DELIVERABLE REPORT

WP7 JRA2 – High precision manufacturing

D7.13

Fabrication and synchrotron characterization of 3D nanomagnets arrangement with sub-100 nm resolution

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Christian David (PSI)

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D7.13	Fabrication and synchrotron characterization of 3D nanomagnets arrangement with sub-100 nm resolution

DELIVERABLE DESCRIPTION

The deliverable aims at fabrication of mesoscopic 3D magnetic structures by laser polymerization of 3D scaffolds and their post-processing to endow them with magnetic properties. The produced structures are examined using high resolution x-ray tomography and their ferromagnetic resonances are experimentally investigated.

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NATURE

P - Prototype

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☒ P - Public
☐ PP - Restricted to other programme participants & EC: (Specify)
☐ RE - Restricted to a group (Specify)
☐ CO - Confidential, only for members of the consortium

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Contents

Executive Summary

Advanced patterning techniques allowing the production of nanoscale structures have enabled breakthroughs in multiple fields of science. In particular, over the past decades, tailoring the shape of magnets on the nanoscale has enabled the study of a large number of novel quasi-static and dynamic phenomena in nanostructured magnetic materials. In recent years, a novel class of magnetic materials – artificial spin ices – has been the focus of intense research because it displays a rich spectrum of emergent phenomena. Artificial spin ices are composed of geometrically frustrated arrangements of interacting nanomagnets and have mainly been used to investigate fundamental aspects of the physics of frustration. They also have the potential to become a class of functional materials with technological applications. Indeed, it has been shown that spin ices support topological defects [1], can be tailored to act as metamaterials for spin waves [2], and even to realize thermal ratchets [3]. However, only 2D 'flat' structures have been studied so far.

The study of magnetism in 3D nanostructures is a young field of research and has mainly been limited to simple three dimensional magnetic nanostructures such as cylinders and nanotubes. Those studies have for example demonstrated that curvature can give rise to novel magnetochiral effects in the presence of magnetic fields [4]. Such effects are promising for applications, in particular for data storage concepts, which rely on magnetic domain walls to store bits of information. In contrast, our goal was to extend artificial spin systems into three dimensions and to study aspects of their collective dynamics on the nanosecond time scale. Indeed, so far only the quasi-static behavior of free-form ferromagnetic 3D structures, such as magnetization reversal and hysteretic behavior, has been investigated [5]. Our study of the GHz dynamics in 3D structures opens the possibility of investigating the influence of finite-size effects on the dynamic response of the magnetization, in particular of spin waves, and of exploring the possibility of creating functional materials, such as reconfigurable magnonic crystals [6].

Investigating such systems requires specific fabrication and measurement techniques.

The deliverable addresses these challenges and aims at:

- DEVELOPING TECHNIQUES ALLOWING FOR FABRICATION OF FREE FORM 3D MAGNETIC STRUCTURES AT THE MICRO/NANO-SCALE;
- USING STATE-OF-THE-ART METHODS TO INVESTIGATE COMPOSITION OF 3D MAGNETIC STRUCTURES AND THEIR MAGNETIC PROPERTIES.

In our approach, the fabrication of 3D magnetic structures is based on high resolution laser scaffolding technique developed previously within NFFA and described in report of MS9 "Sub-100 nm 3D photopolymer structures fabricated by non-linear laser lithography". The reported technique enables production of high quality sub-100 nm resolution free form resist scaffolds. These scaffolds are later uniformly coated by a few nanometer thick conductive layer and electroplated by nickel to obtain a magnetic structure.

Synchrotron-based imaging techniques were used for the structural characterization of the fabricated 3D magnetic samples. In particular, high resolution ptychographic tomography was carried out at the cSAXS beamline (Swiss Light Source) revealing a mostly homogeneous nickel film coating around the polymerized scaffold. For studying the magnetization dynamics, the 3D structures were transferred into microresonators by using micromanipulators and the ferromagnetic response was measured as a function external magnetic field strength and angle with respect to the structure to achieve a full 3D characterization. The recoded complex periodic ferromagnetic resonance signal indicates the effect of the three dimensional structure on the magnetic resonances. Further studies of these architectures should give insights into three dimensional nanomagnetism and provide a basis for tailoring collective behavior, which can be used to design novel functional magnetic micro-devices.

1. Concept

For the past decades, magnetism has mainly been studied in two-dimensional thin films. It is only recently that three-dimensional structures have started to be studied thanks to the development of novel lithography and self-assembly techniques. Based on these developments, it is now possible to experimentally verify theoretical predictions of the novel magnetic properties expected in curved thin films. Indeed, in the presence of an external magnetic field, curvature has been predicted to break chiral symmetry in a ferromagnet [1]. In nanotubes, it should lead to a preferred direction of domain wall propagation [7] as well as asymmetric spin wave dispersion [8]. It has also been shown that ferromagnetic resonances are strongly modified in topographically modulated thin films with spherical curvature [9].

