Experimental Report

04/02/2014

Proposal:	**5-32-786**	**Council:**	10/2012
Title:	Magnetization distribution in anisotropic Janus nanoparticles		

This proposal is a new proposal

Researh Area: Materials

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Samples: FePt@MnO Janus nanoparticles, dispersed in d8-toluene
Fe2O3 nanoparticlesz, dispersed in d8-toluene as well as deposited on Si substrates

Instrument	Req. Days	All. Days	From	To
D33	3	3	15/03/2013	18/03/2013

Abstract:

We propose static polarized SANS measurements on magnetically and sterically anisotropic Janus nanoparticles in an applied magnetic field of up to 5 T. The aim of the experiment is to quantitatively investigate the impact of shape anisotropy and exchange bias (induced by interaction of the FePt and MnO subunits of the hetero-dimers) on the spatial magnetization distribution in these nanoparticles.

As a result, we expect to gain precise information on the impact of exchange interactions on the surface spin canting and thus also the magnetic anisotropy in Janus nanoparticles. The proposed experiments are crucial for the understanding of the magnetization relaxation in such anisotropic nano-hetero-particles currently under investigation.

Magnetization distribution in shape-anisotropic nanoparticles

Magnetic nanoparticles exhibit unique physical properties, such as superparamagnetic relaxation, which finds technological applications in e.g. magnetic imaging or hyperthermia [1]. Combining nanoparticles with different physical properties (such as magnetic, electric or optical properties) leads to novel materials with multiple functionalities [2]. In order to explore such multifunctional nanomaterials for technological applications, understanding of the coupling of the different properties is required.

In the framework of the Marie-Curie project ‘Magnetization dynamics in anisotropic nanoparticles investigated using time-resolved X-ray and neutron scattering’ (FP7-PEOPLE-2011-IEF 298918), we study the influence of shape anisotropy and interface interactions on the magnetization relaxation of shape anisotropic nanoparticles. Janus nanoparticles consisting of ferro- and antiferromagnetic subunits of different size provide tunable exchange bias effect and shape anisotropy and are thus promising for materials with tailored magnetization relaxation properties. In order to understand the magnetization dynamics in detail, precise knowledge of the structural and static magnetic morphology of the samples under study is essential. Here we originally proposed a temperature dependent polarized SANS study of FePt@MnO Janus nanoparticles in order to elucidate the impact of exchange bias on the spatial magnetization distribution in the FePt nanoparticle subunits. As meanwhile carried out experiments suggest (ILL report INTER-245), the Curie temperature in the nanoparticles under study is significantly lower than room temperature. Consequently, very low temperatures and large applied magnetic fields are required in order to study the magnetization distribution in these samples. The sample cells available for liquid samples at the time of the experiment, however, did not allow for cooling inside the large magnetic field cryostat. For this reason, we decided to use the beam time instead for a study of the magnetization distribution in cubic iron oxide nanoparticles which exhibit a sufficient magnetic scattering contribution at ambient temperatures. Exploiting the low temperature option of the available sample environment, we additionally studied the magnetic scattering contribution in long range ordered assemblies of the same nanoparticles in order to elucidate the magnetic correlations in such dense magnetic lattices.

The samples under study consist of highly monodisperse iron oxide nanocubes as well as long range ordered assemblies thereof, obtained by deposition onto Si substrates in a magnetic field induced assembly process [4]. Grazing incidence small-angle scattering (GISAXS) on very similar samples revealed internally structurally coherent mesocrystals which are oriented perpendicular to the substrates, thus forming a 2D powder. The mesocrystal structure is directed by small variations in the particle shape, with a preferred face-to-face arrangement for faceted nanocubes [5,6]. Such long range ordered nanoparticle mesocrystals represent suitable model systems for further investigation of magnetic interactions by polarized neutron or resonant X-ray scattering.

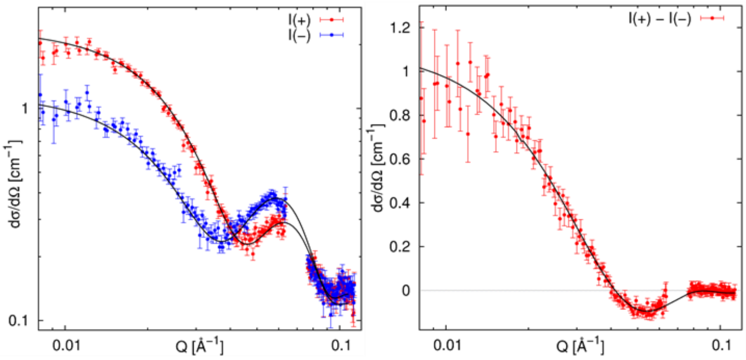

Figure 1: polarized SANS by iron oxide nanocubes. The magnetic contrast variation using a polarized incident neutron beam (left) and the obtained nuclear-magnetic cross term (right) are presented.

