ESRF	**Experiment title:** XMCD in the $L_{2,3}$ fluorescence of Rh in CoRh bimetallic nanoparticles	**Experiment number**: HE-1253
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Report:

In this report, we present the results obtained from XMCD measurements using fluorescence yield detection (FY) at the Rh $L_{2,3}$ edges in nanoscale Co_xRh_{1-x} alloyed systems embedded in organic matrix. These experiments have been made in single bunch mode to demonstrate the feasibility of such experiment regarding the very low polarization rate (4-10 %), the small mount of matter in these nanoscale systems; and to test sample preparation and define the best method to prevent oxidation. This first attempt was successful and some preliminary results have been obtained.

The context of this work concerns the investigation of the influence of size reduction on the magnetic properties of bimetallic ferromagnetic 3d/4d metals nanoparticles in the size range of 1-4 nm[1]. The nanoparticles are synthesised following an organometallic synthesis in mild conditions of temperature and pressure. This synthesis leads to isolated nanoparticles in a polymer matrix with clean surface. In the $Co_{1-x}Rh_x$ system[2], reducing particle size leads to enhanced magnetisation, 2.38 μ_B at 30 T (2.2 μ_B at 7T) for CoRh particles of 1.6 nm diameter, up to two times larger than the bulk phase. The origin of such a strong effect is not yet understood, but a large induced electronic polarisation on Rh would possibly be a consequence of both alloying and size reduction. Thus, selective element experiments like XMCD are straightforward to determine how is distributed the magnetisation, on each atomic specie.

We performed XMCD measurements on several samples with two kinds of preparation. To avoid oxidation, the samples were prepared in a glove box of our laboratory according to

the following methods. The first one consists on a thin film preparation obtained by deposition of a drop of colloidal solution on a copper support. In the second one, samples were pressed in pellets and then deposited on a copper support. In both cases, the sample was protected by a thin organic polymer film of PMMA. Both methods of preparation allowed us to measure a fluorescence spectrum even in the lower concentrated systems. Definitely, a thick sample displaying a large surface with a roughness reduced as much as possible would be required for a next experiment. Our pellet preparation is thus the most appropriate. The PMMA surface layer has revealed to be sufficient to protect against oxidation without diffusing photons, which is important when using fluorescence yield detection.

Preliminary results have been thus obtained on three samples, with Rh concentration less than 10% in mass. Due to the low polarisation of incident photons, 4% at the L_3 threshold and 10% at the L_2 threshold, and the single bunch mode, the measurement for each edge requires about 16 hours. The first sample under study consists in 1.6 nm Co_1Rh_1 nanoparticles (Coll. 1) dispersed in a polyvinylpyrrolidone matrix. The second one contains 1.6 nm Co_3Rh_1 nanoparticles (Coll. 2). Bigger nanoparticles of 4.1 nm of Co_1Rh_1 (Coll. 3) dispersed in polydimethylphenyloxide have also been studied.[3] This set of sample allows to get some information on the size effect and the composition effect in $Co_{1-x}Rh_x$ nanoparticles on the Rhodium magnetic moments.

The measurements at $L_{2,3}$ Rh thresholds were performed in single bunch mode using fluorescence yield detection at the lowest available temperature. The absorption spectra were recorded with the X-rays at normal incidence, parallel to the direction of the magnetisation. Fig. 1 shows the total absorption of Coll. 1, the sum of spectra recorded with the two polarisations of the light, and the difference between the two spectra, for the L_3 and L_2 edges of Rh. Each edge was measured separately and then normalised to a ratio of 3.72:1.41 according to ref. 3.[4] The difference curve has been then corrected for the incomplete polarisation of the X-rays. To avoid any experimental artefact, the direction of the applied magnetic field was reversed from +7T to -7T.

The shape of the total adsorption lines displays unusual features, with probably two

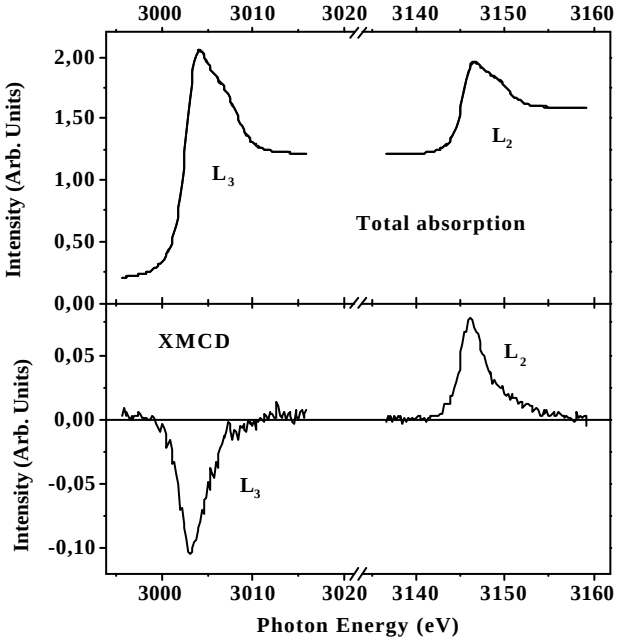

Fig. 1 : *total absorption and XMCD signals at L_3 and L_2 edges of Coll. 1. $\mu_0 H = 7$ T $T < 10$ K.*

contributions. Their origin is not yet identified and may be related to two valence states in Rh atoms.

