ESRF	**Experiment title:** Complementary GISAXS and GISANS studies of the geometrically frustrated magnetic opal-like structures	**Experiment number**: HC-874
Beamline: BM26B	**Date of experiment**: from: 25/04/13 to: 29/04/13	**Date of report**: 30/06/13
Shifts: 12	**Local contact(s)**: Portale Giuseppe	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
N. Grigoryeva*(SPBU), A. Mistonov*(SPBU), I. Dubitskii* (SPBU), I. Shishkin* (SPBU), S. Grigoriev (PNPI)

Scientific background. Geometrical frustration, which arises from the topology of a well-ordered structure rather than from disorder, has recently become a topic of considerable interest [1]. One of the most fascinating aspects of geometrically frustrated magnets is how the spins/moments locally accommodate the frustration of the spin-spin (moment-moment) interactions. A new class of the geometrically frustrated 3-dimensional nanoscale ferromagnetic structures is inverse opals [2], which can be synthesized by filling the voids of opal templates with suitable structure-forming precursors and subsequent removal of the initial microspheres to leave three-dimensionally ordered porous materials. This templating technique allows one to produce the film samples of large-period quasi-2D and quasi-3D structures. The traditional method for studying the nanoscale 3D magnetic structures with the large period is the small angle neutron diffraction [3,4] . Since the samples are films of a few microns thickness the GISAS methods can be very effective to study both their structure properties (GISAXS) and the local magnetization distribution in this structure (GISANS).

Samples and experimental techniques. The samples were synthesized by a template method using as a template the films of polystyrene microspheres organized in opal-like structure (OLS). The OLS films on a conducting substrate were prepared by the vertical deposition of microspheres (diameter ~ 500 nm) from an aqueous suspension. The electrocrystallization of nickel (or cobalt) was performed in a three-electrode electrochemical cell in a potentiostatic regime using the nickel- (cobalt-) containing electrolyte solutions. To prepare the nickel (cobalt) inverse OLS films, the polystyrene microspheres were dissolved in toluene. Thus an inverse OLS can be considered as a set of submicron metallic particles connected to each other via thin and long crosspieces. The shapes of such particles resemble the shapes of the voids of face centred cubic (FCC) structure of opal and have quasi cubic and quasi tetrahedral forms.

The experiments were performed at the BM-26 (DUBBLE) with the photon energy 13 keV and a compound refractive beryllium focusing lenses. A standard configuration of GISAXS experiment was used in combination with transmission SAXS geometry to compare results of different approach (GISAXS and SAXS) and estimate a quality of the crystal structure. Experiments were aimed to study IOLSs of different thicknesses upon the transition from quasi 2D (0.5 – 3.5 layers) to quasi 3D (7 - 30 layers) structures. This knowledge is necessary as complementary for perform the GISANS experiments to determine the local magnetization distribution in the magnetic IOLS.

Results. We studied two series of the inverse opal-like structures based on nickel and cobalt with different number of monolayers. Typical GISAXS and SAXS patterns are presented in Fig. 1(a), (b). While SAXS signal was obtained for all samples, the GISAXS patterns were seen only for quasi 2D IOLS (0.5 – 3.5 layers) at the angle below of the total external reflection. This is connected with both the low penetration depth of X-rays in metals and the increase of the surface roughness with IOLS thickness growth. For instance, 7 vertical stripes can be seen in GISAXS pattern obtained from 0.5 layer sample (Fig. 1(a)) but only

4 stripes are presented for the sample with 3.5 layers (Fig. 1(b)). Moreover stripes do not reveal any structure along vertical (q_z) direction which means that scattering is almost 2-dimensional.

In order to fully understand GISAXS patterns we have simulated the reciprocal space of 2D hexagonal lattice consisted of hemispheres in ISGISAXS package [5]. As a result we were able to separate the form-factor and the structural factor contributions to the scattering. It was found that the form-factor plays the significant role in the scattering from samples which have smooth surfaces. For example, intermediate low intensive peaks obtained from the nickel-based 0.5 layer IOLS arise from the form-factor contribution (Fig. 2). Conversely, no peaks are visible for the cobalt-based 0.5 layer IOLS which has more rougher surface. The structure periods were determined to be 490 ± 15 and 570 ± 15 nm for nickel- and cobalt-based IOLS, respectively. The same values of structure period were found from the analysis of SAXS data for half a layer samples (Fig. 1(c)).

