Experimental report

08/06/2022

Proposal: 5-32-932 **Council:** 4/2021

Title: Evolution of the magnetic coherentlength in bi-magnetic core/shell nanoparticles (Fe3O4/Mn3O4) by polarized neutrons under applied field

Research area: Materials

This proposal is a new proposal

Main proposer: **Josep NOGUES**

Experimental team: Thomas HANSEN
Iurii KIBALIN
Arsen GOUKASSOV

Local contacts: Thomas HANSEN

Samples: Fe3O4/Mn3O4 core/shell nanoparticles

Instrument	Requested days	Allocated days	From	To
D20	5	5	09/07/2021	14/07/2021

Abstract:

In bi-magnetic core/shell nanoparticles with antiferromagnetic interface coupling at high fields the antiferromagnetic coupling is overcome and shell and core align ferromagnetically. However, the details of the coupling remain poorly understood. Here we propose to carry out a polarized powder neutron diffraction (PPND) study of Fe3O4/Mn3O4 core/shell nanoparticles with antiferromagnetic interface coupling. Our preliminary PPND study of the Fe3O4/Mn3O4 particles indicates that that, although at low fields the magnetization of the Fe3O4 and Mn3O4 moieties are antiparallel, at high fields they align parallel. The analysis reveals other unusual phenomena like inhomogeneous canting or unusually small magnetic coherent lengths in the Fe3O4 core. Our experiment did not have sufficient statistics to obtain reliable parameters, hampering any significant conclusions. Thus, we propose to carry out a PPND experiment on the same Fe3O4/Mn3O4 samples with enough statistics to perform meaningful fits. The analysis will allow us to study the evolution of the different parameters as the magnetization of the shell rotates with increasing fields.

Evolution of the magnetic coherent length in bi-magnetic core/shell nanoparticles (Fe3O4/Mn3O4) by polarized neutrons under applied magnetic fields (5-32-932).

We carried out systematic polarized neutron diffraction measurements on some Fe3O4/Mn3O4 and Mn3O4/Fe3O4 core/shell nanoparticles and some reference Mn3O4 nanopartciles in magnetic fields up to 5 T. All results were treated with the Cryspy package – a new soft for the treatment of the powder diffraction patterns measured with polarized neutrons (flipping ration method).

To serve as reference a pure Mn3O4 nanoparticles were first studied.

Typical patterns: sum and difference of the measured profiles "spin-up" and "spin-down" are shown in Figure 1. The average size, evaluated from the peak broadening, is ~ 9.5 nm, crystal structure of Mn3O4 is the tetragonal spinel with the lattice parameters: a = 5.718(2) Å and c = 9.364(2) Å.

