ESRF	**Experiment title:** **EXAFS study of Pt-Co and W-Co alloys in metal-capped Co nanoparticles**	**Experiment number:** HE-2952
Beamline: BM29	**Date of experiment:** from: February 11th, 2009 to: February 16th, 2009	**Date of report:** March 25th, 2009 Received at ESRF:
Shifts: 15	**Local contact(s):** Dr. Sakura PASCARELLI	

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In the proposal of experiment HE-2952 we proposed to perform EXAFS to quantitatively describe the local structure of granular $(Al_2O_3/Co/M)_N$ samples, where M=Pt and W. These granular Co thin film multilayers constitute a family of nanoparticle systems which have been very useful for understanding size effects in magnetism. We have previously studied these properties in Co clusters produced by sputtering of Co on amorphous alumina, both uncapped [1] and metal capped [2], in order to modify the surrounding matrix and study its effect in the magnetic properties of the particles.

Metallic W capping particles show a superparamagnetic behaviour above a blocking temperature T_B which increases with t_{Co} (nominal thickness of Co), similar to those of uncapped, and Cu and Au capping. However, according to magnetization and susceptibility measurements performed in a SQUID magnetometer and XMCD measurements performed at ID12-ESRF beamline, on these W-capped samples the saturation magnetization per atom decreases strongly with decreasing t_{Co}, for a fixed t_W, and it also decreases with increasing width of the W capping, for a fixed t_{Co}, below T_B. These results are consistent with a model that assumes the formation of a magnetic dead shell around the Co core of the nanocluster, of Co:W alloys. The amount of W and the effective surface of the particle surface would modulate the thickness of the dead shell, reducing the size of the magnetic Co core, thereby, modifying the fraction of magnetic Co with respect to the total deposited, and the particle anisotropy.

Instead, capping with Pt has a completely different effect, as Co particles are strongly coupled via the polarized Pt [3]. Magnetization hysteresis curves measured on granular $(Al_2O_3/Co/Pt)$ multilayers show an extremely strong Perpendicular Magnetic Anisotropy (PMA). The coercive field at low temperature is as high as μ0HC=0.5 T at 1.8 K. A model based on particles conformed as a Co core surrounded by a Co_xPt_{1-x} shell, embedded in Pt and coupled magnetically by dipolar or RKKY interaction may explain the phenomenology of this system.

In the HE-2952 experiment, XAS spectra for $(Al_2O_3/Co/W)_{25}$ samples, t_W= 0.6, 1.5, and 4.5 nm, were taken at the Co K and W L_3 edges. Similarly, spectra for $(Al_2O_3/Co/Pt)_{25}$ samples with nominal Pt capping thickness t_{Pt}= 0.6, 1.5, 4.5 and 6.0 nm, were taken at the Co K and Pt L_3 edges. Reference samples were also measured at different edges: uncapped particles $(Al_2O_3/Co)_{20}$ measured at the Co K edge, CoPt and $CoPt_3$ alloys measured at the Co K and Pt L_3 edges, Co_3W alloy measured at the Co K and W L_3 edges, Au capped particles with formula $(Al_2O_3/Co/Au)_{25}$, t_{Au}= 1.5 and 4.5 nm, measured at the Co K and Au L_3 edges, Cobalt film measured at the Co K edge, Pt film measured at the Pt L_3 edge, W film measured at the W L_3 edge and Au film measured at the Au L_3 edge. For each edge measured on each sample, four spectra were taken in order to have enough statistics in data treatment, following a 4s/point count.

Part of spectra measured for the W-capped NPs at the Co K edge are shown in the following graphs.

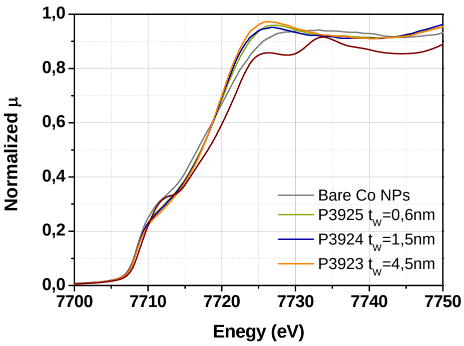

Fig. 1. XANES at the Co K edge on different W capped Co – NPs with a constant t_{Co} = 0.7 nm and comparison with uncapped Co – NPs and Co Foil.

