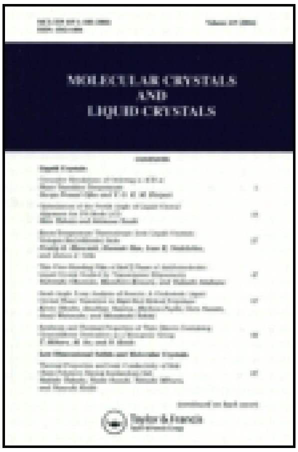

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Multiferroic Behaviour in Mixtures of the Ferroelectric Liquid Crystal and Magnetic Nanoparticles

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Multiferroic Behaviour in Mixtures of the Ferroelectric Liquid Crystal and Magnetic Nanoparticles

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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 (LC) mixtures with magnetic nanoparticles (NPs) to determine the impact of the magnetic nanoparticles on the Goldstone and soft mode and to study the disordering effects on the ferroelectric phase transition. It was verified via SQUID susceptometer that the indirect coupling between the NPs magnetic moments and the LC electrical polarization exists in these mixtures.*

Keywords Liquid crystal; magnetoelectrics; mixtures; nanoparticles

1. Introduction

Magnetoelectric materials are important subgroup of multiferroics and they become recently very attractive topic for research due to their potential in electronics applications. Because in such material it would be possible to control the magnetic properties via electrical ones, and vice versa. It is well known that the single-composite or a single-phase magnetoelectrics, in which the electric and magnetic properties are directly coupled, are rare [1–2]. For this reason the focus has been shifted to the composites, i.e., two phase-composite magnetoelectrics. Here the coupling between the magnetic and electric properties is indirect, but can be much stronger than that in single-phase magnetoelectric. In our case an interest is related to the magnetoelectric states in mixtures of a ferroelectric liquid crystal (LC) and ferromagnetic nanoparticles (NPs). It is known that mixtures of nanoparticles (NPs) and other conventional materials could exhibit special behaviour not found in either of the individual

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components [3]. LCs are soft materials that respond to different external perturbations, i.e., external magnetic or electric field. And also it has been shown [4–6] that the spontaneous onset of liquid crystal ordering could be a way to obtain very well aligned NPs [7]. Our interest is in ferroelectric liquid crystals exhibiting a smectic C^* phase (SmC^*), where the structural ordering of molecules display a helical structure and the electrical polarization appears.

Our experiments are made on mixtures of ferroelectric liquid crystal (LC) and weakly anisotropic ferromagnetic nanoparticles (NPs) in the vicinity of the ferroelectric smectic C^* phase. We will demonstrate potential of such mixtures to form new soft magnetoelectric materials.

2. Experimental Methods

We experimentally investigated the mixtures of a SCE9 LC and maghemite ($\gamma - Fe_2O_3$) nanoparticles. The SCE9 liquid crystal exhibits a broad SmC^* phase near the room temperature and it has a large value of spontaneous polarization [8]. The sequence of all phases in SCE9 with decreasing temperature from the isotropic phase is as follows: isotropic (I), nematic (N), smectic A (SmA) and smectic C^* (SmC^*) and the phase transitions take places at $T_{IN} \approx 392K$, $T_{NA} \approx 360K$ and $T_{AC^*} \approx 334K$. As already mentioned, for the magnetic NPs the maghemite ($\gamma - Fe_2O_3$) nanoparticles (Fig. 1) were used. The typical diameter of NPs was around 20 nm. Maghemite NPs were covered with oleic acid in order to form a stable suspension in toluene. Preparation of magnetic NPs was made in following steps. Hydrophobic particles covered with oleic acid were synthesized by coprecipitation of Fe(II) and Fe(III) cations by ammonia. Next, synthesized suspension of NPs was treated hydrothermally at 200°C for cca. 3 hours to promote NPs growth from, on average, 11 nm

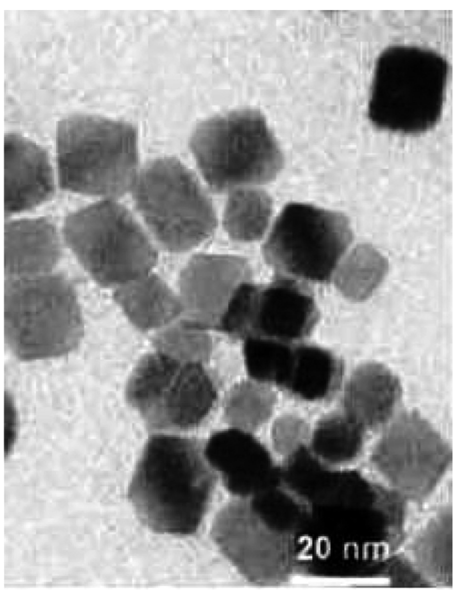

Figure 1. TEM image of maghemite ($\gamma - Fe_2O_3$) magnetic nanoparticles covered with oleic acid and dispersed in toluene.

to 20 nm in size. The hydrophobic nanoparticles were precipitated by adding HNO_3. The particles were soaked in oleic acid and the excess acid was removed by washing NPs with acetone. At the end the NPs were dispersed in toluene.

