	Experiment title: **Magnetism of 4d Nanostructures at Vicinal Pt Surfaces**	**Experiment number**: HE-1541
Beamline: ID08	**Date of experiment**: from: 3.12.03 to: 5.12.03	**Date of report**: 20.2.04
Shifts: 6	**Local contact(s)**: Peter Bencok	*Received at ESRF:*

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Report:

As suggested by the Review Commitee we performed a feasibility test to check wether the magnetism of low-coverage Rhodium and Ruthenium on Pt-substrates can in principle be measured using X-ray magnetic circular dichroism (XMCD) techniques in the range of the M3/2 absorption lines. Some difficulties were expected by the referees since the X-ray absorption spectrum (XAS) of the Pt-substrate exhibits pronounced absorption lines in the spectral range of interest which can complicate the separation of the background signal. The results presented in this report demonstrate that despite the changing slope of the Pt or Ag-background the magnetism of Rh and Ru at sub-monolayer coverages can be readily studied using XMCD techniques at a beamline with high photon flux comparable to ID08. Futhermore we were already able to obtain the result that single Rh atoms deposited at very low temperatures, i.e. in the impurity limit, are essentially non-magnetic on both the substrates Pt(997) and Ag(100).

Although 4*d* metals are non-magnetic in the bulk, the emergence of a resulting magnetic moment is predicted for low-dimensional systems [i][ii] and ascribed to the reduced coordination of the atoms. We therefore proposed to explore the occurrance of magnetism in monatomic, biatomic and multiatomic chains of the 4*d* metals Ruthenium and Rhodium, as well as clusters of varying size and shape by self-organized growth on a vicinal Pt single-crystal surface. XMCD is a technique that has the surface sensitivity needed to investigate the magnetism of these low-coverage systems. In addition, the thereby measured XAS provides important information on the electronic structure of the metals.

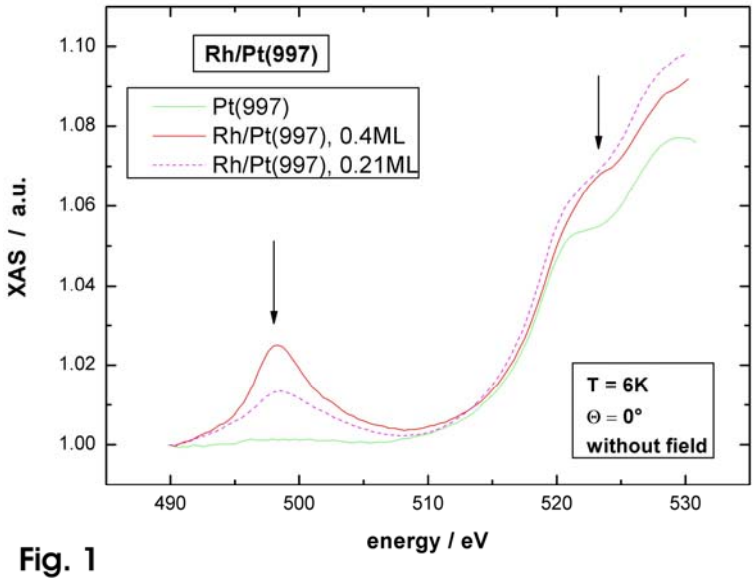

Fig. 1

The feasibility measurements were carried out at the ID08 beamline which provides the necessary high photon flux as well as variable temperatures in the range of 6-300K. In the preparation chamber the used substrates were cleaned and annealed. The regular ordering of the surface step structure was verified using LEED. Due to the very limited experimental time we focussed on the detection of low adsorbate coverages without attempting to obtain the adsorbate structures. The samples were prepared by depositing Rh on Pt(997) and Ag(100) substrates in the magnet chamber at a temperature of a about 6 Kelvin which facilitates preparation and measurement but prevents diffusion and formation of homogenous structures. At sub-monolayer coverages a high concentration of single adatoms will be present together with a fraction of clusters containig a few atoms. Fig. 1 shows the XAS of two Rh/Pt(997) samples at different coverages compared to the signal of the clean substrate. Indicated by the arrows are the M3 and M2 lines of Rh (496.5eV and 521.3eV core-level binding energies[iii]). The spectra show a pronounced Rh-M3 peak whereas the M2 is not as well-defined. At the high energy end of the spectra where the M2 peak ends the signal might be distorted due to artifacts caused by the limited spectral window of the beam at a fixed undulator gap. Since there was no quartz-balance available in the magnet chamber to calibrate the evaporation rate we estimate the coverage *ex post* from the intensity of the Rh-M3 peak with respect to the Pt background. This gives coverages of (0.4±0.1) and (0.21±0.05) ML, respectively, for the shown plots. In this estimate we used a calibration of iron on Pt(997) from our previous XMCD measurements and rescaled the ratio between the M3-peak intensity and the Pt-background using calculated photoionization cross-sections in the dipole approximation for the elements Pt, Fe and Rh [iv].

