Experimental report

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Proposal: 5-53-258 **Council:** 4/2015

Title: Influence of dipolar interactions on the magnetization distribution in iron oxide nanoparticles for biomedical purposes.

Research area: Physics

This proposal is a new proposal

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Samples: S1 (Fe_2O_3/Fe_3O_4)
S2 (Fe_2O_3/Fe_3O_4)
S3p (Fe_2O_3/Fe_3O_4)
S3l ($Fe_2O_3/Fe_3O_4+H_2O$)

Instrument	Requested days	Allocated days	From	To
D33	6	3	09/11/2015	12/11/2015

Abstract:

Use of spin-resolved POLARIS experiments will reveal the influence of dipolar interactions on the spatial magnetization distribution in Fe-oxide (Fe_3O_4 core/Fe_2O_3 shell) Nanoparticles with two different diameters (d = 10-11 nm, d = 5 nm) and hence interrelate dipolar interactions on the nanoscopic and macroscopic level. This is of outmost importance when defining parameters to get a standardization of these nanometric compounds for biomedical applications.

Report: Influence of dipolar interactions on the magnetization distribution in iron oxide nanoparticles for biomedical purposes.

In recent years, utilization of iron oxide nanoparticles (IONPs) for a wide range of biomedical applications was extensively researched [1], prompting the need to standardize the characterization of their physical properties [2]. The aim of the EU NMP FP7 project, NanoMag [3], is to improve, redefine and ultimately standardize existing analysis methods. For that purpose it is necessary to correlate the macroscopically measured quantities of the ensembles with the physical properties of the individual particles on the nanoscale. An open issue is yet to experimentally resolve the influence of local particle interactions within such ensembles on their magnetization behaviour.

In this study, the magnetization behaviour of a dense powder of iron oxide nanoparticles (S2, Fig. 1 (left), average core radius of R = 5 nm and a polydispersity of 7%) was characterized by conventional magnetometry, as well as polarized small angle neutron scattering at the instrument D33 with polarisation analysis (POLARIS [4]). In case of isothermal magnetization measurements, the ensemble behaves at T = 300 K as a superparamagnet (Fig. 1 (right)) and is close to saturation at $\mu_0 H$ = 1T (increase at higher field strengths is mainly due to a paramagnetic contribution of uncorrelated surface spins). This superparamagnetic behaviour originates from the individual particles who are single-domain (atomic spins preferentially parallel to each other). At room temperature the thermal energy is significantly larger than the effective anisotropy energy, resulting in a spin fluctuation. Hence, in zero field the ensemble has no net magnetization.

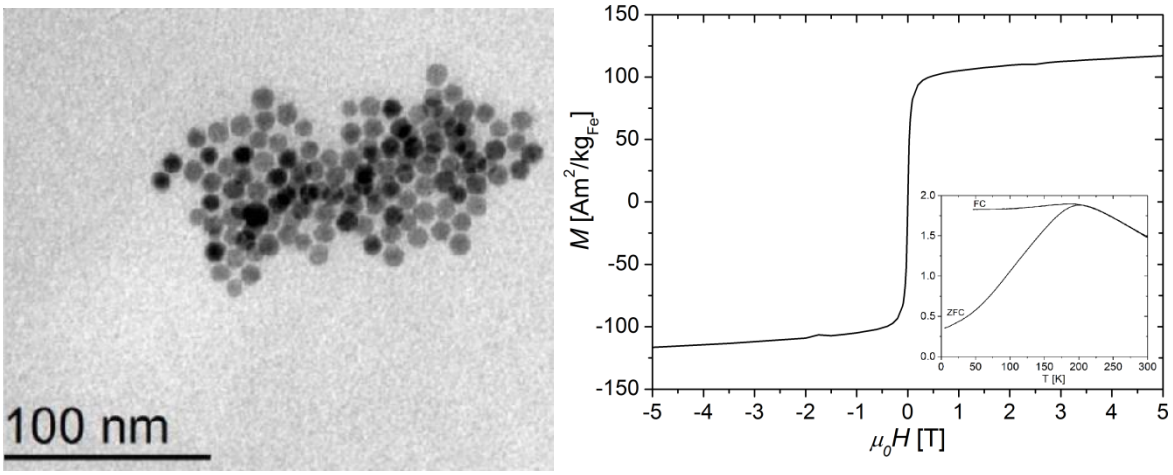

Figure1–left: TEM image of S2. right: Isothermal magnetization measurement of S2 at T = 300 K (inset: Zero field cooled (ZFC)-Field cooled (FC)-measurement).