As a proof of concept for the fabrication of 3D magnetic structures and investigation of their dynamic magnetic properties we have chosen a mesoscopic buckyball structure, composed of an assembly of nanotubes. In this structure, the vertices correspond to the location of the carbon atoms in the C_{60} molecule and the bars connecting the vertices correspond to the molecular bonds. The developed fabrication approach is based on scaffolding by high resolution 3D laser lithography and post processing steps to form high quality magnetic structures. Uniformity and layer quality of magnetic coatings on 3D scaffolds were evaluated using x-ray ptychographic tomography, which allowed us to measure the structure of the fabricated samples with high spatial resolution.

The investigation of the magnetic properties of the mesoscopic buckyballs has focused on their spin wave modes, which were experimentally measured by placing the structures into microresonators. These allow carrying out very sensitive ferromagnetic resonance measurements on single buckyball structures by detecting the oscillations of the magnetization in the 3D structure through excitation with an external magnetic field. The external field direction and amplitude were varied to record the mode spectrum of the structure.

2. Fabrication

2.1 3D scaffold

The fabrication uses multiphoton laser polymerization, which has recently emerged as a high resolution free-form three dimensional structuring technique. The technique provides great flexibility in envisioning and designing structures for various applications and so far has been widely used to produce metamaterials, photonic crystals and scaffolds for tissue engineering [10]. Commercially available three dimensional lithography systems reach sub-micron resolution in the plane perpendicular to the optical axis of the writing beam. However, the resolution along the axis is typically two to three times lower due to a weaker confinement of light along this direction and, as a result, elongated voxels are produced.

In three dimensional laser lithography, high resolution buckyball structures are typically made by properly combining single voxel lines. Nonetheless, in this case, oval rather than round bar cross-sections are obtained, resulting in difficulties to disentangle various magnetic phenomena occurring in the structure. One solution to mitigate the initial voxel elongation is composing the bars of a few overlapping lines, but this increases dimensions of the entire structure. A way around it is first to polymerize larger scaffolds with round cross-sections of the composing bars and then to scale them down by pyrolysis and plasma etching. This size reduction method has been developed previously within NFFA joint research activities and is explained in report of MS9 “Sub-100 nm 3D photopolymer structures fabricated by non-linear laser lithography”. The method is based on mass loss of cross-linked polymer at high temperatures, resulting in uniform shrinkage of the 3D structure; then the resist turns into glassy carbon. The shrunk structure is then further thinned down by isotropic etching in an oxygen plasma to reach the required dimensions.

The investigated buckyball structures were obtained through laser polymerization using commercially available 3D laser lithography system (Photonic Professional GT, Nanoscribe GmbH) and high resolution photoresist IP-Dip (Nanoscribe GmbH). The used resist allows for fivefold size reduction of the polymerized structure preserving its proportions when the cross-linked resist is pyrolyzed at ca. 700 oC and turned into a glassy carbon. Several structures were 3D printed on a single silicon chip and scaled down by pyrolysis and oxygen plasma etching as described in MS9 report. Scanning electron micrographs of the produced scaffold are shown in Fig. 1. The final structure is 5 µm in diameter and the constituent bars are ca. 300 nm thick. As mentioned before, the main challenge in polymerizing these high resolution scaffolds is having close-to-one aspect ratio of the cross-linked resist lines. Nonetheless, due to the applied post-processing steps, we were able to fabricate structures with the composing bars having aspect ratios <1.1. Figure 2 shows a high magnification SEM image of buckyball scaffold illustrating close to perfect aspect ratio of the glassy carbon bars.