Polarized SANS measurements carried out at ambient temperatures in an applied magnetic field of 1.5 T are presented in Figure 1. Analysis of the purely nonmagnetic scattering cross section using a core-shell spherical form factor yields the nuclear scattering length density profile of the nanoparticles consisting of a spherical radius of the inorganic particle core of R_s = 6.00(2) nm, an oleic acid ligand shell of 1.33(1) nm thickness, and a lognormal size distribution of the particle core of 5.6 % FWHM. Using a simple transformation of the spherical radius into the cubic edge length of the particles [6], leads to a cubic nanoparticle edge length of 9.3(1), well in agreement with the edge length inferred from TEM analysis. Analysis of the magnetic contrast and the nuclear-magnetic cross term presented in Figure 1 yields the spatially resolved magnetization distribution which is best described by a magnetic particle core with constant magnetization and a linear shell of decreasing magnetization towards the particle surface [7]. For the sample under study we determined a core magnetization of 0.59(2) μ_B per Fe atom along with a thickness of the surface shell with lower magnetization of 0.3(1) nm. These results are in agreement with recent results on smaller nanoparticles [NJP].

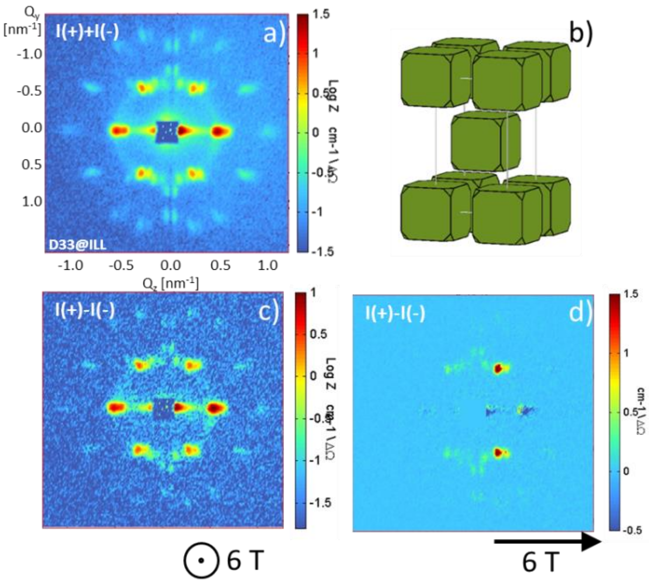

Figure 2: Mesocrystals of iron oxide nanocubes. a) nonpolarized GISANS pattern, b) schematic of the obtained mesocrystal structure, c,d) polarized GISANS with a 6T magnetic field applied parallel and perpendicular to the incident neutron beam, indicating magnetic scattering contributions in most reflections.

Figure 2 presents polarized GISANS measurements on mesocrystals of the same nanocubes, deposited on Si substrates. The nonpolarized GISANS (Fig. 2a) reveals sharp reflections corresponding to a body-centered tetragonal mesocrystal structure with lattice constants a = 13.5(2) nm and c = 23.8(1) nm. Similar to published results [5], the nanocubes are oriented in a *face-to-face* arrangement as indicated in Figure 2b. The nuclear-magnetic cross term I(+)-I(-) measured on this sample with orientation of the applied magnetic field parallel and perpendicular to the incident neutron beam is shown in Figure 2c and d, respectively. We observe clear magnetic scattering contributions in both cases in an applied magnetic field of 6T, which is expected to saturate the sample, corresponding to the expected parallel orientation of the nanoparticle moments parallel to the applied field.

More detailed analysis of these and further scattering patterns at different applied magnetic fields and temperatures is currently ongoing.

References

[1] Q. A. Pankhurst, J. Connolly, S. K. Johnson, J. Dobson, *J. Phys. D: Appl. Phys.* **36**, R167 (2003).

[2] H. Zeng, S. Sun, *Adv. Funct. Mater.***18**, 391 (2008).

[4] A. Ahniyaz *et al.*, *Proc. Natl. Acad. Sci. USA* **104**, 17570 (2007).

[5] S. Disch, E. Wetterskog *et al.*, *Nano Letters* **11**, 1651 (2011).

[6] S. Disch *et al.*, *Nanoscale* **5**, 3969 (2013).

[7] S. Disch *et al.*, *New J. Phys.* **14**, 013025 (2012).