To correlate the macroscopic magnetization with the local magnetization distribution on the nanoscale all four POLARIS cross sections were measured at the field strengths 5 mT, 20 mT, 100 mT and 1000 mT, with $\mu_0 \boldsymbol{H} \perp \boldsymbol{k}$. The detector distance was 6 m and the wavelength 6 Å. Fig. 2 (a) and (b) show exemplarily the spin-leakage corrected 2D spin-flip cross sections at 1000 mT ("saturation": particle spins aligned in field direction) and 5 mT ("zero field": random orientation). It can be observed that the shape and strength of the SF scattering signal changes significantly, going from a (weak) $\mathrm{Sin}^2\theta$ $\mathrm{Cos}^2\theta$-anisotropy, as expected for the fully aligned state, to an enhanced scattering along the applied field direction, which arises from the emergence of transversal magnetization components. In order to get information about the correlation of the spins of neighbouring particles in real space the *I(q)* data was Fourier transformed. Fig. 2 (right) shows the extracted autocorrelation function $C(r)$ for the measured fields of 5 mT, 20 mT, 100 mT and 1000 mT. By reducing the magnetic field, its strength increases, indicating that disorder in the magnetic microstructure grows. At 1000 mT the spins are aligned in field direction and hence not only correlated in the individual particle cores (r ~ 5 nm) but also over a longer range between the neighbouring particles in the dense

powder. The observed maxima at ~ 15 nm corresponds well to the expected position of the nearest neighbours. At 5 mT the macroscopic magnetization of the ensemble is basically zero and hence the expected correlation function in case of non-interacting particles would be the one of a sphere with R = 5 nm (with $C(r > 2R)$ = 0 and l_C ~ 4.5 nm). However, the correlation length (defined as $C(r = l_C)=C(0)/e$) increases from a value of ~ 5 nm at maximum field to 6.1 nm at 5 mT and $C(r > 2R) > 0$. This indicates that within the ensemble a significant number of particle spins is coupled with the nearest neighbour particle due to dipolar interactions.

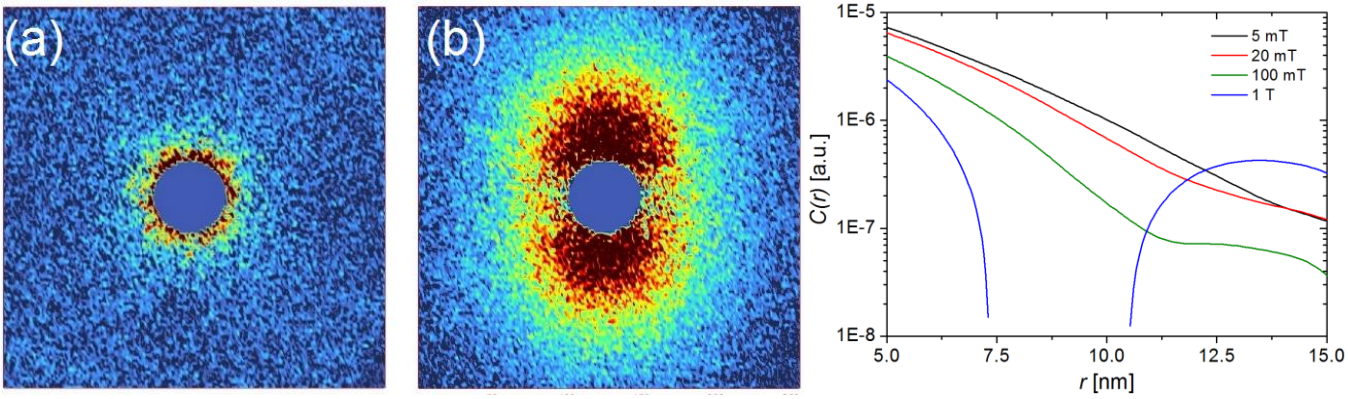

Figure 2: 2D spin-flip POLARIS cross sections of sample S2 for (a) 1000 mT and (b) 5 mT at 300 K. For both plots the same linear intensity scale was used. The magnetic field was applied in vertical direction. right: Correlation function $C(r)$ of the radially averaged SF cross section at 5, 20, 100 and 1000 mT.

Additionally to S2 a second sample of iron oxide nanoparticles (S1) was characterized by SANSPOL at different field strengths ($\mu_0 H$ = 5 mT - 5000 mT) and temperatures (300 K and 5 K). The diameter of these particles was identical to S2 but they were coated with ~9 nm thick silica shell. Hence, in this case dipolar interactions are negligible. A further data analysis on this sample, will allow to extract the spatial magnetization profile within the individual particle cores.

Perspectives:

Of particular interest is to clearly resolve the coupling of neighbouring particle spins due to dipolar interactions. As stated in [5] "*local quantitative observations of dipolar magnetism in nanomaterials are lacking due to stringent experimental requirements*". This gap can be closed by the performed polarized SANS experiments. These results will be important e.g. for understanding the role of dipolar interactions in hyperthermia experiments, where the collective heating of iron oxide nanoparticle ensembles due to spin relaxation in alternating fields is analysed. So far, there exist conflicting results/models regarding the influence of dipolar interactions on the relaxation dynamics, in particular due to the unknown arrangement of the spins in close-packed assemblies, as discussed e.g. in [6].

For a successive experiment it would be beneficial to determine the POLARIS cross sections for more fields - in particular within the 'initial slope' of the magnetization curve 5 mT - 200 mT - as well as dependent on the temperature. It would be of great interest to examine if the particle coupling increases while approaching the blocking temperature (for this sample ~ 200 K, see ZFC-FC measurement in Fig 1 (right)).

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2. S. Bogren et al., *Int. J. Mol. Sci.* **16**, 20308-20325 (2015).
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7. S. Mørup et al.,*Beilstein Journal of Nanotechnology* **1**, 182-190 (2010).