ESRF	**Experiment title:** "Magnetism of compact surface-supported Fe nanoclusters"	**Experiment number**: HE 2212
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Report:

The aim of proposal HE 2212 was to study the magnetic properties of relaxed 3d metal nanoclusters on different surfaces in order to compare them with epitaxially grown clusters of comparable size and density. Experimentally, this was realized by studying the magnetism of clusters fabricated by buffer layer assisted growth (BLAG) [1] on metal surfaces. During BLAG, clusters are formed on a Xenon layer of several monolayer thickness, which covers the substrate surface. With this method, compact and relaxed clusters can be studied both while still situated on the Xenon layer and in contact with surfaces after desorbing the Xenon layer. This method, thus, is substantially different from the molecular beam epitaxy (MBE) approach: in the latter the growth is mainly governed by the interaction of single impinging atoms with the substrate and, with increasing coverage, by the lattice mismatch leading to strain. The results in this report show on the one hand the clear difference between clusters prepared by MBE and BLAG. On the other hand the influence of the substrate on the magnetic anisotropy of the clusters becomes evident. In the case of Co cluster, Pt(111) and Ag(111) substrates induce an out-of plane and in-plane magnetic easy axis direction, respectively.

Experimental

The substrates were cleaned under ultra-high vacuum (UHV) ($<10^{-9}$mbar) conditions by Ar ion beam sputtering/surface annealing cycles. Cleanliness and surface order was verified using Auger and LEED. In order to prepare 3d metal clusters on surfaces using the BLAG technique a retractable 20cm long doser tube with a Xe inlet system was added to the magnet chamber. For adsorption of Xe at temperatures of 30K the end of the doser tube was positioned at a distance of 1cm away from the substrate. The Xe thickness on the substrate could be well controlled by the inlet system, which defined the amount of Xe gas flowing through the tube with a pressure gradient of $3x10^{-3}$mbar. A triple evaporator was also mounted on the magnet-chamber to allow subsequent Co or Fe deposition onto the Xe layer at low temperatures. After deposition the sample was warmed up to 120 K to desorb the Xe and bring the 3d metal clusters in contact to the substrate. The final cluster size depends on the Xe coverage and the amount of 3d metal evaporated on top. Larger amounts of Xe and/or 3d metal lead to larger cluster sizes. Systematic STM studies done in the run-up to the HE 2212 beamtime allows us to control the cluster size and density within a wide range. The 3d metal coverage was chosen in the range of 0.1 and 0.6ML, while the Xe thickness was varied. X-ray absorption spectra (XAS) at the $L_{2,3}$ edge were recorded for circularly polarized light as a function of angle with the surface normal, of the applied magnetic field, and of temperature. The spectra are taken in the highly surface sensitive total electron yield (TEY) mode. Along the magnetic easy axis and hard axis directions magnetic magnetization curves up to fields of 4.5T were measured. Possible oxygen contaminations during the BLAG procedure were excluded measuring the oxygen K-edge at 543.1eV.

Results

Table 1 gives an overview of the prepared samples measured during HE 2212. From previous XMCD experiments on 3d metals on Pt(111) we are able to estimate the amount of evaporated 3d metal from the intensity of the XAS signal at the $L_{2,3}$ edge. For all samples the amount of adsorbed Xe was monitored by looking at the $M_{3,2}$ absorption lines shown in the inset of Fig. 1.

Table 1

		Xe exposure time	Estimated Xe thickness	Easy axis after desorption
#1	0.1MLCo/Pt(111)	2 minutes	7 ML	polar
#2	0.1MLCo/Ag(111)	2 minutes	7 ML	in-plane
#3	0.1MLCo/Ag(111)	20 minutes	70ML	in-plane
#4	0.6MLFe/Pt(111)	20 minutes	70ML	in-plane

Before desorption of the Xenon the 3d metal clusters exhibited no preferred magnetic direction as shown in Fig. 1 for the case of 0.1MLCo/Xe/Ag(111). Moreover, no remanence was observed at 30K in any of the samples at the stage before Xe-desorption. This suggests that 3d metal clusters on cold Xe-layers stay rather small due to slow diffusion, leading to a superparamagnetic behavior with blocking temperatures much lower than 6K. We want to point out that it is rather surprising that despite the insulating Xe layer the quality of the 3d metal XMCD signal remained rather good. Nevertheless, small charging effects in the TEY due to lack of grounding can not be excluded at this stage of evaluation.

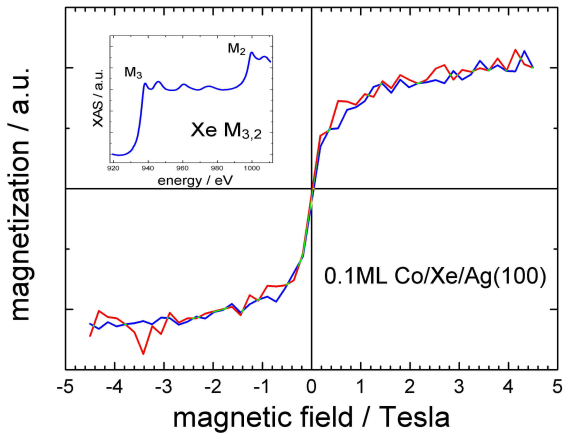

Fig. 1:
Magnetization curve of Co ontop of a Xe buffer layer measured on the Co L_3 line at 30K. The inset shows the Xenon signal measured at the Xe $M_{3,2}$ edge.