Fig. 2 shows the XAS at a Rh coverage of 0.4ML using positive and negative circular polarized light in a magnetic field of 6T at polar geometry (0° angle of the incident beam). The resulting XMCD signal shows no dichroism, e.g. no magnetization of the adsorbates. We want to stress the fact that the XMCD signal remains zero (within the error given by the random noise) over the entire spectral range suggesting that the onset of the Pt-N3-edge at 519.5eV[iii] (changes in the Pt-XAS are about 8%) does not introduce any significant artifacts. Further measurements at different angles and samples with lower Rh-coverages down to about 0.15ML also did not show any dichroism. Given the small noise in the XMCD of about 2% of the M3-peak intensity, the expected moments of around $1\mu_B$ per atom at sub-monolayer coverages [i] should be detectable: For a moderate moment per hole of the order of $0.2\mu_B$ we could detect the magnetism down to coverages of at least 10% of a monolayer. Hence, the absence of dichroism at 0.15ML gives us an upper limit for the moment per hole of $0.1\mu_B$. Here we clearly take advantage of the high flux and stability of the ESRF beamline.

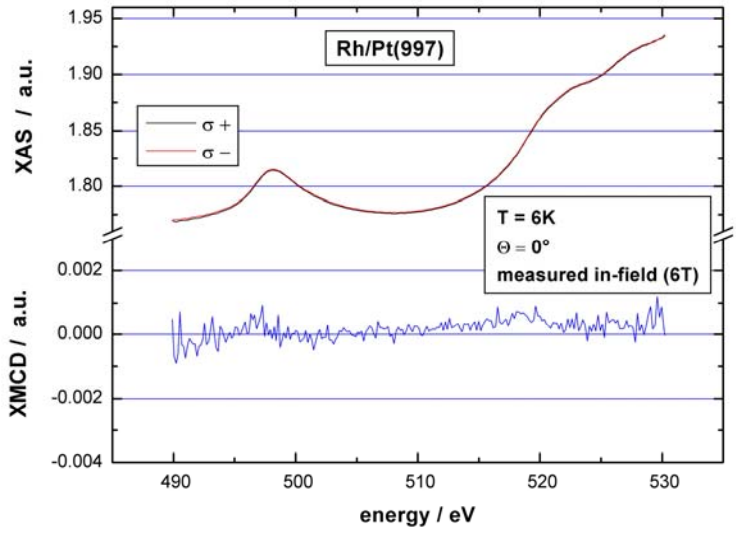

Fig. 2

For the Ru experiments we could only obtain preliminary results because the filament of the evaporator failed before we could attempt the deposition on a well-prepared Pt(997) surface. Nevertheless we have obtained a rough XAS spectrum of Ru evaporated on a strongly contaminated Pt-substrate. Fig. 3 shows this spectrum of Ru/Pt(997) together with the background of the clean Pt(997)-substrate in the same spectral range. No magnetic field was applied. The Ru-M3/2 lines indicated by the arrows can be clearly distinguished from the Pt-background which changes only about 2%

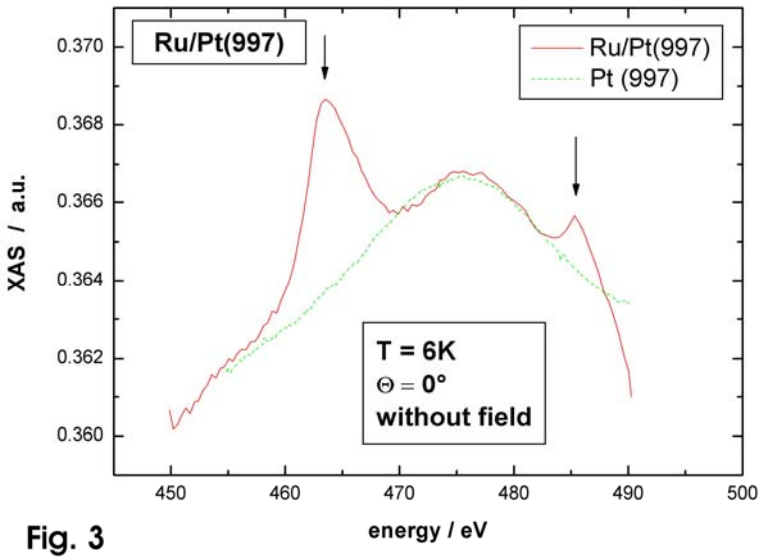

Fig. 3

between 450eV and 490eV. Assuming the same noise-level in the XMCD we expect that magnetism of Ru should be detectable even in the sub-monolayer regime, especially since theory predicts magnetic moments twice as large compared to Rh [i].

