ESRF	Experiment title: Magnetism of Rh and Ru nanoclusters on inert Xe buffer layers and in contact with Ag(001) surfaces studied by X-ray circular dichroism (XMCD)	Experiment number: HE-2679
Beamline: ID08	**Date of experiment:** from: 05/03/2008 to: 11/03/2008	**Date of report:** 21.7.08
Shifts: 18	**Local contact(s):** Dr Carsten Tieg	*Received at ESRF:*

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Report:

Motivation and summary

The aim of the present proposal was to study the effect of cluster-substrate hybridization on the magnetic properties of compact 4d metal nanoclusters. Our previous results from *HE-1541* have shown that submonolayer coverages of Ru/Rh directly deposited on Ag(001) are not magnetic [1], in contrast to theoretical predictions [2]. A possible reason for the absence of magnetism is the extreme sensitivity of small magnetic clusters to the local arrangement of the atoms on the surface as well as the electronic configuration of the substrate which determines hybridization effects.

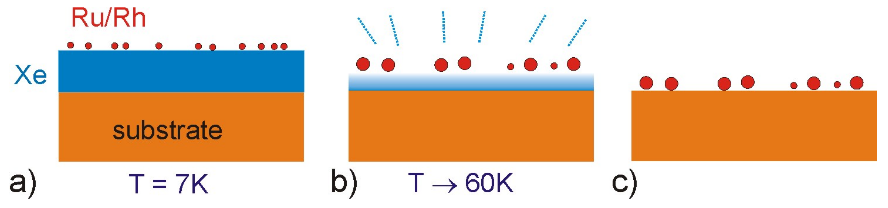

Fig.1: Buffer layer assisted growth (BLAG). a) 0.1ML Ru/Rh is evaporated onto the Xe buffer layer at low temperatures. b) At $T \sim 60$K Xe starts to desorb and cluster growth is triggered. c) Clusters in contact with the substrate.

Here we investigated this problem by comparing the magnetism of nanoclusters of Ru and Rh prepared by Xe buffer layer assisted growth (BLAG) [3] before and after they get in contact with the substrate (see **Fig 1**).
In this way we could model the two cases in which the clusters are decopuled or coupled with the substrate. For the clusters still situated on the inert Xe buffer layer we found a dependence of the magnetic moment on the cluster size similar to the one measured on free clusters in the Stern-Gerlach experiment [4]. During desorption of the Xe-layer the nanoclusters grow in size and make contact with the substrate, which leads to a full quenching of the magnetic moment, similar to what we found for small clusters in *HE-1541*.

Experimental

The substrate preparation was done by standard ion bombardment/annealing cycles, the cleanliness being directly verified by looking at the XAS of oxygen. Xenon buffer layers of about 50 Langmuir (L) thickness are adsorbed onto the surface at lowest temperatures in the magnet chamber, using the procedure from *HE-2212*. Then Ru/Rh is evaporated onto the Xe buffer layer at T = 10K by thermal evaporation from a rod using a UHV port at the magnet chamber.
The dichroic signal was measured at the $M_{3,2}$ absorption edges of Ru (450 - 500 eV) and Rh (480 - 540 eV) for different Rh and Ru coverages. After measuring the XMCD of Ru or Rh nanoclusters on the Xe at lowest temperatures of 7K (**Fig. 1a**) the sample is gradually warmed up to 150K. This triggers two different processes: first, between 10 and 50K the Xenon layer is intact and the clusters grow in size because of

thermally activated diffusion. Above 60K Xenon starts to desorb in two steps. First the desorption of the 'bulk' Xenon is observed. To desorb the last monolayer of Xe on the Ag substrate temperatures of 150K are requiered. XAS/XMCD measurements have been performed at T = 10K after several annealing steps. The amount of remaining Xe on the substrate can always be monitored by measuring the Xe M-edge around 0.9keV (see *HE-2212*). Once the Xe layer is fully removed (by annealing the substrate up to 150K), XAS/XMCD spectra are once again measured for the clusters in contact with the substrate (**Fig. 1c**).