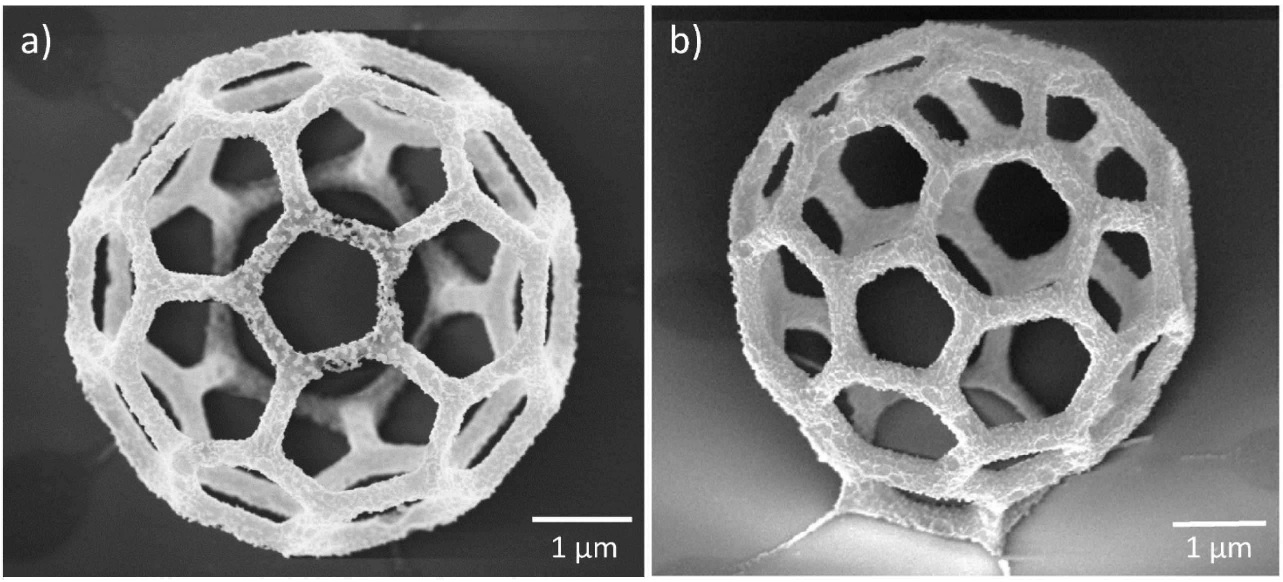

Figure 1 – SEM images of produced glassy carbon scaffold: a) top view; b) 45^{o} tilt view.

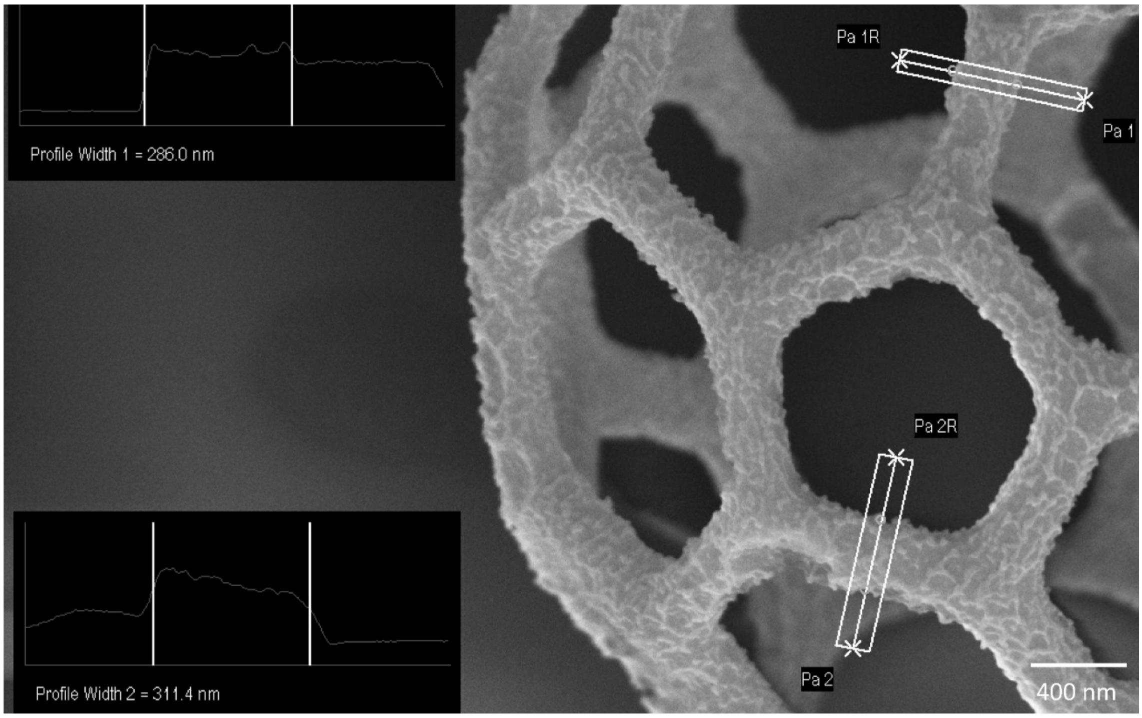

Figure 1– Close up image of the buckyball scaffold showing close-to-one aspect ratio of the composing bars.

2.2 Magnetic coating

The polymerized resist is nonmagnetic and post-processed scaffolds need to be further altered to endow them with magnetic properties. In the past this has been done by sputtering laser polymerized scaffold with a magnetic material, for example cobalt [11]. However, in that case, the scaffold coverage by sputtered Co film was irregular due to shadowing effects. To produce a structure with a more homogeneous magnetic coating, an alternative fabrication technique has been developed in the framework of this deliverable.

In our approach, electroplating instead of sputtering was employed to avoid shadowing effects and to form homogeneous magnetic coatings. Growing a film on 3D structure from an electrolyte solution via electrodeposition requires good electrical conductivity of the surface being plated. However, in our case, the buckyball scaffolds were highly resistive. We thus first coated the polymer scaffold with iridium using atomic layer deposition technique. The technique allows for homogeneous coating of various 3D structures with a possibility to control the film thickness at the sub-nanometer level. In our case, a few nanometer thick iridium layer was sufficient to form a conductive electroplating base over the entire 3D structure. Figure 3 shows SEM images of buckyball scaffolds uniformly coated by an Ir layer.

