ESRF	Experiment title: **Maximizing the magnetic anisotropy of rare-earth atom-sized magnets at surfaces using axial ligand fields**	**Experiment number**: **HC 1557**
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Shifts: 18	**Local contact(s)**: Kurt Kummer	*Received at ESRF:*

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Report:

A) Overview

This projects aimed at maximizing the magnetic anisotropy and relaxation time of individual rare-earth (RE) atoms by using oxide surfaces with dominant axial coordination as supporting substrates. Two critical ingredients must be optimized in order to achieve long spin-relaxation time. First, a high uniaxial anisotropy with a negligible transverse terms is required to minimize the probability for magnetization reversal by quantum tunneling. This ensures that ground-state switching may occur via thermally activated and, possibly, magnetic-field-assisted process only and requires to overcome the entire anisotropy barrier. The second crucial aspect which determines slow spin relaxation is the decoupling from the electrons, nuclear spins and lattice vibrations of the substrate. All these perturbations induced by the surrounding environment can easily destabilize the localized magnetic moments of single atoms.

Many efforts have been devoted to reach the ultimate size limit, ideally a single atom, for a quantum magnet with long spin relaxation time and large magnetic moment. The majority of research so far has focused on 3*d* transition metal atoms and followed the route of reinforcing the impurity spin-orbit interaction which gives rise to magnetic anisotropy and taking advantage from the reduced atomic coordination number at surfaces [1-3]. However, this approach is intrinsically limited by the strong hybridization of the 3*d* electrons with the substrates which determines a very efficient electron-electron scattering and lowers the spin relaxation time [4]. This severely weakens the potential of 3*d* elements as single-atom magnets and suggests to radically change the approach to the problem.

In this proposal we have tried to extend our investigation of the magnetic anisotropy energy of 3*d* metal atoms to the RE series, for which the strong spin-orbit interaction in the 4*f* shell could give, for atoms with large spin and orbital moments, a magnetic anisotropy energy even larger than for transition metals. Moreover, the hybridization with the substrates is strongly suppressed for lanthanides due to the robust localization of the 4*f* states.

Recent experiments on single RE atoms on metallic surfaces showed controversial results and no signs of slow relaxation behavior were obtained in x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) experiments [5, 6]. Thus, we focused our attention on RE single atoms on a thin

insulating film in order to further suppress interaction with the substrate conduction electrons. We used ultra-thin-films (1-3 atomic layer thick) of MgO(100) grown on Ag(100) and probed the magnetic properties of Ho impurities. On the one hand, the large band gap of MgO films (of about 8 eV [7]) ensures an excellent electronic decoupling from the supporting metal crystal. On the other end, the dominant axial coordination to O adsorption sites determines an optimal symmetric environment for crystal field protection against the spin switching of adatoms [8].

B) Quality of measurement/data

By using morphological and structural characterization obtained by STM and LEED, we could successfully calibrate the growth parameters to obtain atomically-flat thin MgO layers on Ag(100). We performed a precise thickness calibration of the MgO film by cross-checking STM data in the sub-monolayer regime with XAS spectra at the K-edge of Mg (Fig. 1). Ho atoms were deposited on the thin insulating film with the sample surface kept at 6.5 K. At this temperature, the impurities stick at the the adsorbing site without diffusing on the surface, as indicated by low-temperature STM measurements performed in collaboration with H. Brune's group at the EPFL (see inset of Fig. 1). Coverages as small as 1-3 % on monolayer were studied. We acquired XAS and XMCD spectra in the Total Electron Yield mode at the $M_{5,4}$ edges of Ho in order to access to the ***L*** and ***S*** moments. The complex shape of the XAS backgrounds at the Ho edge (Fig. 2) required the acquisition of a significant number of spectra (8 or more) to be mediated per photon polarization, thus impeding measurement of other RE atoms different from Ho. However, we expect similar measurements in future runs to be easier, since an issue at the monochromator cooling present during this experiment has been later solved. Nonetheless, the vacuum conditions guaranteed samples with unmodified XAS and XMCD spectra for at least 4-5 hours of experiment.

