ESRF	**Experiment title:** Structure analysis of the magnetic opal-like structures by the small-angle scattering of synchrotron radiation	**Experiment number**: HC-1723
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Scientific background. Three-dimensional geometrically frustrated systems called spin ice are of great scientific interest due to their promising properties [1-3]. The ordering of magnetic moments of the rare-earth ions in the nods of pyrochlore-like lattice of the spin ice gives rise to residual entropy [4], magnetic quasimonopoles [3] and other interesting phenomena. Because of that, there are many attempts to find or synthesize such structures. A lot of investigators also tries to create nanoscale analogues of the spin ice [5,6]. However great number of these artificial spin ice structures are mostly two-dimensional [6] or quasi-three-dimensional [7] and hence does not totally mimic the original spin ice.

Inverted opal-like structures (IOLS) can be considered as a three-dimensional nanoanalogue of the spin ice due to their spatial anisotropy. It was proposed, that like in conventional spin ice distribution of the magnetization in IOLS is described by "ice-rule", stated, that number of the magnetization vectors going in the nod-like structural elements of the IOLS and ones, going out should be equal [8]. This model can be verified to some extent by small-angle neutron diffraction. In order to interprete the results of neutron experiments correctly, one has to determine the spatial structure. Microradian diffraction of synchrotron radiation is the best way to attack this problem.

Samples and experimental techniques. The samples were synthesized by template method using as a template the films of polystyrene microspheres organized in opal-like structure (OLS). The OLS films on a conducting substrate (silicon covered by gold) were prepared by the vertical deposition of the 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 close packed structure of opal and have quasi cubic and quasi tetrahedral forms. Thickness of the samples is defined as a number of initial opal's hexagonal close packed layers, which were filled by metal. The thicknesses of studied samples are from 0.5 to 26 layers.

The experiments were performed at BM-26 (DUBBLE) with the photon energy of 13 keV (λ = 1.033 Å) and a compound of 7 refractive beryllium focusing lenses, for high resolution. Sample to detector distance was about 7 meters. Photonic Science Detector with pixel size of 22.7 x 22.7 μm^2 was used for diffraction maps capturing. Initially the samples were mounted so that the substrate was perpendicular to the beam. Vertical axis corresponds to the direction of meniscus moving at the stage of OLS synthesis. In order to determine a type of packing we have performed angle scans around vertical axis in the range of -60 ÷ 60 degrees (ω-scans, where $\omega = 0°$ is starting position) with the step of 0.5°.

Results. We studied two series of the inverse opal-like crystals based on nickel and cobalt with different number of layers. Diffraction pattern of Co-based sample with the thickness of 26 monolayers at $\omega = 0°$ is presented in Fig. 1. One can see well-resolved Bragg peaks, meaning long-range order in the sample. ω-scans allowed us to determine a type of packing and obtain different slices of the reciprocal space.

At $\omega = \pm 19°$, $\omega = \pm 35°$, $\omega = \pm 54°$ we observed diffraction patterns, corresponding to slices of the reciprocal lattice of the face-centered cubic (fcc). Couples of reflexes, which are symmetrically related to $\omega = 0°$ appears due to twinning. In ideal single-crystal only one reflex of the couple would be present in the reciprocal space. By the intensity ratio of these reflexes one can determine the fraction of corresponding twins. Thus, for all the samples with the thickness more than 3 layers fcc structure dominates, herewith the twinning takes place. Having this knowledge we can introduce the system of axes and thereby index all the reflexes (Fig.1). The vertical direction corresponds to $[20\bar{2}]$ axis, while the direction along the beam is [-1-1-1] axis.

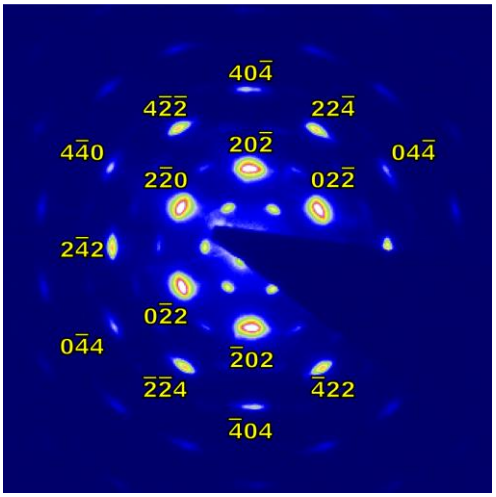

Fig. 1. Diffraction pattern for Co IOLS with thickness of 26 layers.