After forming the plating base, the scaffolds were placed in a nickel plating bath for deposition of the magnetic layer. The submerged samples were agitated to remove air trapped in the middle of the 3D structure. Then the plating was done in a pulsed mode at 2.11 Hz and pulse amplitude of 25 mA. The final result was mesoscale 3D structures composed of magnetic nanotubes. Figure 4 shows SEM images of magnetic buckyballs composed of nickel tubes of 300 nm – 450 nm in diameter and having sidewall thickness of 20 nm – 50 nm. Several samples were prepared for characterization.

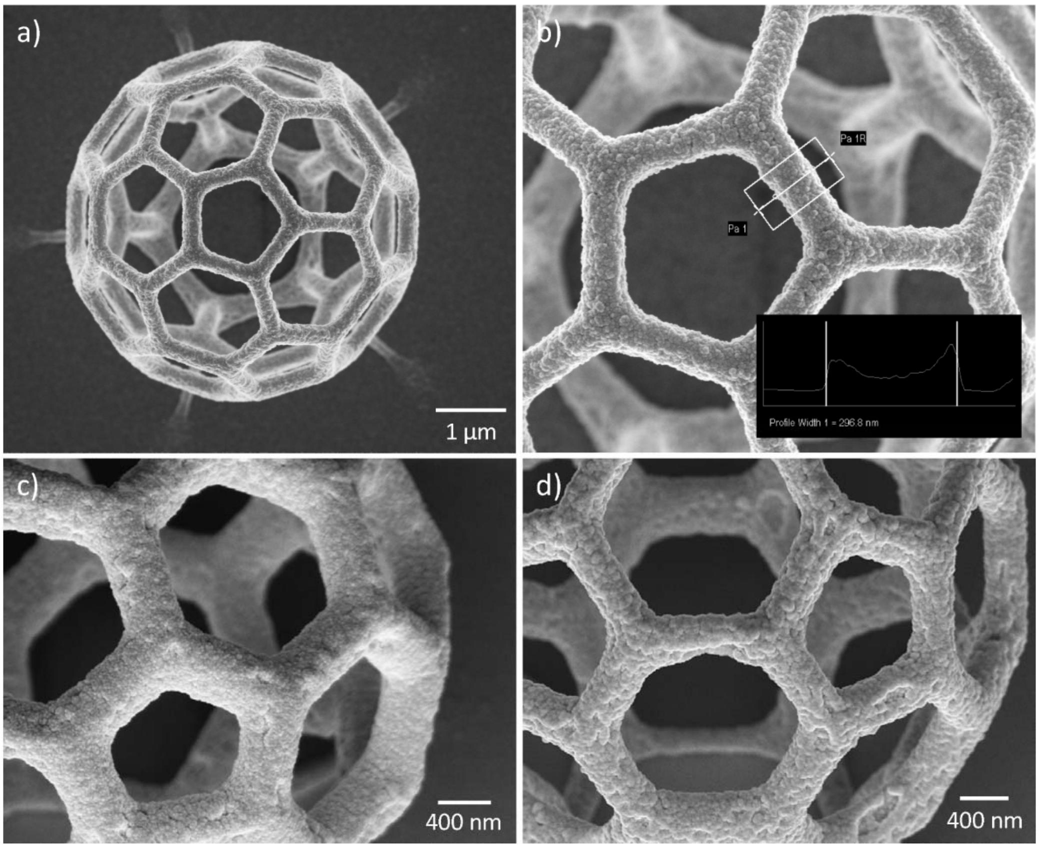

Figure 3 – SEM images of iridium coated scaffolds: a) and b) – top view; c) and d) - view at 45° angle.

