XANES and XMCD Studies of FeRh and CoRh Nanoparticles

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Element-selective magnetic properties of new core-shell bimetallic MRh (M=Fe or Co) nanoparticles (NP) of 50/50 composition with either M@Rh or Rh@M core/shell order and an average diameter of ~2 nm have been investigated by X-ray Absorption Spectroscopy (XANES) and X-Ray Magnetic Circular Dichroism (XMCD) technique. XANES spectra at the Rh L\textsubscript{2,3} edges exhibit the same characteristic features for all systems having the Rh metal enriched shell. XMCD experiments at the same edges have shown that 4d states of Rh atoms acquire a magnetic moment as a result of hybridization with iron or cobalt 3d states. As expected the value of this induced moment depends on the 3d transition metal and on the core/shell chemical order in the nanoparticle.

1. Introduction
Magnetism of small ordered clusters is now in the focus of experimentalists and theoreticians due to a variety of new phenomena. The most attractive of them are an enhancement of spin and orbital magnetic moments of atoms in comparison with bulk materials and the presence of strong magneto-crystalline anisotropy [1].

Current progress in chemistry offers the possibility to produce very small bimetallic nanoparticles with well defined core/shell segregation. As an example of 3d-4d bimetallic NPs, core/shell Fe\textsubscript{x}Rh\textsubscript{100-x} and Co\textsubscript{x}Rh\textsubscript{100-x} nanoparticles with Rh-enriched core have been investigated [2-4]. More recently, a new chemical method was developed that allows to reverse the core/shell order in the FeRh nanoparticles and to obtain NPs with an Fe rich core and Rh rich shell, by a kinetic control of the decomposition of two precursors [5]. Significant changes in the electronic structure and magnetic properties of the FeRh NPs depending on composition and chemical order have been observed.

This new method has now been applied to produce nanoparticles with Co rich core and Rh rich shell in the same size range. It is noteworthy that the NPs with a 3d-transition metal core and a Rh noble metal shell are of great interest for technological applications as the Rh shell provides a greater stability in air to the nanosystems contrary to 3d transition metal surface since strong oxidation.

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It is essential to study the effect of the chemical order on the electronic and magnetic properties of the CoRh nanosystem and compare these results to those already obtained for the FeRh ones, thus evidencing the effect of the nature of the 3d-transition element.

In the current report we focus mainly on the induced magnetism of Rh 4d states in small (~2nm) bimetallic FeRh and CoRh nanoparticles of 50/50 composition containing about 500 atoms in average, and with a Co or Fe rich core and a surface enriched in Rh. For clarity purposes these samples will be referred to as M@Rh (M=Fe or Co). Their properties will be discussed in comparison to those of NPs presenting a reverse chemical order at identical composition and size, hereafter called Rh@M NPs.

2. Experimental details

2.1. Sample Preparation and Macroscopic Characterization

All manipulations were carried out under argon atmosphere; each reactant was weighted inside a glove-box (less than 1ppm O$_2$ and H$_2$O) and thoroughly dried and degassed before use.

Fe@Rh NPs were prepared according to reference [5]. Co@Rh systems were obtained by following procedure: Co[N(SiMe$_3$)$_2$]$_2$ and [Rh(η$_3$-C$_3$H$_5$)$_3$]) precursors in a 1/1 molar proportion and 2 equivalents of amine-borane complex were added to a heptane solution of tetramethylpiperidine at very low temperature. The mixture was allowed to warm up to room temperature and the final NPs were isolated by evaporation of the solvent after 12h. The black powder thus obtained (~ 55mg) was stored in a glove-box.

TEM images were done on a Jeol JEM1011 (100 kV). A Gaussian fit of the size distributions of nanoparticles gives the average diameter as 2.2nm for Fe@Rh and 1.8nm for Co@Rh NPs.