Before LC-NPs mixture preparation the SQUID susceptometry measurements were made to check the quality of NPs. It was found that the blocking temperature of NPs is well above 400 K, i.e., in temperature range of interest. We prepared mixtures of concentration $x = 0.10$ and $x = 0.14$, where $x = m_{NP}/(m_{NP} + m_{LC})$. Here m_{NP} is mass of NPs and m_{LC} is mass of SCE9. The preparation procedure of LC&NPs mixtures was as follows. The LC was dissolved in toluene together with the magnetic NPs. Then a solution was mixed at around 393 K to allow all the solvent to evaporate and to achieve homogeneous dispersion which was stable for at least several months. Stability of the mixture was checked by X-rays scattering (SAXS) at synchrotron Trieste. X-rays data (Fig. 2) obtained on a more than six months old mixture show rather narrow size distribution of particles centred around 17.7 nm and with standard deviation less than 6 nm. This results are in good agreement with the particle size distribution obtained from the transmission electron microscopy (TEM). This demonstrates that the mixture remains stable, practically aggregates free and very uniform even after six months time. After preparation of mixtures, a dielectric spectroscopy, magnetic susceptibility, and high-resolution calorimetry measurements have been done. In case of dielectric measurements, a cell of two glass plates covered with ITO electrodes was used and it was filled with the mixture of LC and NPs. The cell thickness was 120 μm. For dielectric measurements, a HP4284A Precision LCR meter [9] was used. For magnetic measurements a mixture was inserted into thin glass tubes and the magnetic properties were measured with a commercial SQUID-based magnetometer with a 5 T magnet (Quantum Design MPMS XL-5). In case of calorimetric measurements the mixture was placed in a silver cell. The calorimetric method is described elsewhere [10–12].

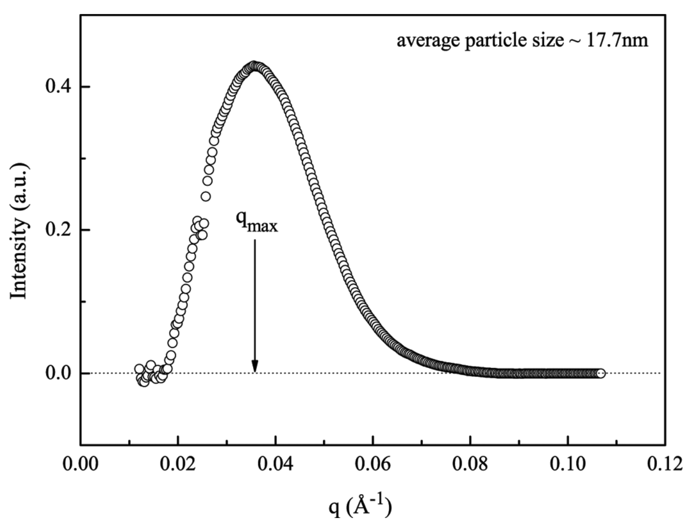

Figure 2. SAXS scattering intensity as a function of the wave vector q. Relatively narrow distribution between 11 nm and 25 nm indicates that the mixture remains stable and free of aggregates even after six months time.

3. Results and Discussion

Frequency dependent dielectric constant of SCE9 and NPs mixture was measured between 400 Hz and 300 kHz in temperature range between 300 and 360 K and a cooling rate of 400 mK/h. Results at two different electric fields are presented in Figure 3. The both soft and Goldstone mode anomalies are similarly suppressed and smeared as in case of aerosils mixtures [9]. The electric field strongly suppresses the Goldstone mode which is still present in the 10% mixture.

Calorimetric and magnetic susceptometry measurements were made in the temperature range near the bulk SCE9 SmA-SmC* phase transition, i.e., from 325 K to 337 K. Specific heat data (see Fig. 4) show similar disordering effect as in case of the aerosils [13–14]. In case of SQUID susceptometry a sample was first heated to 320 K in a zero magnetic field. At 320 K 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. As shown in Figure 4, the excess heat capacity data (ΔC_p) and Δm (Fig. 5) anomalies both appear at SmA-SmC* transition temperature of bulk LC SCE9 at around 330 K ($T_{AC} = 330$ K). The shape of the Δm anomaly closely resembles temperature evolution of the molecular tilt, i.e., the primary SmC* order parameter in the vicinity of the SmA to SmC* phase transition. These results demonstrate that the observed anomaly in Δm is a consequence of the coupling between the magnetic NPs and LC director field. The data can be well modelled within the assumption of perpendicular ordering of the magnetic NPs with the respect to the average molecular director. As a consequence, a net $\Delta m \neq 0$ response closely following the temperature dependence of the molecular tilt is observed under a small magnetic probing field.