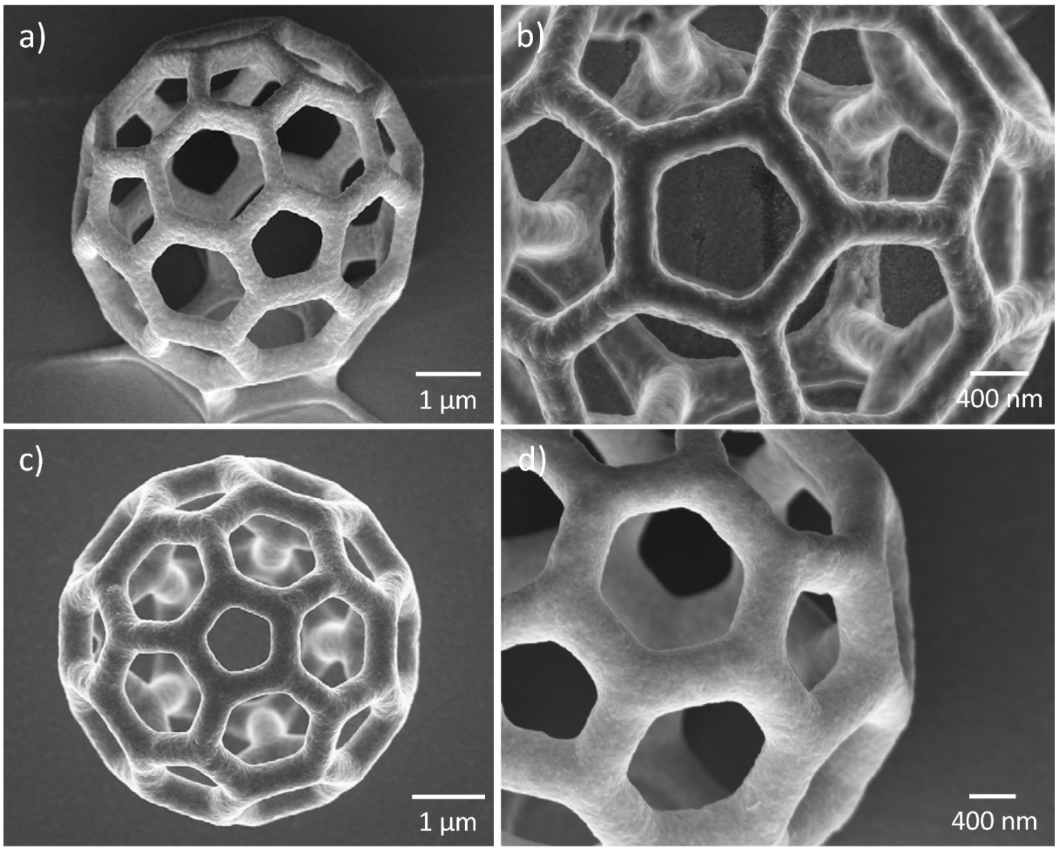

Figure 4 – SEM images of plated buckyballs: a) and b) - structure composed of ca. 300 nm in diameter nickel tubes with the sidewall thickness of ca. 20 nm; c) and d) - structure having bar width of ca. 450 nm and ca. 50 nm thick nickel coating.

2.3 Transfer into microresonators

In order to experimentally investigate feromagnetic resonances of the fabricated magnetic strcutures, the buckyballs had to be transfered from the initial silicon substate into the measurement microresonators. The transfer has been done in a FIB/SEM chamber using a set of micromanipulators (Kleindiek Nanotechnik GmbH). The microresonators and silicon chip with plated buckyballs were placed together in the chamber. The buckyballs were then detached from the substrate by grabbing with the micromanipultor needles and gently lifting them up (Fig. 5a). Each buckyball was individually moved into separate microresonator and fixed in place by focused ion beam induced deposition of platinum. Figure 5b shows an SEM image of the transfered structure that is placed into the coil microresonator and ready for the experiments.

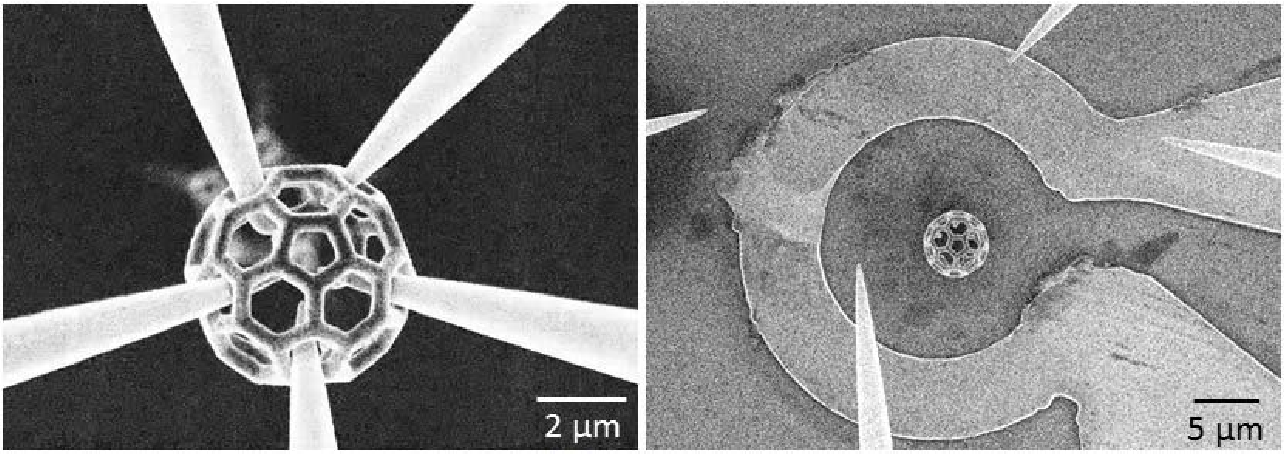

Figure 5 – Transfer of the plated structures into the microresonators: a) a buckyball grabbed by a set of micromanipulator needles and lifted from the silicon substrate; b) the structure placed in the coil microresonator and ready to be measured.

