Experimental report

06/02/2022

Proposal: **INTER-528** **Council:** 4/2021

Title: Diffusion in the liquid interface region of IONPs

Research area:

This proposal is a new proposal

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Samples: Fe3O4

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	15/03/2021	18/03/2021

Abstract:

Water dynamics on iron oxide nanoparticles

Experiment INTER-528

1. Scientific background

Nanoparticles (NPs), although already in common use today, still come along with many open questions. This concerns even basic properties like their defect inventory and a structural surface relaxation of direct relevance for their growth, as well as the structure of the interfaces when in solution. In general, the situation is more complex as NPs are stabilized by ligands, which attach to the surface to limit particle growth and avoid NP agglomeration. In a recent attempt, we tried to make the ligand shell visible in SANS experiments. However, the results were inconclusive, as we did not succeed in a satisfactory description of the data by involving core-shell models. We argue that is due to a more complex ligand solvent structure, which involves e.g. an unknown surface density and a complex geometry of the ligand due to steric arrangements on the flat surfaces, edges and corners of the NPs, as well as an infiltration of the ligand by the solvent. A direct measurement of the ligand-solvent structure is challenging, although we have recently made a significant contribution by proving a restructuring of the water reaching out to some three layers through a careful PDF analysis. However, the infiltration of the solvent into the ligand shell remains unknown. With QENS as a different approach the derivation of structural evidence from dynamical information, in particular for the ligand-water interface is possible. It is to expect that motions of water present in the ligand or local motions of ligand units should become apparent in fixed window scans in backscattering spectroscopy, both in the elastic and inelastic mode. Those motions could become observable as intensity steps of characteristic shape at specific temperature values, depending on the water content or the type of ligand with different amounts of hydrogen.

2. Experiment

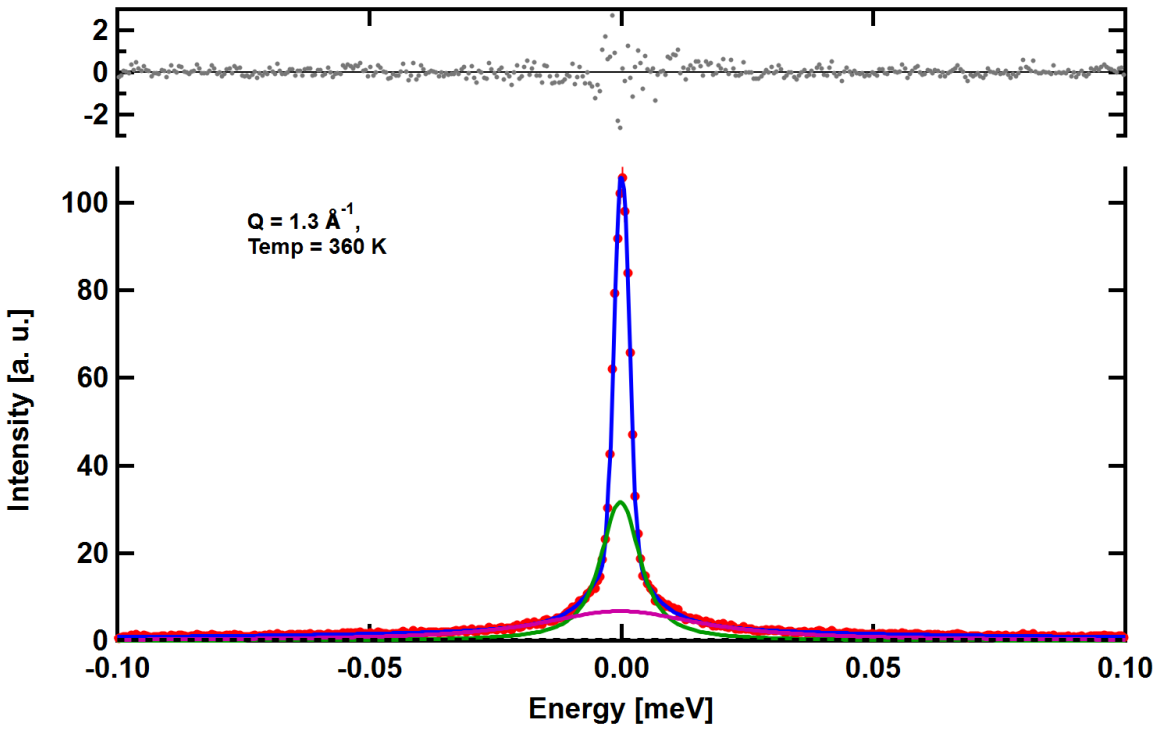
Based on preliminary FWS data collected during EASY-636, we have carried out BATS measurements on selected samples during INTER-528.

The samples studied were a powder of citrate capped iron oxide NPs which was equilibrated at three different relative humidities (8, 75 and 85 % RH) in an aluminium sample holder sealed with Indium wire. QENS spectra were recorded at various temperatures in the range from 2 K to 330 K. Furthermore, a vanadium standard for background correction and an empty can measurement were performed.

3. Preliminary results

The QENS data have been properly normalized given the sample composition as determined from TGA and CHN analysis on the samples before and after the beamtime. The quasielastic signal in the QENS spectra clearly shows a correlation with both temperature and relative humidity, which can be modelled with a combination of a delta function (instrumental resolution) and one or two Lorentzian curves. Unfortunately, the recently recruited PhD student for the project quit the project and we are looking for a postdoc to fully analyse these QENS data.

The figure shows an example of a fit (blue) of the data (red dots with error bars) by the sum of 2 Lorentzians (magenta and green) and a delta function, all convoluted with the experimental resolution function. Note that the experimental energy range is from -143 to 186 µeV.


2
0
-2
100
80
60
40
20
0
Intensity [a. u.]
Q = 1.3 Å-1,
Temp = 360 K
-0.10
-0.05
0.00
0.05
0.10
Energy [meV]