An average first metal-metal distance was estimated from the position of the first maximum in the Radial Distribution Function (RDF) measured with a Wide-angle X-Ray scattering (WAXS). For the Co@Rh compound the first metal-metal distance was found to be 2.69Å. For Fe@Rh nanoparticles the first metal-metal distance was found to be 2.70Å. In all cases the atomic packing is close to a polytetrahedral arrangement, except for the Rh@Fe NPs which clearly adopt a fcc packing.

Blocking temperatures were determined via classical zero-field cooling / 1mT field cooling measurements carried out with a SQUID magnetometer. For both systems blocking temperature was found to be rather low: ~5 K for Co@Rh NPs and ~7 K for Fe@Rh NPs.

For further XMCD measurements the powders of NPs were diluted in boron nitride, pressed into 5 mm diameter pellets and fixed on a specially designed air-tight sample holder.

2.2. XANES and XMCD Experimental Setup

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 [6]. 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 and cobalt (7.1 and 7.8 keV) have been recorded under the same experimental conditions. All necessary details about the experimental set-up, XMCD technique and spectra analysis can be found in our previous paper [7] and references therein.

3. Results and discussions

3.1. XANES and XMCD at the Fe and Co K edges

Variations of the local electronic structure and magnetic polarizations of the 4p states of either iron or cobalt as a function of the NPs chemical order have been studied with XANES and XMCD spectroscopy at the Fe and Co K-edges. However these results are out of the scope of this presentation and will be published separately. The only important result that should be declared here is that XANES spectra have shown neither any X-ray irradiation damage of nanoparticles nor presence of any Fe and Co oxides in the investigated NPs.
3.2. XANES and XMCD spectroscopy at the Rh L\(_{2,3}\) edges

The XANES spectra recorded for Fe@Rh and Co@Rh nanoparticles at the Rh L\(_{2,3}\) absorption edges, corresponded to 2p \(\rightarrow\) 4d dipole allowed transitions, are presented at left panels of figure 1 and figure 2. Spectra exhibit the tendency expected for NPs with predicted Rh-enriched shell: there is a shoulder at the high energy side of the so-called “white line” in the XANES spectra. This feature clearly reflects significant changes in the Rh 4d density of states for NPs and is attributed to the interaction of the Rh atoms located on the surface of the NPs with the stabilizing organic matrix used during the synthesis of the NPs. No such effect was observed at Fe or Co edges, as these elements are buried in the core of the NPs. For the sake of comparison we have also added the Rh L\(_2\) edge XANES spectrum from pure Rh NPs of the same diameter, prepared in the same chemical environment.

![Figure 1](image1.png)

**Figure 1.** XANES (left panel) and XMCD (right panel) spectra at the Rh L\(_{1}\) and L\(_2\) absorption edges for FeRh nanoparticles with a different core/shell order. Spectra were recorded at 10 K and under 6 T field. Corrections for the incomplete circular polarization rate and self-absorption have been applied.

![Figure 2](image2.png)

**Figure 2.** XANES (left panel) and XMCD (right panel) spectra at the Rh L\(_2\) absorption edge for CoRh nanoparticles with a different core/shell order. XANES spectra were recorded at 10 K and zero field. XMCD spectra have been measured at the same temperature and under a field of 6 T. Further XMCD spectra were corrected for the circular polarization rate and self-absorption effects.

Rather intense XMCD signals have been found for all investigated nanoparticles, indicating that Rh atoms acquire a sizeable magnetic moment in these bimetallic NPs. For the FeRh systems it was possible to estimate via sum rules analysis [9] the values of spin and orbital contributions to the total magnetic moment [8]. For NPs with Rh enriched shell we have found a spin magnetic moment of 0.35\(\mu_B\) with a very small orbital contribution the order of 0.01\(\mu_B\).

The case of Co\(_{50}\)Rh\(_{50}\) NPs is more delicate: since we have experimental results only for the Rh L\(_2\) absorption edge we cannot apply the sum rules for the determination of magnetic moments. But still,
we can compare XMCD spectra qualitatively. From figure 2 (right) one can see, that XMCD signal is much stronger for NPs when the Rh lies in the core and is surrounded by Co atoms rather than when it seats at the surface of the NPs. This is contrary to what was observed in the case of FeRh NPs, where the XMCD signal at the Rh L_2 edge and the total induced magnetic moment is stronger for NPs with an Rh enriched shell.