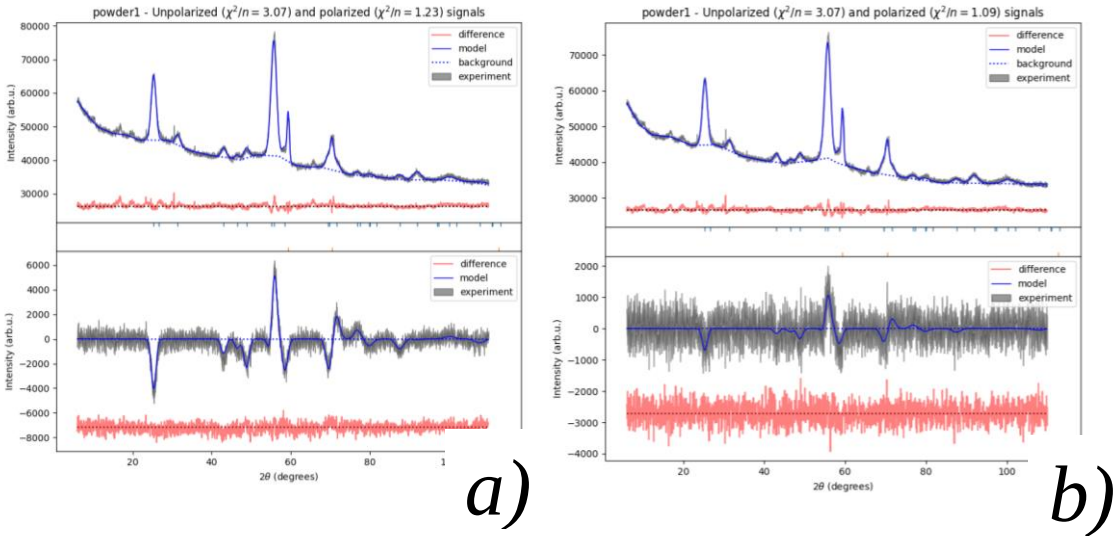

Figure 1. Refined profiles: sum (upper panels) and difference (low panels) of the measured profiles "spin-up" and "spin-down" in magnetic fields 5.0 T (*a*) and 0.5 T (*b*).

As the magnetic field is increased, the magnetic moments in the random oriented crystallites aligns along the applied field and an average ferromagnetic moment appears. This moment is proportional to the parameter "polarization", which is refined by the Cryspy program. The field dependence of this parameter is shown in Figure 2 together with the magnetic moment measured by SQUID. It is seen that both dependencies practically coincide, which confirms the correctness of the calculations.

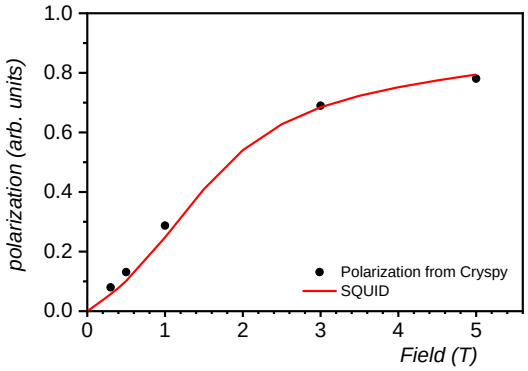

Figure 2. The polarization vs. magnetic field. The black squares – from Cryspy package, red lines – from SQUID hysteresis loop.

In the current version of the Cryspy package, the size of the nanoparticle and the size of the magneto-ordered area are assumed to be equal. This parameter vs. applied magnetic field, refined from the peak broadening, is shown in Figure 3. We can see that the magnetic correlation length increases for larger fields, since magnetic field aligns the disordered surface spins.

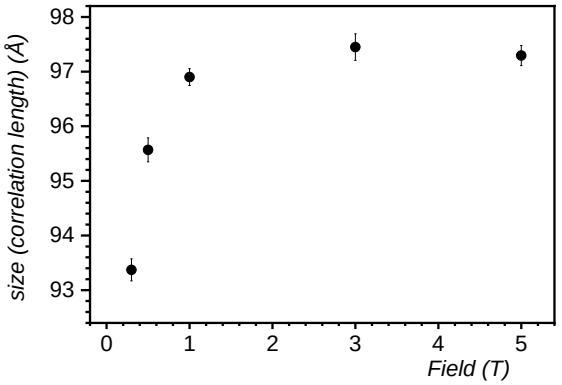

Figure 3. The nanoparticle size (correlation length) vs. applied magnetic field.

The evolution of the local susceptibility ellipsoids with applied magnetic field, refined by Cryspy from the sum and difference of "spin-up" and "spin-down" patterns, is shown in Figure 4. The symmetry of the A-site limits the orientation of the corresponding local susceptibility ellipsoids along the z-axis only, while for ellipsoids corresponding to the B-site, the symmetry allows some

