ESRF	**Experiment title:** **Orbital contribution to the induced magnetism of the Rh 4*d* states in *magnetically independent* Fe@Rh@ligand nanoparticles**	**Experiment number**: HE-3006
Beamline: ID12	**Date of experiment**: from: 09.06.2009 to: 16.06.2009	**Date of report**: 23/10/2009
Shifts: 18	**Local contact(s)**: A. Smekhova	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

C. Amiens*[1], D.Ciuculescu[1], N.Atamena[1] , K. Fauth[2], B. Muenzing[2], M. Respaud[3]

[1] Laboratoire de Chimie de Coordination, UPR 8241-CNRS, Toulouse Cedex 04, 31077, France ;

[2] Faculty of Physics and Astronomy, Würzburg University, Am Hubland, 97074, Würzburg, Germany;

[3] LPCNO, 135 Avenue de Rangueil, 31077 Toulouse Cedex 04;

Report: The aim of this experiment was the measurement of the spin and orbital contributions to the magnetic moment of Rh atoms in magnetically independent Fe@Rh@ligand nanoparticles containing less than 500 atoms in average (less than 2 nm in diameter), i. e. nanoparticles with an iron core, a rhodium shell and ligand coating. A set of organic coating agents has been specifically designed to insure that the nanoparticles were spatially well separated, thus preventing any magnetic dipolar couplings to set in. In this way, the measurement of the properties of an assembly of nanoparticles offers the possibility to access the individual magnetic properties of the nanoparticles.

XANES and XMCD experiments have been performed at the ESRF beamline ID12, dedicated to polarization dependent X-ray spectroscopy in the energy range from 2 to 15 keV. X-ray absorption spectra at the $L_{2,3}$ absorption edges of rhodium (3 ÷ 3.2 keV) as well as at the K-edges of iron (7.1 keV) have been recorded under the same experimental conditions.

Extreme care was taken to prevent the NPs oxidation prior to XMCD experiments. Samples in the form of pellets were mounted under argon atmosphere into special aluminum capsules covered with a 25 μm thick kapton foil. For each sample we used a separate capsule which was attached to a cold finger of a constant flow He cryostat. The latter was inserted in a bore of superconducting magnet providing a magnetic field of 6 Tesla.

Prior checking the Rh $L_{2,3}$ edges, we performed XANES measurements at the Fe K edge to prove the absence of NPs oxidation. The important result was that XANES spectra have shown neither any X-ray irradiation damage of nanoparticles nor presence of any Fe oxides in the investigated NPs.

XMCD signals at the Rh $L_{2,3}$ edges (Fig.1) were obtained as a direct difference of X-ray absorption near-edge structure (XANES) spectra recorded with left and right circularly polarized X-rays using total fluorescence yield detection mode. The experimental spectra were then corrected for incomplete circular polarization rate of the incoming X-rays. To make sure that the final result is free from any experimental artifact, we checked that the same XMCD spectra but of opposite sign have been obtained for opposite direction of magnetic field. All measurements were done at low temperature of about 10K, which is somewhat higher than the blocking temperature of the NPs.

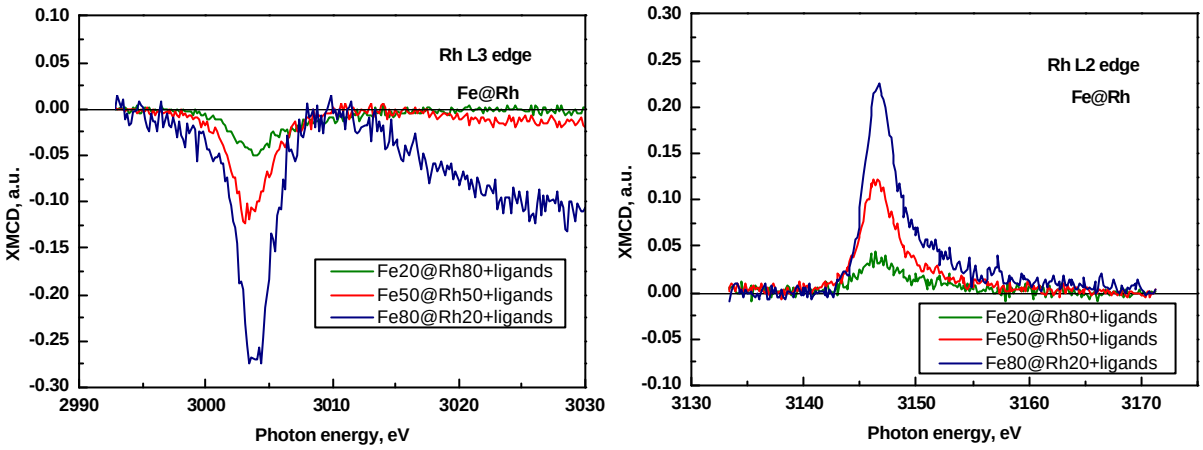

Fig.1 XMCD spectra at the Rh $L_{2,3}$ absorption edges for Fe20@Rh80, Fe50@Rh50 and Fe80@Rh20 NPs. All spectra presented after incomplete polarization rate and "branching ratio" corrections.
No self-absorption corrections have been applied since PPO stabilizing matrix contains only light elements.

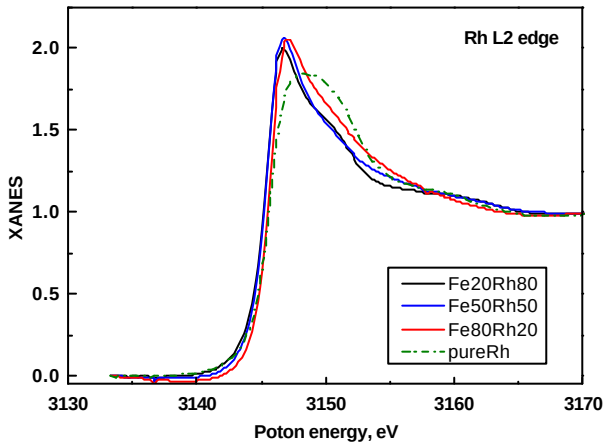

Fig.2 XANES spectra at the Rh L_2 edge for all investigated Fe@Rh@ligand NPS.
XANES for pure Rh nanoparticles of the same size are shown for the comparison.

The main outcomes of the performed experiment can be formulated as follows:

-- XANES spectra (Fig.2) show the presence of at least 2 different types of Rh atoms: the "metal-like" one (with the maximum on the white-line around "main" peak) and the "surface Rh with ligands", to which we attribute the feature at the high energy slope of XANES spectra;

-- via Sum Rules analysis we determined the total induced magnetic moments at Rh atoms for all compositions:

composition	magnetic moment in μ_B
Fe80@Rh20 +ligands)	0.626
Fe50@Rh50 +ligands)	0.320
Fe20@Rh80 +ligands)	0.160

(assuming 2.4 holes in the 4d band for all samples);

-- inspite we obtained a reasonable tendency in the induced magnetic moments (which correlates with the amount of Fe in the NPs), these data should be corrected furher since only "metallic-like" Rh atoms contribute into the dichroic magnetic signal.

A paper is under preparation.