Results

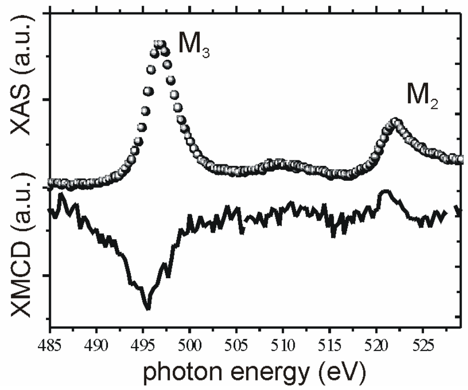

Fig. 2: XAS and XMCD for 0.05ML Rh on the Xenon buffer layer.

First we analized the magnetic properties of Rh clusters decoupled from the substrate. In **Fig. 2** the XAS at the Rh M_{32} adsorbtion edge is plotted for 5% of ML Rh on the Xenon layer, together with the XMCD. Due to the very low amount of magnetic moment in Rh, the dichroic signal is rather weak. In order to exclude possible artifacts we verified the change of sign in the XMCD when changing the field direction as a consistency prove of the measurements.

In **Fig. 3a** the ratio between XMCD and XAS is calculated at the M_3 (black dot) and M_2 (red dot) edges as a function of the increasing coverage. This trend reflects the behavior of the magnetization as a function of cluster size and it resembles qualitatively what was observed in the Stern-Gerlach experiments [3]. Due to an increase of the Rh-Rh coordination with cluster size the magnetic moment progressivly approaches the zero value found in the bulk.

In **Fig. 3b** we plotted again the XMCD/XAS at the M_3 edge measured at 10K after several annealing steps, from 10K up to 150K. The decrease of the magnetic moment upon annealing to 40K is possibly due to an increase of the cluster size promoted by cluster diffusion on the solid Xenon layer. At 70K though the signal drops to zero, in coincidence with the desorption of the bulk part of the Xenon layer. This shows how the interaction with the substrate leads to quenching of the magnetization in the nanoclusters.

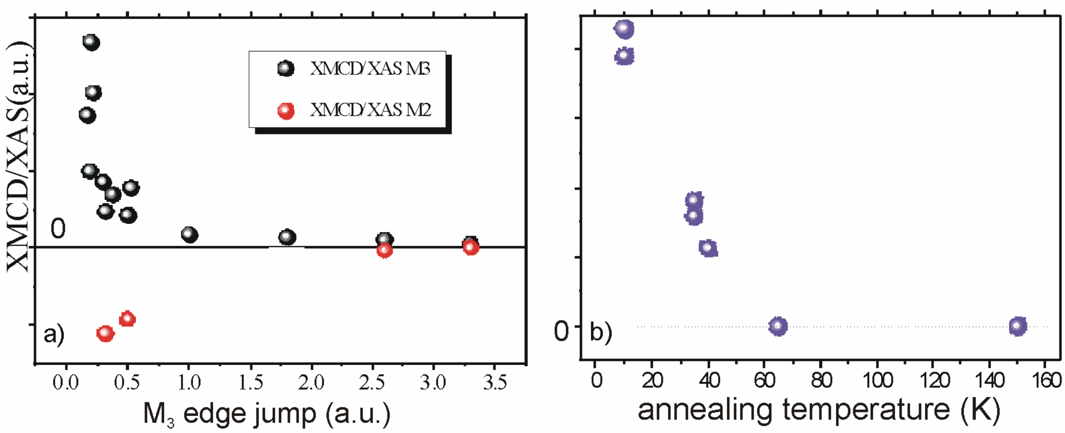

Fig 3: a): XMCD/XAS at the M_2 (red) and at the M_3 (black) Rh edges vs M_3 edge jump, showing the behavior of the magnetic moment with cluster size; b) XMCD/XAS at the M_3 edge for 0.03ML and 0.05ML measured at 10K after annealing steps indicated in the plot. From this trend is clear that the magnetization is quenched from the moment the clusters get in contact with the substrate on (Xenon starts to desorb at about 65K).

In conclusion we have shown a way to measure the magnetism of low-coordinated 4d nanoclusters on a weakly coupling substrate. The choice of the substrate revealed though to be crucial. For the future, it could be interesting to repeat the experiments with Rh clusters in regular arrays of an semi-insulating boron-nitride nanomesh, a substrate that may not influence the electronic structure of the clusters but pins the clusters up to room temperature.

References

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