3. Characterization

3.1 Tomography

Structural characterization of the Ni film was performed using hard X-ray nanotomography in order to determine the uniformity of the nickel coating. Indeed, electroplating is well-suited for coating two-dimensional surfaces and it was not clear if the nickel film would be uniform around the 3D structure due to: 1) the larger distance of certain regions of the buckyball from the flat electrode and 2) the possibility that the buckyball structre formed a Faraday cage, thus hindering plating.

Ptychography based nanotomography [12] was performed at an energy of 6.2 keV at the cSAXS beamline of the Swiss Light Source. Measurements of the strucutre were performed for ca. 500 different angles covering an angular range of 180 degrees. This allowed us to achieve a spatial resolution of ca. 20 nm in three dimensions. The identification of the different materials (glassy carbon, iridium, nickel, air) was achieved based on segmentation of the reconstructed electron densities within the sample. Fig. 6a shows the reconstructed sample, which has a diameter of 5 µm. In Fig. 6b, the different phases are distinguished based on the measured electron densities. Two main results were obtained:

- THE THICKNESS OF THE ELECTROPLATED NICKEL FILM WAS FOUND TO BE RATHER UNIFORM ACROSS THE BUCKYBALL HEIGHT, WITH 50% MORE NICKEL ELECTRODEPOSITED ON THE EXTERIOR OF THE STRUCTURE, AS COMPARED TO THE INTERIOR OF THE STRUCTURE. THIS IS MOST LIKELY DUE TO PARTIAL SHIELDING OF THE ELECTRICAL FIELD AT THE CENTER OF THE BUCKYBALL.
- NICKEL FILM IS PRESENT ON BOTH SIDES OF THE IRIDIUM COATING, THUS LOCALLY CREATING DOUBLE-WALLED NICKEL TUBES. THIS CAN BE EXPLAINED BASED BY THE FACT THAT THE PYROLIZED POLYMER WAS POROUS, LEADING TO A POROUS AND PERMEABLE IRIDIUM COATING.

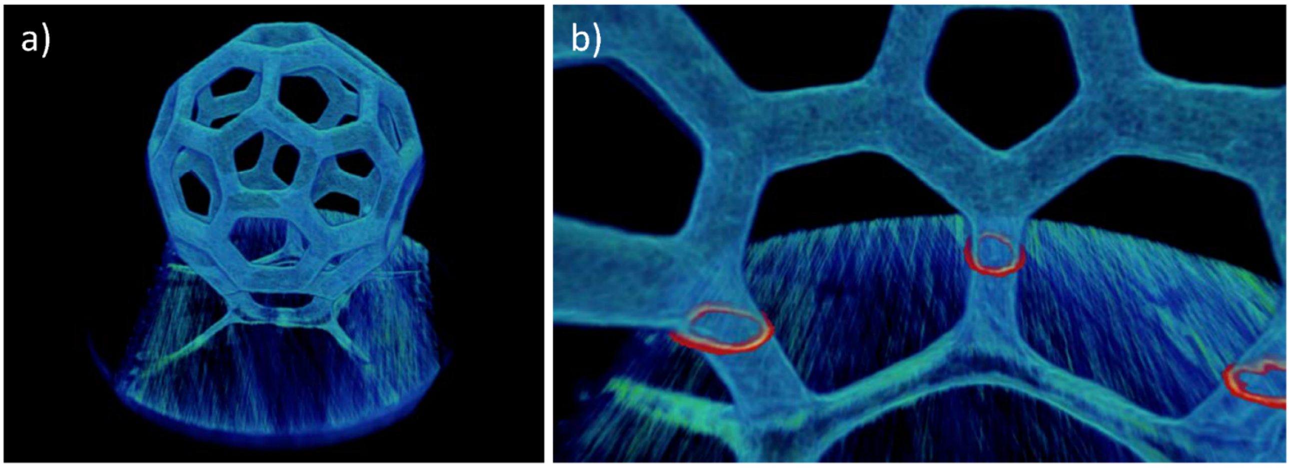

Figure 6 – a) Reconstructed mesoscopic buckyball structure based on ptychographic tomography. Its diameter if of 5 **μm.** b) The coloured cutplane shows material segmentation based on electronic densities: the yellow rings correspond to iridium, while the red rings correspond to nickel, defining magnetic nanotubes. It can be seen that nickel is not only present outside the Ir coated region, as would be expected. It is also occasionally present inside the nanotubes, owing to the porous nature of the polymer scaffold and, consequently, of the iridium film.