The moments of Rh and Ru structures were, however, calculated on Ag(100) and not on Pt(997)[i][ii]. We therefore decided to grow a sample of Rh on an available Ag(100)-substrate. Fig. 4 shows the according results of a 0.4ML Rh/Ag(100) sample prepared using the above described procedure. Again no dichroism was found at this coverage, however this time both the Rh-M3/2 absorption lines are well-defined. Like for the case of Rh/Pt(997) the low noise level in the XMCD-signal allows us to study magnetism at sub-monolayer coverages.

In conclusion we have shown that XMCD measurements of both Rh and Ru deposited on Pt(997) and on Ag(001) can be performed without substantial problems at the ID08 beamline even for sub-monolayer coverages down to 0.1ML. The absence of a dichroic signal for low-temperature deposited Rh at coverages between 0.15 and 0.4 ML on Pt(997) and 0.4 ML on Ag(100) indicates that the structures prepared by 6K deposition are essentially non-magnetic. We cannot exclude, however, that clusters of certain geometries or chains which are present as a small fraction of the coverage exhibit magnetism. The low-coverage Rh/Pt(997) measurements certainly indicate that single Rh-adatoms have a moment per hole below $0.1\mu_B$.

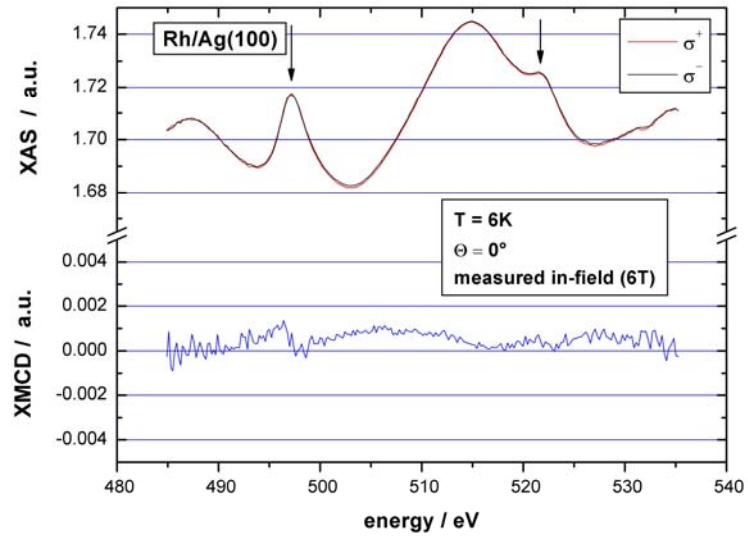

Fig. 4

Based on the results of this feasibility test it would be highly interesting to measure the magnetic behavior of chains or islands of Rh as well as Ru in contrast to the limit of single adatoms: The theory predicts a strong dependence of the magnetic behavior on the geometry of the 4*d*-metal coordination [i]. Experimentally this can be done by increasing the temperature during the evaporation process which allows the self-assembly of adsorbates via surface diffusion. The magnetic investigation of chains as well as larger islands of 4*d*-metals on Pt(997) and Ag(100) will be subject of a new proposal. We want to gratefully thank the ID08-team at this point for the good support during the measurements.

[i] K. Wildberger, V.S. Stepanyuk, P. Lang, R. Zeller, and P.H. Dederichs, Phys. Rev. Lett. **75**, 3, 509 (1995)

[ii] V.S. Stepanyuk et al., Solid State Commun. **92**, 755 (1994)

[iii] J.C. Fuggle *et al.*, *Core-Level Binding Energies in Metals*, J. Electron Spectrosc. Relat. Phenom., **21**, 275 (1980), J. A. Bearden *et al.*,*Reevaluation of X-RayAtomic Energy Levels*, Rev. Mod. Phys ., **39**, 125 (1967),

[iv] J.J. Yeh, *Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters*, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993 and J.J. Yeh and I.Lindau, *Atomic Data and Nuclear Data Tables*, **32**, 1-155 (1985).