



	Experiment title: Induced magnetism of Rh 4d states in FeRh bimetallic nanoparticles	Experiment number: HE – 2538
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Fe_xRh_{100-x} (x = 50, 80) nanoparticles (NPs) with an average diameter of ~2 nm were prepared by simultaneous decomposition of stoichiometric quantities of Fe[N(Si(CH₃)₃)₂]₂ and Rh(C₃H₅)₃ using two different routes: a standard hydrogenation procedure and a new one based on use of amino-borane as reducing agent. All samples were found to be superparamagnetic with blocking temperature below 10K. Results of X-Ray Magnetic Circular Dichroism (XMCD) experiments at the Fe K-edge and the Rh L_{2,3} edges have shown that not only iron but also rhodium atoms are magnetic as a result of hybridization of Fe 3d states with 4d states of Rh. The total induced magnetic moment of Rh atoms as well as its spin and orbital contributions are shown to depend on chemical composition of NPs and the preparation method. "XMCD Studies of FeRh Nanoparticles" by A. Smekhova, D. Ciuculescu, P. Lecante, F. Wilhelm, C. Amiens, A. Rogalev and B. Chaudret, *IEEE*, Nov 2008.

Report:

The experiment HE – 2538 proposed to investigate the 4d induced magnetic moment of Rh atoms in core-shell Fe@Rh and Rh@Fe nanoparticles embedded in an organic matrix. We have studied bimetallic Fe_xRh_{100-x} nanoparticles (x = 50, 80) prepared via two different routes. Firstly, Fe₈₀Rh₂₀ and Fe₅₀Rh₅₀ nanoparticles were prepared according to a hydrogenation process of metal organic precursors. The second route was to prepare nanoparticles (NPs) with the same chemical compositions Fe₈₀Rh₂₀ and Fe₅₀Rh₅₀ but by using a different reducing agent, namely an amine-borane complex: iPr₂NH.BH₃ (1mmol). The mean size of these nanoparticles has been determined by TEM. Wide Angle X-Ray Scattering showed that independently of the chemical procedure and chemical composition of the nanoparticles, the first metal-metal distances was found to be 2.67 ± 0.03 Å.

Blocking temperatures were determined via classical Zero-Field Cooling – 1 mT Field Cooling measurements carried out with a SQUID magnetometer. The iron rich nanoparticles have rather different blocking temperatures depending on synthesis: 3 K for the ones prepared via hydrogenation and 7.6 K for those prepared with amino-borane. Surprisingly, Fe₅₀Rh₅₀ nanoparticles have about the same blocking temperature of 7.1 ± 0.1 K.

We report here the results of XMCD measurements performed at the Fe K-edge and the Rh L_{2,3} edges in these Fe_xRh_{100-x} nanoparticles.

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 aluminium capsules covered with a 25 µm thick kapton foil, which was attached to a cold finger of a constant flow He cryostat. The latter was inserted in a core of superconducting magnet providing a magnetic field of 6T.

We have reproduced on Fig. 1 the Fe K-edge XANES spectra for all four samples. The absence of an additional peak at the pre-edge region clearly shows that there is no significant amount of Fe oxides in the nanoparticles. The stability of the nanoparticles in the capsule was confirmed by excellent reproducibility of the Fe K-edge XANES spectra during the whole period of XMCD measurements.

The XMCD spectra at the Fe K edge recorded on three samples are presented Fig. 2. The spectral shape of the spectra recorded on hydrogenated NPs is typical for metallic Fe but their amplitude is about two times less than for bulk Fe. The main XMCD peak corresponding to 1s to 4p dipolar transitions and reflecting the orbital magnetization of the 4p states is found to be practically the same for all three samples. One can therefore tentatively conclude that the 4p orbital moment of Fe in these NPs is reduced by a factor of 2 compared to bulk Fe and is independent of preparation method.

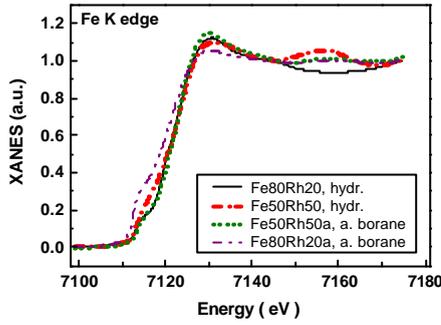


FIG. 1. Isotropic Fe K-edge XANES spectra of $\text{Fe}_x\text{Rh}_{100-x}$ NPs recorded at 10K.