3.2 Feromagnetic resonance

Ferromagnetic resonance measures the precessional motion of the magnetization in an external field. While bulk ferromagnets display a uniform precessional mode, in laterally-confined nanostructures, additional modes are present owing to the inhomogeneous magnetostatic field created by the magnetization at the edges of the film, giving rise to edge modes. A recent study of two dimensional artificial spin ice systems, which consist of magnetostatically coupled nanomagnets, has shown that these can exhibit well-defined edge modes as well as mode splitting depending on their local magnetic state [13]. The interest in these modes comes from the fact that the spin wave mode spectrum can reveal the existence of topological defects (such as charge monopoles) within such systems without the need for directly imaging them. Surprisingly, it has been found that the mode spectrum is also related to the zero point entropy of spin ice systems [14]. The mesoscopic buckyball is thus an ideal 3D artificial spin system, allowing to study the role of geometry and magnetic state in three dimensions.

For the characterization of the spin wave excitations of the system, ferromagnetic resonance was performed using planar microresonators (Fig. 5b) that significantly enhance the sensitivity of the technique, allowing the detection of the spin wave stpectrum at fixed frequency as a function of static magnetic field strength in single buckyball structures [15]. The measurements were performed in the framework of a collaboration with the Helmholtz Zentrum Dresden Rossendorf. These measurements allow determining magnetic anisotropy and magnetization relaxation. Fig. 7 shows a spectrum obtained using a buckyball with a 20 nm nickel coating. The spectrum displays the same five-fold symmetry as the buckyball structure, reflecting the fact that shape anisotropy plays a doinant role in defining the spin wave modes of the system. Micromagnetic simulations are presently being perfomed in order to elucidate the origin of the measured modes.

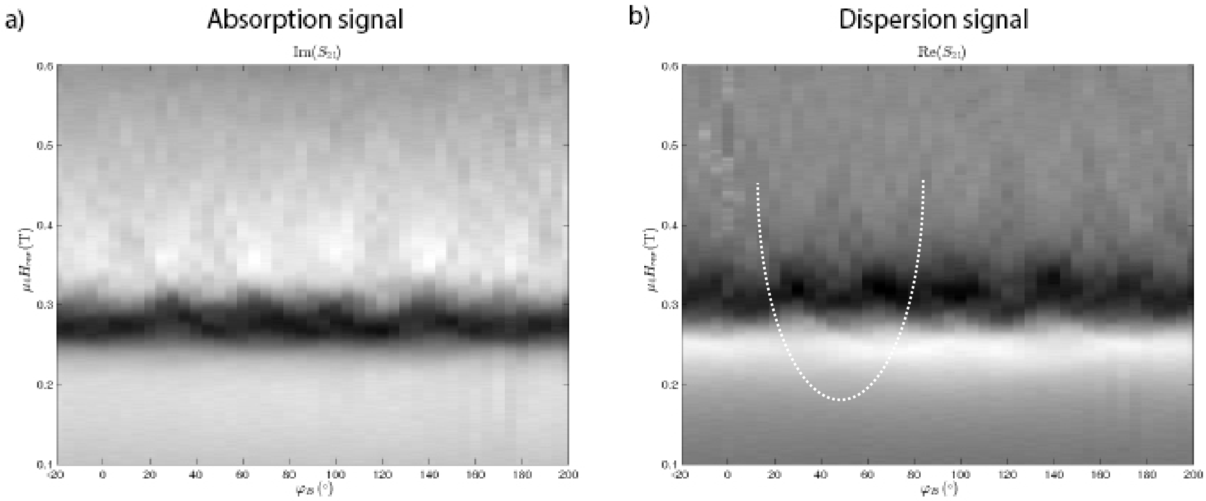

Figure 7 - Field-dependence (μ_0H) of the (a) microwave resonant absorption intensity and (b) dispersion signals measured at 13.9 GHz for a single buckyball as a function of field angle φ (between -20 degrees and 200 degrees), covered by a 20 nm thick nickel film. The white dotted parabola is an eye guiding line to better visualise five-fold symmetry of the spectrum. The rather faint signal is due to the low nickel film thickness. We are presently measuring buckyballs with 50 nm nickel film thicknesses, which are expected to yield a stronger signal.

4. Conclusions

Fabrication of mesoscale 3D magnetic structures has been successfully demonstrated by producing high resolution 3D scaffold and electroplating of nickel. Uniformity of the nickel coating was determined by structural characterization using hard X-ray nanotomography with a spacial resolution of ca. 20 nm. The tomography revealed homogeneous Ni coating inside and outside of the 3D architecture. However, the thickness of the magnetic coating was lower in the inner side of the structure, most probably due to shielding effects during the elecroplating.

Characterization of the spin wave exitations in magnetic buckyball was carried out by measuring ferromagnetic resonance of the 3D structure. The plated buckyballs were transferred into microresonators to enhance the measurement sensitivity. As expected, the recorded feromagnetic resonance spectra display five-fold symmetry and indicating the fact that shape anisotropy plays a doinant role in defining the spin wave modes of the system. Further studies of these architectures should give insights into three dimensional nanomagnetism and provide a basis for tailoring collective behavior, which can be used to design novel functional magnetic micro-devices.