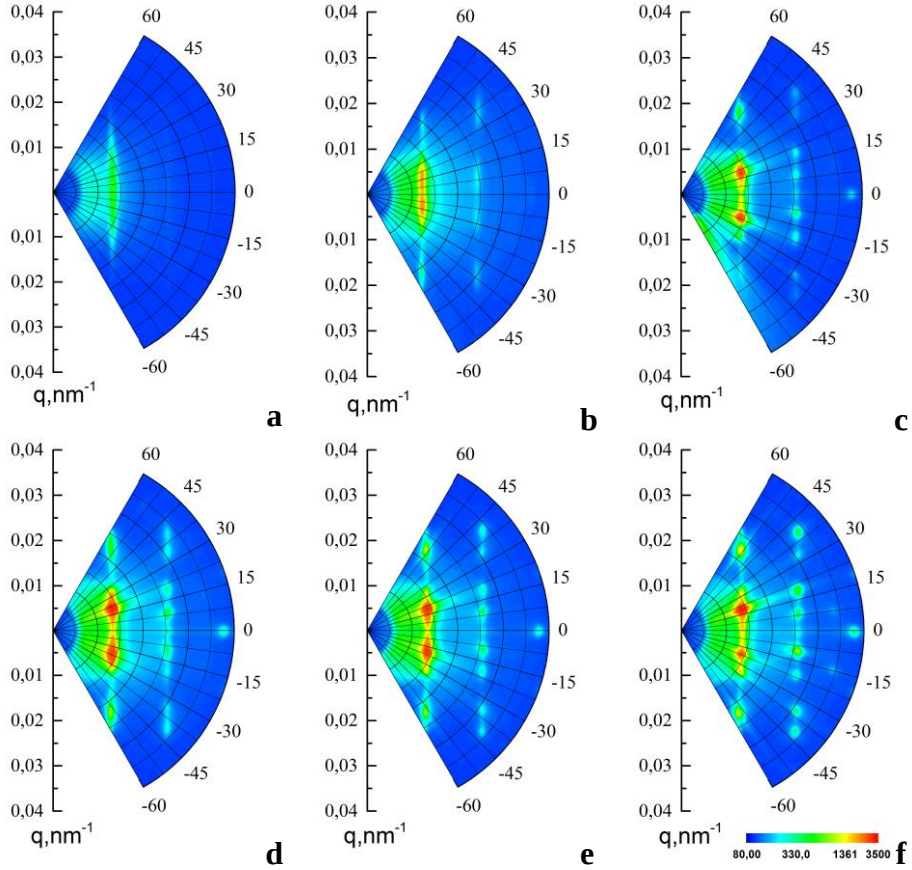

Fig. 2. Slice of the reciprocal space in plane $(h0\bar{h})$ for the IOLS based on Co with number of layers of 0.5(a), 2(b), 7(c), 17(d), 20(e), 26(f)

By analysis of reciprocal space slices taken in $(h0\bar{h})$ plane (Fig. 2) we conclude, that the quality of the crystal increases with the thickness increasing. It is confirmed by the high amount of well-resolved reflexes and low level of diffuse scattering for the thick samples on the contrary to the thin ones.

Besides the Bragg reflexes in the reciprocal space one can see also some extended features – so called Bragg rods (Fig.2a,b). These rods can appear due to stacking faults of the OLS layers or surface scattering [9].

Since the rods evolve to individual peaks with the sample thickness increasing, one can suppose, that the surface scattering is the dominant mechanism, while the stacking faults has minor contribution. However only detailed analysis of the intensity along the rods allows to determine contributions of these two sources.

Overall IOLS structure was successfully determined. All investigated samples demonstrate the set of diffraction patterns. The scattering intensity is adequately described by Bragg reflection indexes of the fcc structure for the thick IOLS films (7 - 26 layers).

References

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