4. Conclusions and Perspectives

A dielectric spectroscopy, magnetic susceptibility and high resolution calorimetry measurements were made near the ferroelectric smectic C*-smectic A phase

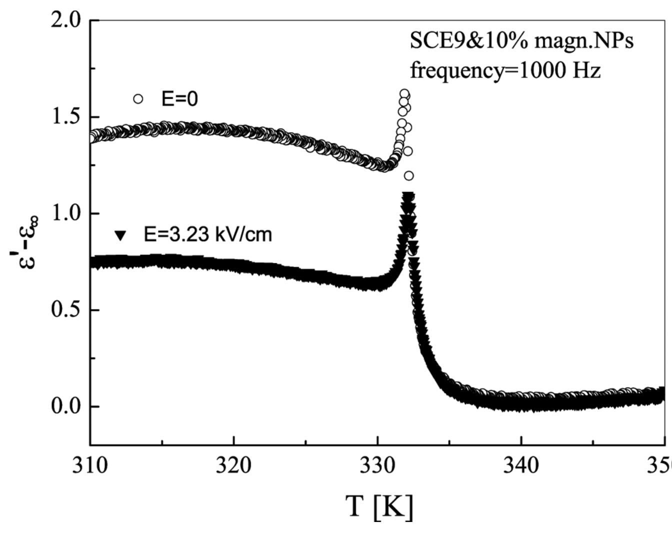

Figure 3. Temperature dependence of the real part ε' of the dielectric constant at two different electrical fields on mixtures of SCE9 LC and magnetic nanoparticles. $\varepsilon_\infty = 4.5$ was subtracted from all data.

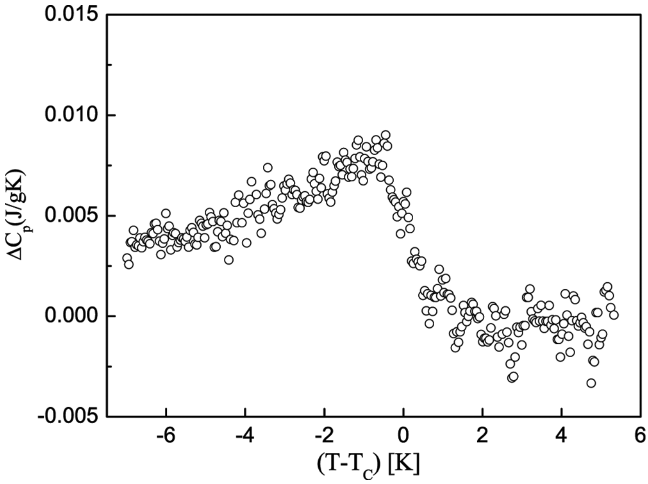

Figure 4. Excess heat capacity ΔC_p of SCE9 LC mixtures with magnetic nanoparticles of diameter 20 nm with $x = 14\%$. The SmA-SmC* transition temperature $T_{AC^*} = T_C = 330$ K.

transition of SCE9 ferroelectric liquid crystal mixtures with weakly anisotropic magnetic nanoparticles.

The dielectric measurements show that the magnetic nanoparticles have significant impact on the soft and Goldstone mode. In the vicinity of the ferroelectric phase transition the similar disordering effects were observed as for aerosils mixtures. The anomalies of both modes are strongly suppressed and smeared [9].

The calorimetry and magnetic susceptibility measurements demonstrate that the orientation of magnetic nanoparticles and the liquid crystal molecular director field

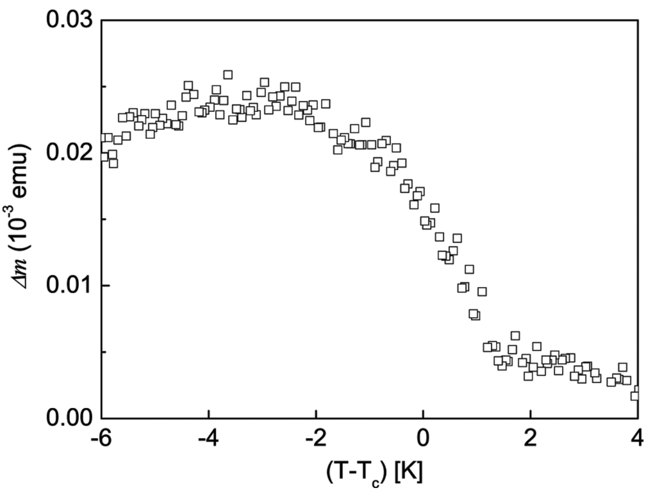

Figure 5. Excess heat magnetization $\Delta m = m\text{-}m_L$ of SCE9 LC mixtures with magnetic nanoparticles of diameter 20 nm with $x = 14\%$; m_L represents the linear temperature dependence of magnetization in SmA phase extrapolated to low temperatures. The SmA-SmC* transition temperature $T_{AC^*} = T_C = 330$ K.

are directly coupled. Such coupling allows possibility of indirect coupling between the magnetic and ferroelectric order. Due to this, the mixtures of ferroelectric LC and magnetic NPs are candidates for soft indirect magnetoelectrics.

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