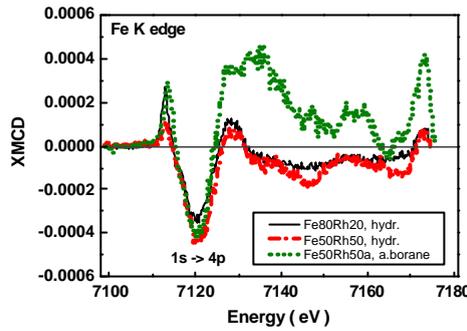


FIG. 2. Fe K-edge XMCD spectra of $\text{Fe}_x\text{Rh}_{100-x}$ NPs recorded at 10K and applied magnetic field of 6 Tesla.

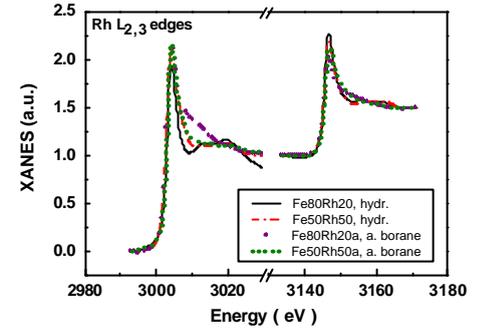


FIG. 3. The Rh $L_{2,3}$ XANES spectra of $\text{Fe}_x\text{Rh}_{100-x}$ NPs at 10K.

The XANES and XMCD spectra recorded at the Rh $L_{2,3}$ absorption edges, corresponding to $2p_{3/2} \rightarrow 4d$ (~ 3004 eV) and $2p_{1/2} \rightarrow 4d$ (~ 3146 eV) dipole allowed transitions are shown Fig. 3 and Fig. 4. There is a strong redistribution of the white line intensities at the Rh L_2 and L_3 edges between samples prepared by the different ways. This redistribution clearly reflects significant changes in the Rh 4d density of states. A plausible interpretation could be that it is related to changes in the core-shell structure of NPs: hydrogenation leading to Fe rich surfaces, while amine-borane reduction would lead to Rh rich surfaces. Rather intense XMCD signals have been observed at the $L_{2,3}$ -edges of Rh (Fig. 4). The negative (positive) sign of XMCD signal at the L_3 (L_2) absorption edge reveals the induced magnetic moment to be parallel to an applied magnetic field and therefore to the Fe magnetic moment.

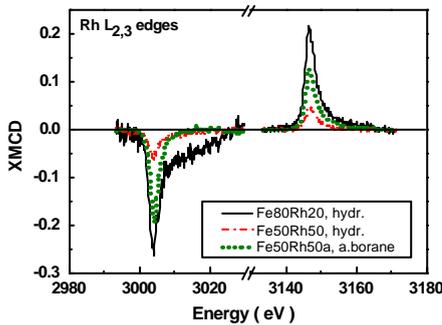


FIG. 4. The Rh L_3 and L_2 XMCD spectra of $\text{Fe}_x\text{Rh}_{100-x}$ NPs recorded at 10K and under 6 Tesla field. Spectra are corrected for circular polarization rate.

TABLE I
THE ORBITAL AND SPIN MAGNETIC MOMENTS OF RH,
TOTAL MAGNETIC MOMENT AND THE RATIO M_L/M_S FOR DIFFERENT NPs.
ALL VALUES OF MAGNETIC MOMENTS ARE IN μ_B .

	$\text{Fe}_{80}\text{Rh}_{20}$, (hydr.)	$\text{Fe}_{50}\text{Rh}_{50}$, (hydr.)	$\text{Fe}_{50}\text{Rh}_{50}$, (a.borane)
M_L	0.07	0.01	0.01
M_S	0.65	0.16	0.35
$M_{\text{tot}} =$	0.72	0.17	0.36
$M_L/M_S =$	0.11	0.06	0.03

The spin and orbital magnetic moments carried by 4d states of Rh are obtained assuming 2.4 holes in the 4d band for all samples and are summarized in Table I.

The results were presented at the Intermag'08 conference in Madrid and at the MISM'08 in Moscow, main conclusions can be found in the paper "XMCD Studies of FeRh Nanoparticles" by A. Smekhova, D. Ciuculescu, P. Lecante, F. Wilhelm, C. Amiens, A. Rogalev and B. Chaudret, *IEEE*, Nov 2008.