Experimental report

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Proposal: 5-32-798 **Council:** 4/2014

Title: Formation of coated bcc-Fe magnetic nanoparticles

Research area: Materials

This proposal is a new proposal

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Samples: fe (bcc)

Instrument	Requested days	Allocated days	From	To
D22	1	1	18/06/2015	19/06/2015
D20	1	0		

Abstract:

Fe bcc nanoparticles coated with a biocompatible surfactant, Poly-TetraMethylene-Glycol, have been produced by the microemulsion method using inverse micelle microreactors. The reaction can be done: type 1, by adding a solid reduction agent, or type 2, by mixing with a secondary microemulsion carrying the reduction agent. Nanoparticles obtained by the two methods have different properties as higher saturation magnetization and thermal stability for those of type 2. However, X Rays, TEM and magnetic measurements (coercivity and ZFC-FC curves) are unable to clearly distinguish such features as size, shape and distribution of the Fe MNPs. We propose a "in situ" study of the evolution of the MNPs for both types of reaction and different micelle size in appropriate environments of deuterated solvents to enhance the contrast of the micelles or the Fe MNPs. 1 day in D20 will be used for the size evolution, while another day in D22 can give the final shape and distribution of the MNPs as well as the coating.

ILL Proposal 5-32-798 – Experimental Report

Title: "Formation of coated bcc-Fe magnetic nanoparticles"
Proposers: Irene URCELAY, José Manuel BARANDIARAN[1], Nagore PEREZ, Marie-Louise SABOUNGI
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The original proposal was intended for "in situ" studying the microemulsion reaction for producing Fe nanoparticles, because X Rays, TEM and magnetic measurements (coercivity and ZFC-FC curves) are unable to clearly distinguish features such as size, shape and distribution of the Fe MNPs during particle formation: "*... we intend to use high flux wide angle diffraction and SANS to investigate in situ the formation of coated bcc Fe MNPs, by following the micelles in the (i) starting microemulsions, (ii) during the reaction, and (iii) the resulting nanoparticles. For this experiment we estimate that 1 day on D20 and 1 day on D22 are required.*"

Only D22 was accorded, so it became clear that the insitu studies were not possible (the high flux of D20 was necessary), and the samples prepared in the laboratory some months ago got oxidized and useless for experiment. We decided then to swithch the experiment and study **magnetosomes** and **magnetite nanorods**. Magnetosomes were biomineralized, between 7h and 24h, by *Magnetospirillum gryphiswaldense* bacteria. These bacteria synthesize, after 72 h, chains formed by 20-25 single crystal magnetite (Fe_3O_4) nanoparticles with cubo-octahedral shape and a mean size of 30-50 nm. These magnetosomes were obtained by **Prof. Mª Luisa Fernández Gubieda** and coworkers at the University of the Basque Countrry (UPV/EHU) Bilbao. The samples were carrefully characterized prior to the experiments by X-ray diffraction and magnetic measurements.

SANS experiments were performed at the instrument D22. For this experiment the bacteria were harvested from the culture medium by centrifugation after initial growth times of > 7h and mechanically crushed to a powder-like substance. Measurements after 7h and after 24h show basically identical behavior. The slightly higher absolute values of the scattering intensity of the 24h samples are probably due to a slightly increase of the particle density in the probed volume. The particle structure (e.g. particle size, cluster size), however, is not changed.

The results for 7 hours are displayed in fig 1, together with a fit performed by **Dr. Philipp Florian Bender**, University of Cantabria, Santander. As can be seen in Fig. 1 the circular averaged scattering intensity I(q) displays a distinct q-dependency, dominated by the iron oxide nanoparticles.

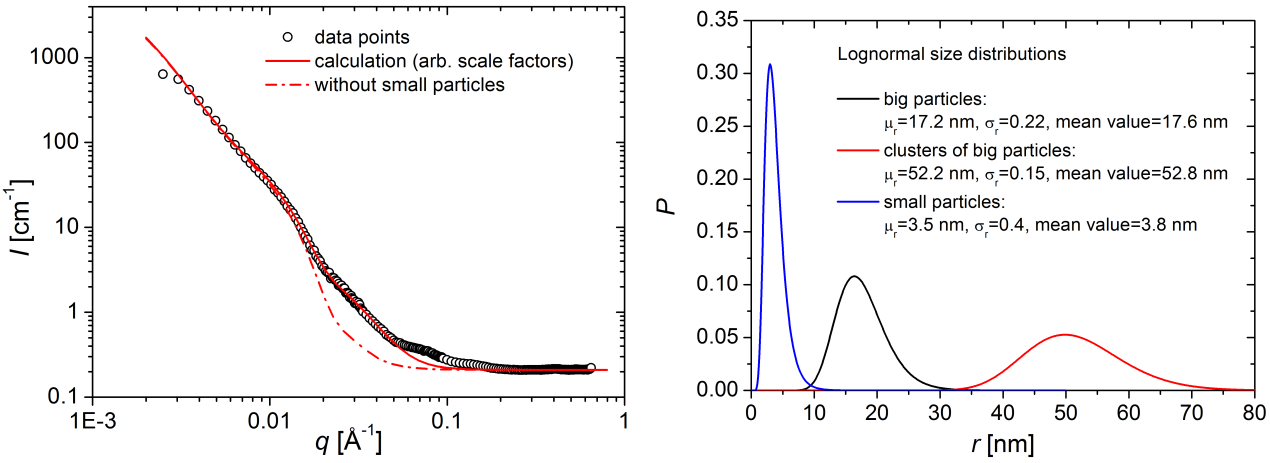

Fig 1.- *Left: Circular averaged SANS intensity of the magnetosomes and calculated intensity using a mass fractal model. Right: Distribution densities used for the calculated SANS intensity*

