Experimental report

13/02/2017

Proposal: 5-32-836 **Council:** 4/2016

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

Research area: Physics

This proposal is a continuation of 5-53-258

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Samples: Fe2O3/Fe304

Instrument	Requested days	Allocated days	From	To
D33	6	4	02/09/2016	06/09/2016

Abstract:

Use of spin-resolved POLARIS experiments will reveal the influence of dipolar interactions on the spatial magnetization distribution in densely packed assemblies of Fe-oxide nanoparticles (r ~ 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, such as hyperthermia.

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

In recent years, the potential application of iron oxide nanoparticles (IONPs) in a wide range of biomedical areas was subject of a large number of experimental and theoretical studies [1]. In particular hyperthermia - collective heating of IONP ensembles due to spin relaxation in alternating fields for hyperthermic treatment of cancer cells [2] - is an intensively investigated research topic. The heating behaviour of the IONP ensembles critically depends on a multitude of interrelated structural and magnetic parameters, prompting the urgent need to eventually standardize the characterization of their physical properties.
The aim of the Nanomag consortium (18 institutions funded by a EU-FP7 project [3]) is to improve and redefine existing analysis methods to establish standard measurements, which define the properties of a given batch of IONPs. To this day, a heavily discussed issue is the influence of particle interactions on the macroscopic magnetization behaviour of such ensembles and ultimately on hyperthermia experiments [2].
With classical techniques the local coupling of neighbouring particle spins due to dipolar interactions cannot be directly resolved. For that purpose, a dense powder of a project sample was analyzed in a previous experiment (no. 5-53-258) by SANS with polarization analysis (POLARIS) at the ILL instrument D33, in order to resolve spin correlations between particles. For this experiment sample **S2** (Fig. 1) was used. The preliminary results, summarized in [4], are very promising, and show that SANS might provide unique and valuable information on the spin microstructure and interparticle correlations.

To improve the study, however, it was necessary to increase the q-range to lower q, since the maximum of the scattering intensity at low q is barely observed. Therefore we repeated the measurements of **S2** at two different detector distances (d_1 = 13.4 m, d_2 = 3 m, wavelength 6 Å) for $\mu_0 H$ = 2, 20, 100 and 1000 mT.
Furthermore, we intended to analyze the spin-coupling dependence on temperature. For this purpose, we measured the spin-resolved SANS signal at 300 and 200 K (blocking temperature T_B = 200 K of the ensemble **S2**, Fig. 1). Additionally, we detected the POLARIS cross sections of sample **S1** at 300 K for 2 and 1000 mT, as a reference system with significantly reduced dipolar interactions compared to **S2** (reduced blocking temperature T_B, Fig. 1).

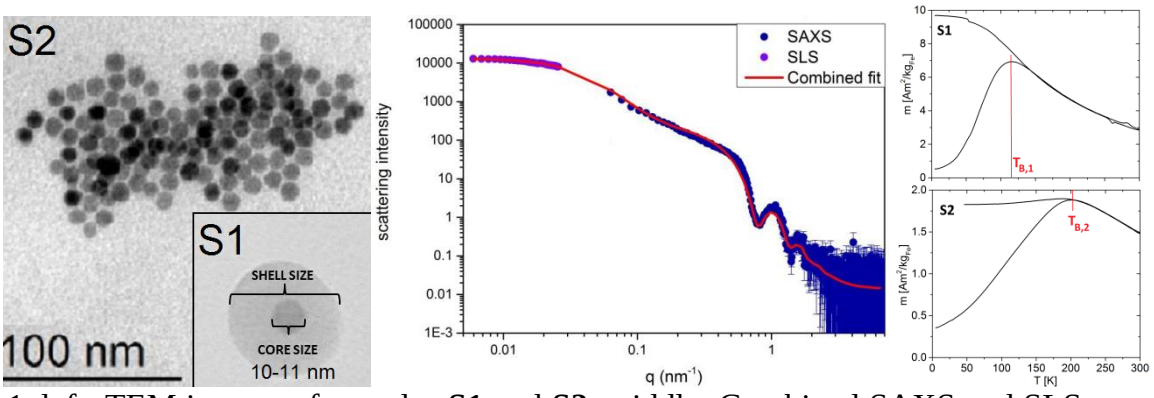

Figure1–left: TEM images of samples **S1** and **S2**. middle: Combined SAXS and SLS measurement of the **S2** in dispersion. right: Zero field cooled (ZFC)-field cooled (FC)-measurements of **S1** and **S2**.