The L_2 and L_3 XMCD signals are of the same order of magnitude, with opposite signs, indicating that the orbital contribution (L_z) is small compared to the spin one (S_z). Using the Thole and Carra's sum rules,[5] we calculate the ratio $L_z/S_z = 0.066$. The determination of L_z and S_z requires the determination of n_{4d}/σ_{tot}, number of holes in the 4d band and the absorption cross section for $2p \rightarrow 4d$ transitions using unpolarised light, and the measurement of a reference sample.

The XMCD was also measured at a fixed energy of 3.146 keV at the L_2 threshold as a function of the magnetic field. Fig. 2 displays the magnetisation loop of Coll. 1 measured at the lowest available temperature.

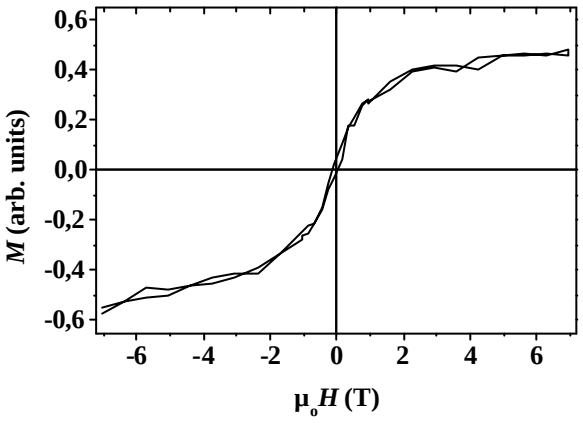

Fig. 2 : *Magnetization loop of Coll.1 measured at the L_2 threshold (3.146 keV). T < 10 K*

Considering the experimental error bars, we can consider that the magnetisation follows a superparamagnetic behaviour. Considering that the blocking temperature is around 10K in a quasi static experiment, the coercive field would vanish for a sample temperature above 8 K. A strong high field differential susceptibility is noticeable in agreement with the macroscopic SQUID measurements.

The XMCD was measured for Coll. 2 and Coll. 3 only at the L_2 threshold due to short beamtime allocated. Fig. 3 displays the influence of the Rh atomic content for the same particle size (Φ = 1.6nm). The integrated XMCD signal is twice bigger for $Co_{0.75}Rh_{0.25}$ than for $Co_{0.5}Rh_{0.5}$. If one assumes that the L_z/S_z is the same in both cases, the magnetic moment

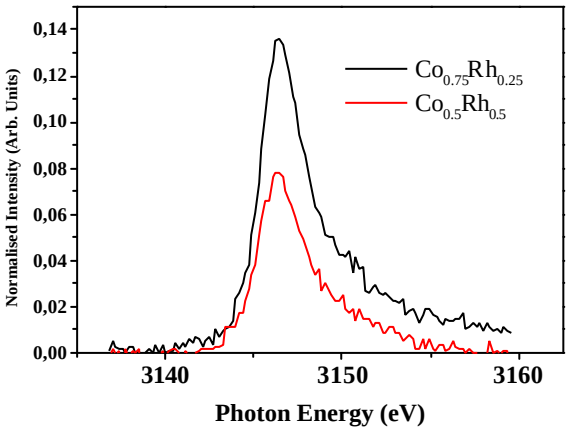

Fig. 3 : *XMCD signals at L_2 edges for Coll. 1 and Coll. 2. $\mu_0 H$ = 7 T, T < 10 K*

carried out by Rh atoms would be twice bigger in $Co_{0.75}Rh_{0.25}$ than in $Co_{0.5}Rh_{0.5}$. By

comparing the signals related to Coll. 1 and Coll.3, we can observe that the increase of particle size leads to a reduction of the magnetic moment on Rh atoms.

In conclusion, these experiments have allowed to observe for the first time the magnetic polarization of a 4d element in nanoscale alloyed 3d/4d ferromagnetic particles. The qualitative analysis of the recorded data shows a polarisation which decreases with size and Rh content. The quantity L_z/S_z has been estimated for Coll. 1. Further experiments are necessary to precise the orbital and spin contributions of each system, including the measure of a reference sample, in order to differentiate the role of size reduction and alloying on the magnetism of Rh. These results will be included in the next conference presentations (ICM 2003) and related publications.

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