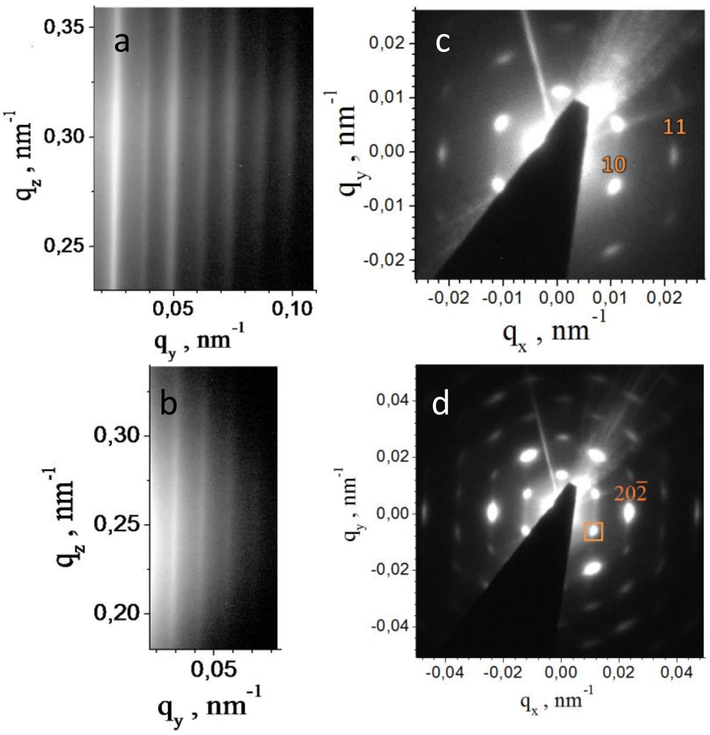

Fig. 1. GISAXS patterns obtained from 0.5 (a) and 3.5 (b) layers IOLS and corresponding SAXS patterns (c), (d).

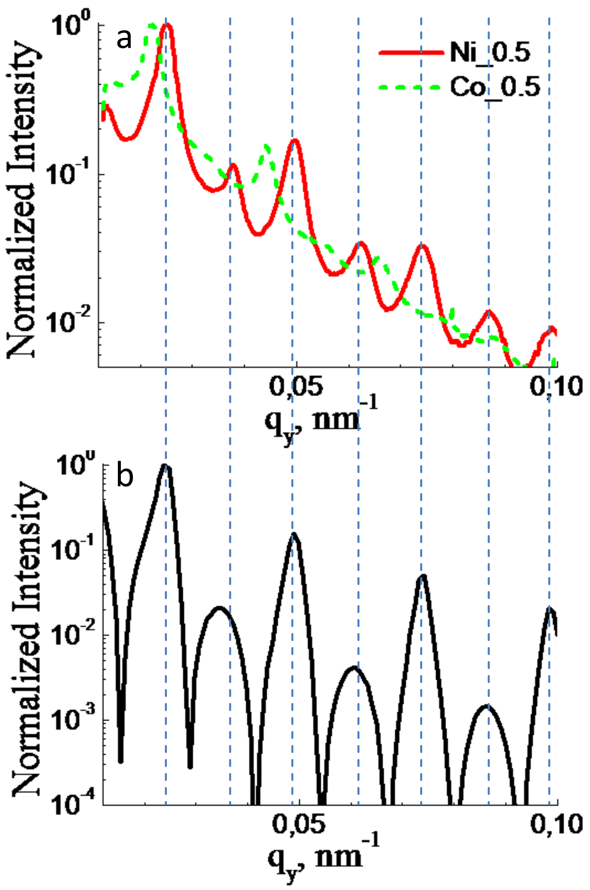

Fig. 2. GISAXS horizontal line slices from 0.5 layer cobalt and nickel IOLS (a) and modelling results for ideal structure (b).

Thus, SAXS and GISAXS techniques are able to provide the complementary information about surface and bulk structure of IOLS due to high surface sensitivity of GISAXS. The structure periods that were found by SAXS and GISAXS coincide well for half a layer samples and reveal small discrepancy (30 nm) for 3.5 layers ones (Fig. 1(d)).

Overall, the GISAXS patterns were fully interpreted. The limits of applicability for GISAXS techniques were determined. All investigated samples demonstrate the set of diffraction patterns in the ordinary SAXS geometry. The scattering intensity in these patterns is adequately described by Bragg reflection indexes of the two-dimensional hexagonal structure for the thin IOLS films (0.5 - 2 layers), and FCC structure for the thicker IOLS films (3.5 - 26 layers).

References

[1] C. Nisoli, C., et. al.,. Rev. Mod. Phys., **85**(4), 1473, (2013)
[2] A. A. Mistonov, et. al., PRB, **87**(22), 220408, (2013)
[3] S. V. Grigoriev, et. al., PRB, **79**(4), 045123, (2009)
[4] N. A. Grigoryeva, et. al., PRB, **84**(6), 064405, (2011)
[5] R. Lazzari, J Appl Crystallogr **35**, 406 (2002).