Preliminary results

To correlate the macroscopic magnetization with the local magnetization distribution on the nanoscale in all cases all four POLARIS cross sections were measured with $\boldsymbol{H} \perp \boldsymbol{k}$. In the following data analysis is focused on the spin flip intensities.
Fig. 2 exemplarily shows the radial averages of the spin flip channels measured at T = 300 K for $\mu_0 H$ = 2, 100 and 1000 mT and measured at T = 200 K for $\mu_0 H$ = 2 mT. The measurement at T = 300 K for $\mu_0 H$ = 20 mT is not shown, because it is nearly identical to the measurement at 2 mT.
To analyze the spin coupling the pair distance distribution functions were determined by indirect Fourier transforms (IFT) of the 1D intensities using the approach by S. Hansen [5].
Of particular interest were the *P(r)*'s at 2 mT. As shown in Fig. 3, at 2 mT the macroscopic magnetization of the ensemble is still nearly zero at T = 300 K. The *P(r)* determined at 300 K, however, deviates from the

P(r) of a single sphere, which would be expected for *P(r)* in case of non-interacting and statistically oriented particles. The observed *P(r)* resembles in the low *r* range the *P(r)* of dimer-like structures. Additionally, negative values in the large *r* range are observed. Altogether, this indicates a coupling between the moments of neighboring particles.
Interestingly, at 20 mT the extracted *P(r)* is quite similar to the *P(r)* at 2 mT in the low *r* range. This strongly emphasizes the assumption that the observed correlations between spins of neighboring particles (*r* = 0-22 nm) are not induced by the external field but by internal (dipolar) interactions.

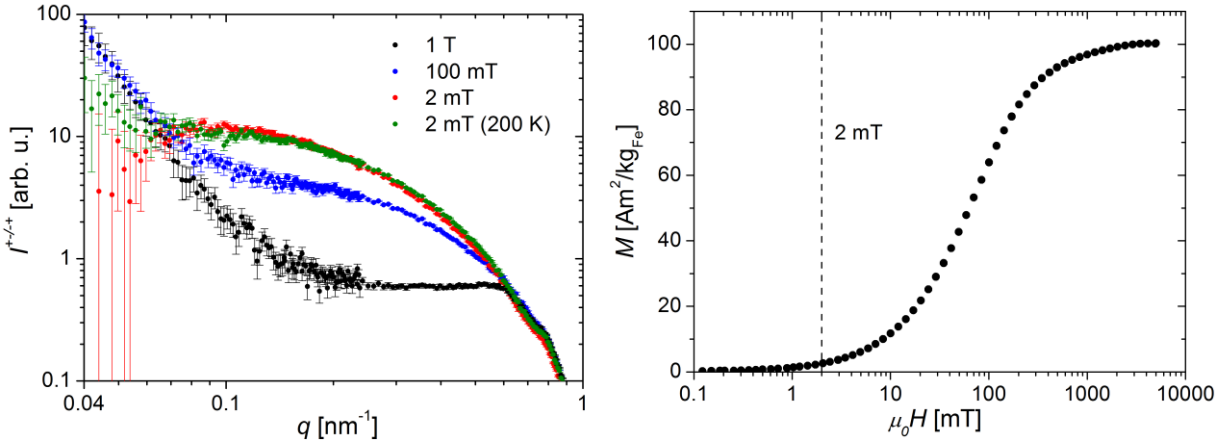

Figure 2: Left: Radial averages of spin flip intensities of sample **S2**. Right: Isothermal magnetization curve of sample **S2** measured at T = 300 K.

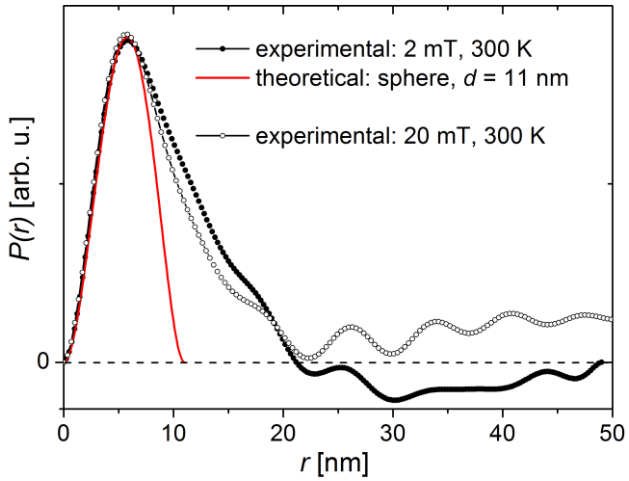

Figure 3: Pair distance distribution functions *P(r)* determined by IFT of the radial average of the spin flip intensities measured at 2 mT and 20 mT (300 K).

It is planned to analyze all measured spin flip intensities by IFT's. Do gain additional insight into the magnetisation distribution and coupling of the magnetic nanoparticles, the anisotropy of the scattering behavior will be also taken into account by analysing the scattering intensities as a function of Θ (angle between ***q*** and ***H***).

In a further step, it would be interesting to analyze the spin coupling of the particles in alternating magnetic fields by stroboscopic (TISANE [6]) experiments. This could help to unravel the influence of dipolar interactions on their relaxation behavior and hence hyperthermia experiments.

References

[1] Q. Pankhurst et al., *J. Phys. D Appl. Phys.* **36**, R167–R181 (2003).
[2] M. Verde et al., *AIP Adv.* **2** 032120 (2012).
[3] http://www.nanomag-project.eu/ (12 Feb. 2015).
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[5] S. Hansen, *J. Appl. Cryst.* **33**, 1415-1421 (2000).
[6] P. Bender et al., *Nanoscale.* **7**, 17122-17130 (2015).