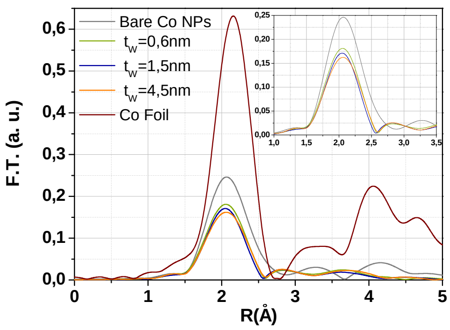

Fig. 2. Fourier Transform of EXAFS signal at the Co K edge on the samples showed in Fig. 1. Inset: Zoom of the first coordination shell peak for the Co –NPs systems.

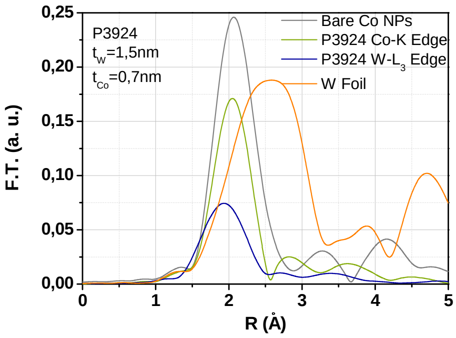

Fig. 3. Comparison of peaks in the Fourier Transform of EXAFS signal both at the Co K edge and W L_3 edge for one of the W - capped samples, uncapped Co – NPs and a W foil.

Fig 1 shows XANES spectra at Co K edge for uncapped and W-capped Co NPs with a constant t_{Co} = 0.7 nm, as well as for Co foil. It can be noticed how the intensity of the pre-edge decreases while the white line increases significantly in the Co NPs systems, especially in W-capped Co NPs, compared to those in Co foil.

Structural analysis that can be extracted from EXAFS signal is better studied by its Fourier Transform, shown in Fig 2. It can be seen that position and shape of the peaks in Co-NPs and Co foil are very similar, not only for the first coordination shell, but also for outer shells, showing how cobalt in Co/Al_2O_3 aggregates in a similar structure as metallic Co, as it has been reported in literature [4]. However, peaks for outer coordination shells are different in W- capped NPs, possibly given by a change in the Co coordination because of the presence of alloying between Co – W. Intensities of all peaks are greater in the Co foil than in the particulate systems, as it is expected from the reduction in Co coordination. This trend is also observed among the W-capped NPs (Fig 2 - inset), having a reduction of the peak amplitude as the W layer gets thicker, from t_W= 0 nm (Bare Co NPs) to t_W=4.5nm (P3923), which might be an evidence of less Co coordination given by a **reduction in the Cobalt core size**. This result is in agreement to the model of creation of a magnetic dead shell around the Co-NPs proposed after magnetic measurements on these systems.

Following this preliminary analysis of EXAFS data obtained in experiment HE-2952, we have compared spectra taken both at the Co K edge and W L_3 edge for one W-capped sample (t_W=1.5nm and t_{Co}=0.7nm), with spectra taken for uncapped Co - NPs and W foil. These data is shown in Fig 3. It can be seen how spectrum taken at W L_3 for W – capped Co – NPs has changed, compared to that of metallic W, possibly due to a change in W neighbourhood by the presence of Co and Co:W alloying.

We have asked for a continuation on experiment HE-2952 to perform similar EXAFS measurements on granular $(Al_2O_3/Co/Pd)$ multilayer samples at the Co K edge and the Pd K edge with the aim of completing the structural analysis on $(Al_2O_3/Co/M)_N$ multilayer samples and to correlate magnetism results with their nano-structure.

References

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