C* phase of SCE9 ferroelectric liquid crystal mixtures with magnetic nanoparticles of average 20 nm.

The dielectric experiments show that the magnetic and ferroelectric nanoparticles have similar disordering effects in the vicinity of ferroelectric phase transition on soft and Goldstone mode as aerosils. The anomalies of both modes are strongly suppressed and
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smeared. The magnetic susceptibility and heat capacity measurements show that besides the disordered effect of magnetic nanoparticles on the director field the orientation of magnetic nanoparticles is directly coupled to the liquid crystal molecular director field. Such coupling between the direction of liquid crystal molecules and the direction of magnetic nanoparticles allows possibility of indirect coupling between the magnetic and ferroelectric order, thus making these mixtures candidates for soft indirect magnetoelectrics.

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References