Previous calculations performed on CoRh nanoclusters [3, 10, 11] predicted such a behavior for Rh induced magnetic moment: the case of Rh@Co NPs has more reasons for enhanced induced magnetism than Co@Rh. Magnetic polarization of 4d Rh states is due to hybridization with 3d band of Co, so the number of Co atoms and the effective width of their 3d-band in the Co-Rh interface is crucial for induced magnetic moment. For Co@Rh systems the number of Co atoms in the Co-Rh interface is less and their 3d-band less localized, therefore the 4d states of Rh atoms hold smaller magnetic moment than Rh@Co. This should also apply to FeRh systems, however, Fe is much more sensitive than Co to any changes in both structure and lattice parameters. Here, due to the large lattice expense and fcc environment experienced by the Fe atoms when located on top of a Rh core (i.e. at the surface of the NPs), their average magnetic moment is dampened (only 0.21\(\mu_B\) as determined by XMCD [5]) and the effective polarization transfer to the Rh atoms is thus much less.

4. Conclusion
The new chemical route with amine-borane complexes has been developed for the preparation of small bimetallic CoRh nanoparticles with a surface enriched in Rh atoms. XANES spectroscopy at the Rh L_2 absorption edge reveals the same characteristic features as for previously studied Fe@Rh, in good agreement with the location of Rh atoms at the surface of the NPs and, hence, in chemical interaction with the organic matrix. Element-selective XMCD measurements have shown considerable magnetic polarizations of 4d Rh states in both FeRh and CoRh nanosystems, but different tendencies of these induced polarizations have been obtained depending on the 3d- transition metal and core/shell order in the NPs.

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References
[1] Bansmann J, Baker S H, Binns C, Blackman J A et al. 2005 Surf. Sci. Rep. 56 189-275
[2] Ciuculescu D, Amiens C, Respaud M, Falqui A, Lecante P, Benfield R E, Jiang L, Fauth K and Chaudret B 2007 Chem. Mater. 19 4624–26
[3] Muñoz-Navia M, Dorantes-Dávila J, Zitoun D, Amiens C, Chaudret B, Casanove M.-J, Lecante P, Jaouen N, Rogalev A, Respaud M, Pastor G M 2008 Faraday Discuss. 138 181
[4] Zitoun D, Respaud M, Fromen M.-C, Casanove M.-J, Lecante P, Amiens C and Chaudret B 2002 Phys. Rev. Lett. 89 037203
[5] Ciuculescu D, 2007 PhD dissertation, University Paul-Sabatier, Toulouse, France
[6] Rogalev A, Goulon J, Goulon-Ginet Ch and Malgrange C 2001 Lecture Notes in Physics 565 Berlin: Springer Verlag
[7] Smekhova A, Ciuculescu D, Lecante P, Wilhelm F, Amiens C, Rogalev A and Chaudret B 2008 IEEE Trans. On Magnetics 44 2776-79
[8] Fromen M.-C, Lecante P, Casanove M.-J, Bayle Guillemaud P, Zitoun D, Amiens C, Chaudret B, Respaud M, Benfield R E 2004 Phys. Rev. B 69 235416
[9] Thole B T, Carra P, Sette F and van der Laan G 1992 Phys. Rev. Lett. 68 1943-46; Carra P, Thole B T, Altarelli M and Wang X 1993 Phys. Rev. Lett. 70 694-7
[10] Munoz-Navia M, Dorantes-Davila J, Zitoun D, Amiens C, Jaouen N, Rogalev A, Respaud M and Pastor G M 2008 arXiv: 0809.3638v1 [cond-mat.mtrl-sci] 22 Sep
[11] Fromen M.-C, Morillo J, Casanove M.-J and Lecante P 2006 Europhys. Lett. 73 885-91