C) Results

We prepared more that 10 different samples to cross check the the magnetism of Ho on its coverage, the thickness of MgO film and the data reproducibility. Some interesting results are already clear and summarized below:

- For Ho atoms on a 3ML MgO, the magnetization loop acquired with the field perpendicular to the sample surface (i.e. along the magnetization easy axis) shows a small opening at 6.5 K (Fig. 3), even if the corresponding coercive field is still small. This observation suggests that first-order spin excitations between the lowest spin doublet are forbidden, e.g. as a result of a suitable combination of the J_z ground state and crystal field symmetry.
- Despite the extremely low coverage, the signal to noise ration of the XAS spectra is good enough to identify clear multiplet structures (Fig. 4, left panels). Combined information from natural and magnetic linear dichroism spectra could be used as a guide to run multiplet calculations which were cross-checked against sum rule analysis. Multiplet calculations (Fig. 4, right panels) show that spectra obtained for a ground state $<J_z>= 4.8$ and a zero-field-splitting of 4.4 meV best reproduce experimental findings. The four-fold symmetric term of the crystal field operator only connects quantum states separated by $\Delta J_z= 4$, thus only a reduced subset of states is mixed. The resulting ground state doublet is a superimposition of different quantum states with the largest fraction having $J_z= 7$. This state fullfils the condition for impeding magnetization reversal from first-order electron scattering.
- For a MgO thickness lower than 3 ML, the oxide layer decouples less effectively the magnetic atoms from the conduction electrons of the underneath metal support and, in turns, the opening in the hysteresis loop vanishes. On the other end, we observe that, for very thick MgO layers (>5 monolayers), the easy axis direction flips from out- to in-plane. This could indicate a change in the coordination environment for Ho adatoms, in line with the increasing roughness (i.e. higher density of step sites) of the MgO surface.

In conclusion, this results represent the first unequivocal evidence of single atom magnets showing finite remanence and coercivity on the timescale of minutes. The data suggest that thin insulating layers, such as those obtained depositing MgO on Ag(100), can efficiently decouple the 4f states from the electrons of the metallic surface, opening interesting opportunities for achieving long spin lifetimes for single magnetic atoms. Further investigation (i.e. different 4f configurations, crystal field environments) is needed to clarify and disentangle the specific roles played by the decoupling layer and the protection given by the crystal field symmetry.

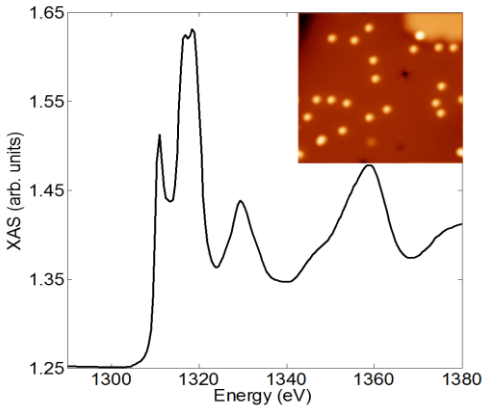

Fig. 1. XAS spectra at the K-edge of Mg for MgO/Ag(100). In the inset, a STM image (20x20) nm^2 of Ho atoms on MgO/Ag(100) acquired at 4.7 K

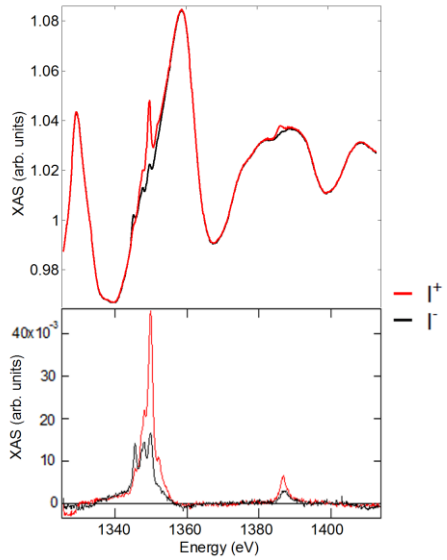

Fig. 2. XAS spectra before (upper panel) and after (lower panel) background substraction acquired at the Ho $M_{5,4}$ edge for Ho/MgO/Ag(100) at normal incidence of the photon beam with respect to the sample surface. Ho Coverage is 1% of monolayer. T= 6.5K, B= 8.5T.

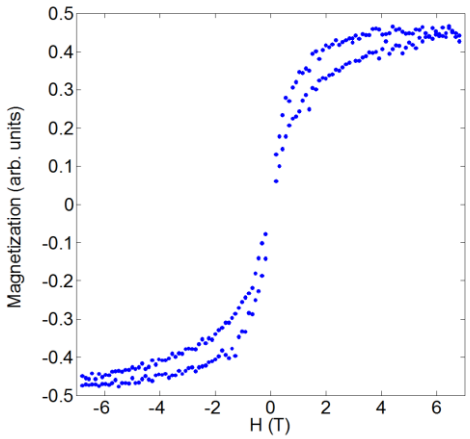

Fig. 3. Magnetization curve for Ho/MgO/Ag(100) acquired at normal incidence of the photon beam with respect to the sample surface. Ho coverage is 1% of monolayer. T=6.5 K.