The crushing of the bacteria resulted in a destruction of the chain-like agglomerates. The adjustment of the data was then performed by applying a conventional mass fractal model [4]. The best agreement with the experimental data was achieved for a fractal dimension D = 3 and the size

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distributions displayed in the right panel of Fig.1. Additionally a second collection of very small spherical particles (without structure factor) had to be superimposed to get a reasonable agreement between the model and the experimental data in the high q-range. These small particles can be small ferritine cores which are already initially present in the bacteria prior to the actual growth of the magnetite particles. However, it has to be mentioned, that for the data analysis the magnetic scattering contribution had to be omitted.

A proposal for studying full bacteria in suspension at a different set of times for magnetosome growth is in preparation to overcome these issues.

A second sample consisting of magnetite nanorods dispersed in deuterated toluene was also measured. The rods were synthetized and characterized by **Dr. Javier Alonso** and collaborators, at the Laboratory of **Prof. Hariharan Srikanth** in South Florida University, Tampa, USA. Average length of the rods was 71 nm and average diameter 11.6 nm. The SANS results are displayed in fig 2 with theoretical calculations by **Dr. Bender**, assuming the rods are single domain and the distribution of the long rod axes with respect to the neutron beam and detector is isotropic. The scaling factor of the calculated scattering intensity was manually adjusted.

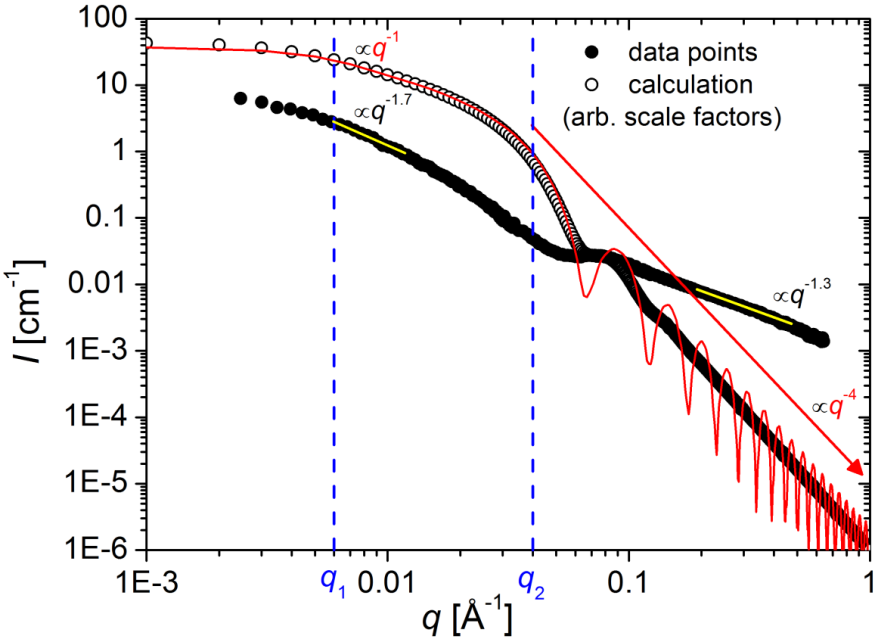

Fig 2.- *Experimental and calculated intensity. The red line is the 1D (orientational average) intensity for a cylinder with l=71nm and d=11.6nm, and the open symbols that of an isotropic ensemble with normal size distributions for diameter and length (PD=0.2)*

Results are quite difficult to interpret:

1) **High q-range:** A scattering intensity I ~ q^{-4} is expected for smooth surfaces. An exponent between 3-4 is expected for rough surfaces. The extremely small observed exponent 1.3 indicates either a deficient subtraction of the background or additional scattering contributions from very small structures.

2) **Low q-range:** For an isotropical distribution of linear structures (e.g. rods but also chain-like agglomerates) a I ~ q^{-1} behavior in the low q-range ($q<q_1$) would be expected [Hammouda, J. Appl. Cryst. 43 (2010) 716]. However, an exponent of ~1.7 is determined. This indicates an, at least partial, agglomeration of the rods. Another explanation could be a significantly different magnetic scattering contribution.

In conclusion: At the current state a correct adjustment of the data is not possible. In particular the unknown magnetic scattering contributions makes the SANS analysis too cumbersome. Also, the agglomeration of the rods could be a problem.

We plan to apply for more beamtime to analyze dilute dispersions of these magnetite nanorods, to improve the deagglomeration, and using polarized neutrons to differentiate between nuclear and magnetic scattering cross sections.