The influence of the substrate on the magnetic properties reveals itself after desorption of Xenon. A direct comparison of samples #1 and #2 grown with the same BLAG parameters are shown in Fig. 2, where the magnetization curves measured at angles 0° and 70° are shown at a temperature of 6K. While in the case of Pt(111) the Co clusters exhibit a pronounced out-of-plane (0°) easy axis, they prefer the in-plane direction on Ag(111). In addition, the Pt(111) substrate stabilizes the magnetization leading to a remanent magnetization at zero fields. In the case of Ag(111) the cluster stay superparamagnetic in all directions even at the lowest temperature of T = 6K. In both cases the spin and orbital moments per Co atom along the easy axis measured at maximum fields of 4.5T were calculated to m_S = 2.01μ_B and m_L = 0.35μ_B, respectively. This is in very good agreement with the literature on free relaxed Co nanoclusters of about 1-2 nm diameter [2]. As expected the moments are substantially enhanced compared to bulk values (m_{total} = 1.6-1.7 μ_B for bcc and fcc structures) due to the reduced average coordination of Co.

Magnetization curves of sample #1 and #2 were measured up to higher temperatures. For the 0.1MLCo/Pt(111) system the observed remanence is lost in the range of of 10-15K. At higher temperatures both sample #1 and #2 gradually lose the degree of magnetic saturation at maximum fields due to thermal excitations.

With increasing cluster size the blocking temperature should shift to higher temperatures. This is indeed observed for sample #3 prepared with a larger Xe thickness of about 20MLs (the signal from the Ag(111)

substrate undeneath was no more observable). Due to the increase of the cluster size with increasing Xe buffer layer remanence appears also on Ag(111) at T = 6K as shown in Fig. 3. Thereby the easy axis remains in-plane like seen earlier in the case of smaller Co cluster (sample #2). With increasing temperature the remanence is reduced and disappears at around 30K as shown in the inset of Fig. 3.

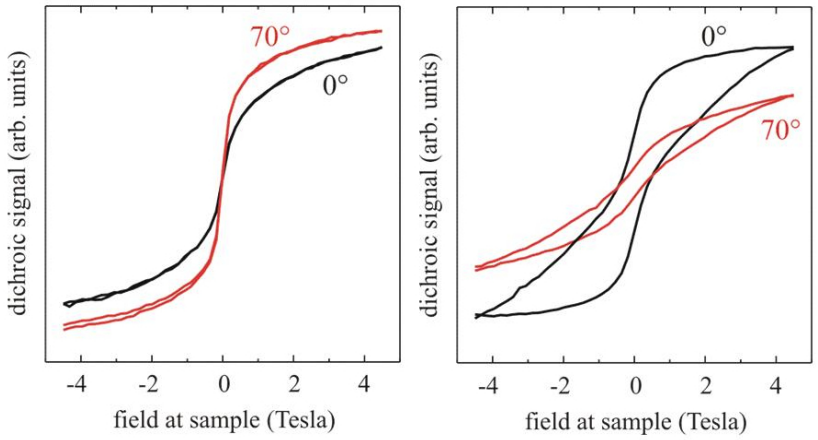

Fig. 2:
Magnetization curves of 0.1MLCo/Pt(997) (right panel) and 0.1MLCo/Ag(100) (left panel) after desorption of the Xenon buffer layer. The curves were measured at T = 6K along angles of 0° and 70°.

In the case of sample #4 the cluster size is expected to be even larger compared to that of sample #3: while the Xenon buffer layer is similar the amount of 3d metal material, in this case Fe, is increased by a factor 6. The results for sample #4 not shown here follows the trend found for Co clusters. Due to the increase of the cluster size remanence can be observed up to elevated temperatures of around 40K. A low-spin phase reported for epitaxially grown Fe islands on Pt(111) is not observed in sample #4.

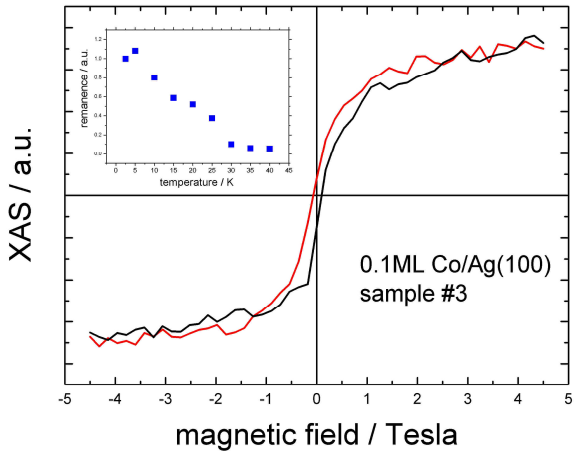

Fig. 3:
Observed remanence at T = 6K along the in-plane direction (easy axis) for Co/Ag(100)(sample #3) after Xe desorption. The sample was prepared using a larger Xe buffer layer thickness to increase the cluster size.

In conclusion during HE 2212 we showed the successful implementation of the BLAG method at beamline ID08 for the magnetic study of *in situ* grown relaxed 3d metal clusters. It is even possible to measure the magnetic behavior of the clusters on the Xenon buffer layer. After the clusters make contact with the substrate the preferred magnetic direction was found to depend on the substrate. The evaluation of the data so far clearly indicates the strong tendency of Pt(111) to stableize the magnetization of the clusters in the out-of plane direction, while Ag(111) promotes the in-plane direction. With increasing cluster size the blocking temperature of the 3d metal clusters is increasing as expected. First quantitative evaluations of the moments of the smallest Co clusters are in good agreement with theoretical and experimental values found for free, relaxed clusters of the size of 1-2nm in diameter.

1. J.H. Weaver, G.D. Waddill, Science **251**, 1444 (1991); Ch. Haley, J.H. Weaver, Surf. Sci. **518**, 243 (2002)
2. J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991)