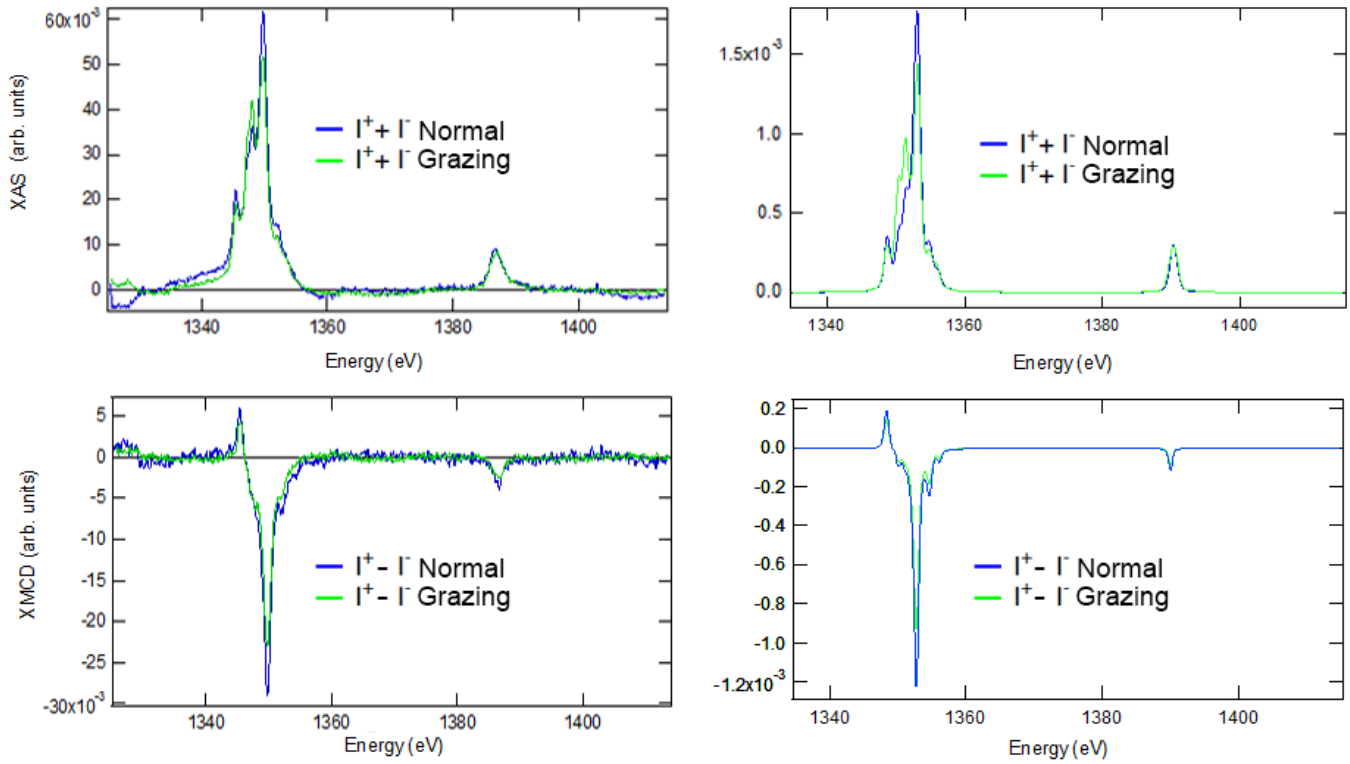

Fig. 4. Comparison between experimental (left panels) and calculated (right panels) x-ray absorption spectra at the Ho $M_{5,4}$ edge for Ho/MgO/Ag(100) at normal and grazing incidence of the photon beam with respect to the sample surface. Ho Coverage is 1% of monolayer. T= 6.5K, B= 8.5T.

D) References

[1] P. Gambardella, S. Rusponi, M. Veronese *et al.*, Science 300, 1130 (2003).

[2] P. Błoński, A. Lehnert, S. Dennler *et al.*, Phys. Rev. B 81, 104426 (2010).

[3] I. G. Rau, S. Baumann, S. Rusponi *et al.*, Science 344, 988 (2014).

[4] A. A. Khajetoorians, S. Lounis, B. Chilian *et al.*, Phys. Rev. Lett. 106, 037205 (2011).

[5] T. Miyamachi, T. Schuh, T. Markl *et al.*, Nature 503, 242 (2013).

[6] F. Donati, A. Singha, S. Stepanow *et al.*, Phys. Rev. Lett. 113, 237201 (2014).

[7] S. Schintke, S. Messerli, M. Pivetta *et al.*, Phys. Rev. Lett. 87, 276801 (2001).

[8] C. Hübner, B. Baxevanis, A. A. Khajetoorians *et al.*, Phys. Rev. B 90, 155134 (2014).