The main results obtained in the course of the joint research activity on this deliverable have been published in the following papers:

- G. SENIUTINAS, A. WEBER, C. PADESTE, I. SAKELLARI, M. FARSARI, C. DAVID. "BEYOND 100 NM RESOLUTION IN 3D LASER LITHOGRAPHY - POST PROCESSING SOLUTIONS." *MICROELECTRONIC ENGINEERING*, 191, 25-31 (2018);
- S. GLIGA, G. SENIUTINAS, A. WEBER, C. DAVID. "ARCHITECTURAL STRUCTURES OPEN NEW DIMENSIONS IN MAGNETISM". *MATERIALS TODAY* (ACCEPTED MANUSCRIPT).

References

[1] E. Mengotti, L. J. Heyderman, A. F. Rodríguez, F. Nolting, R. V. Hügli, H. B. Braun, *Real-space observation of emergent magnetic monopoles and associated Dirac strings in artificial kagome spin ice,* Nature Physics,7(1), 68, 2011.

[2] E. Iacocca, S. Gliga, R. L. Stamps, O. Heinonen, *Reconfigurable wave band structure of an artificial square ice,* Physical Review B,93(13), 134420, 2016.

[3] S. Gliga, G. Hrkac, C. Donnelly, J. Büchi, A. Kleibert, J. Cui, A. Farhan, E. Kirk, R. J. Chopdekar, Y. Masaki, N. S. Bingham, A. Scholl, R. L. Stamps, L. J. Heyderman, *Emergent dynamic chirality in a thermally driven artificial spin ratchet,* Nature Materials,16(11), 1106, 2017.

[4] R. Hertel, *Curvature-induced magnetochirality,* Spin, World Scientific Publishing Company, 3(3), 340009, 2013.

[5] L. Keller, M. K. Al Mamoori, J. Pieper, C. Gspan, I. Stockem, C. Schröder, S. Barth, R. Winkler, H. Plank, M. Pohlit, J. Müller, M. Huth, *Direct-write of free-form building blocks for artificial magnetic 3D lattices,* Scientific Reports,8(1), 6160, 2018.

[6] M. Krawczyk, D. Grundler, *Review and prospects of magnonic crystals and devices with reprogrammable band structure,* Journal of Physics: Condensed Matter, 26(12), 123202, 2014.

[7] M. Yan, C. Andreas, A. Kákay, F. García-Sánchez, R. Hertel, *Chiral symmetry breaking and pair-creation mediated Walker breakdown in magnetic nanotubes,* Applied Physics Letters, 100(25), 252401, 2012.

[8] J. A. Otálora, M. Yan, H. Schultheiss, R. Hertel, A. Kákay, *Asymmetric spin-wave dispersion in ferromagnetic nanotubes induced by surface curvature,* Physical Review B, 95(18), 184415, 2017.

[9] J. Sklenar, P. Tucciarone, R. J. Lee, D. Tice, R. P. H. Chang, S. J. Lee, I. P. Nevirkovets, O. Heinonen, J. B. Ketterson, *Ferromagnetic resonance in a topographically modulated permalloy film,* Physical Review B, 91(13), 134424, 2015.

[10] M. Malinauskas, A. Žukauskas, S. Hasegawa, Y. Hayasaki, V. Mizeikis, R. Buividas, S. Juodkazis, *Ultrafast laser processing of materials: from science to industry,* Light: Science & Applications, 5(8), e16133, 2016.

[11] C. Donnelly, M. Guizar-Sicairos, V. Scagnoli, M. Holler, T. Huthwelker, A. Menzel, I. Vartiainen, E. Müller, E. Kirk, S. Gliga, J. Raabe, L. J. Heyderman, *Element-specific X-ray phase tomography of 3D structures at the nanoscale*, Physical Review Letters, 114(11), 115501, 2015.

[12] M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen, E. Färm, E. Härkönen, M. Ritala, A. Menzel, J. Raabe, O. Bunk, *X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution*, Scientific Reports, 4, 3857, 2014.

[13] S. Gliga, A. Kákay, R. Hertel, O. G. Heinonen, *Spectral analysis of topological defects in an artificial spin-ice lattice,* Physical Review Letters, 110(11), 117205, 2013.

[14] S. Gliga, A. Kákay, L. J. Heyderman, R. Hertel, O. G. Heinonen, *Broken vertex symmetry and finite zero-point entropy in the artificial square ice ground state,* Physical Review B, 92(6), 060413, 2015.

[15] H. Cansever, R. Narkowicz, K. Lenz, C. Fowley, L. Ramasubramanian, O. Yildirim, A. Niesen, T. Huebner, G. Reiss, J. Lindner, J. Fassbender, A. M. Deac*, Investigating spin-transfer torques induced by thermal gradients in magnetic tunnel junctions by using micro-cavity ferromagnetic resonance*, Journal of Physics D: Applied Physics, 51(22), 224009, 2018.