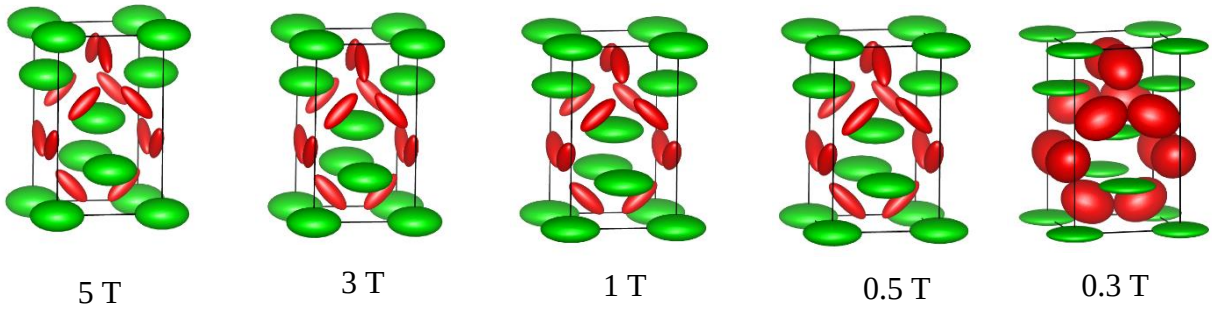

Figure 4. Evolution of the local susceptibility ellipsoids vs applied magnetic field. In green – A (tetrahedral) and in red – B (octahedral) sites.

inclination.

It can be seen that the local susceptibility in the A-site remain similar for all the fields, maintaining the platelet form. However, for the B-site, a transition from a needle to a platelet form between 0.5 T and 0.3 T is clearly observed, which indicates a drastic change in the local anisotropy. The profile refinement performed with measured patterns does not give enough accuracy to define the field dependence of the lattice parameters. However, the refinement of the position of the nuclear peak 101 clearly shows a change of the corresponding inter-lattice distance at low fields, that confirms a structure transition (Figure 5).

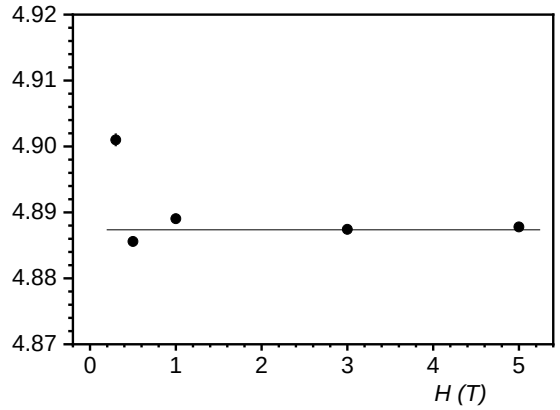

Figure 5. Inter-lattice distance corresponding to the nuclear peak 101 vs. applied magnetic field. Error does not exceed the symbol size.

A similar transition between 0.5 and 0.3 T was reported for the bulk Mn3O4 (Y. Nii et al., PRB 87, 195115, 2013 and M. C. Kemei et al., PRB 90, 064418, 2014) and we observe it for the first time in nanoparticles.

2. Core/shell nanosystem Fe3O4/Mn3O4.

The data treatment of the results from this sample is in progress. A problem with getting reliable data from our polarized neutron experiments is the small amount of the sample. An additional issue with the data refinement is that the shell of Mn3O4 is a layer that consists of nanoparticles of an anisotropic form covering a core of Fe3O4. The smaller dimension of the nanoparticle, which is close to the shell thickness, leads to a broad peak, while the lateral dimension of the shell nanoparticle is defined by a narrow peak located at the same diffraction angle,which makes the results difficult to refine.

However, the thickness of the shell can be evaluated from the refined volume fractions of a shell and a core, refined from the diffraction profile. Here we assume a core to be a sphere with a size, refined from a peak broadening, while a shell is considered as a uniform layer, covering a sphere. In our case, refined volume fractions of 87 % and12 %, for the core and the shell, respectively, are obtained. The calculated “average” thickness of the shell was estimated to be 0.2 nm, i.e., we deal with the thin shell.

3. Core/shell nanosystem Mn3O4/Fe3O4.

Unfortunately, the synthesis of this sample resulted in a very small amount of sample. Moreover, the diffraction patterns show the presence of some impurities (of unknown origin), consequently the results of the analysis are limited. From the neutron diffraction experiments, it is impossible to define the dimensions of the constituted nanoparticles. So, we used data from TEM as input. The refinement of the sum "spin up" and "spin down" profiles gives an average size (correlation length) of a shell of 4 nm, while from the ratio of the volumes, a thickness of 2 nm was evaluated. We are still trying to further analyze these results and correlate the results with magnetization measurements.