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Names and affiliations of applicants (* indicates experimentalists):

Sebastian Stepanow*[$], Jan Honolka*[$], Lucia Vitali*[$], P. Gambardella*[&], Klaus Kern[$&], and Mario Ruben[%]

[$]Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

[&]Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

[%]Institute of Nanotechnology, Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany

Report:

The purpose of the experiment was the characterization of the magnetic properties of monolayers and thin films of $Tb(Pc)_2$ single-molecule magnets on metal surfaces. $Tb(Pc)_2$ represents a new class of molecular magnets with a single Terbium ion located between two phthalocyanine (Pc) units that exhibit slow relaxation of the magnetic moments below 40 K in SQUID measurements [1]. The measurements aimed at the identification of the electronic ground state of the Tb center and its magnetic anisotropy that should be detectable due to the high degree of molecular orientation on the surface. Furthermore, the aim was to investigate if the molecules show magnetic hysteresis in the adsorbed layers and in slowly sweeping fields in XMCD measurements.

The sample preparation relied on a stamping technique that had been developed in the laboratory in Stuttgart [2]. This represents the first attempt to deposit single-molecule magnets in a controlled and dry environment to the surface. However, the quality of samples that we could obtain at the preparation chamber of ID08 was not sufficient for further XAS studies. The samples were characterized by STM and LEED measurements and did not show the expected order of adsorbed molecules. We concluded that this delicate sample preparation procedure was not applicable at the ESRF facilities, therefore we decided to move on with the back-up experiments.

We obtained results on a $Tb(Pc)_2$ powder sample as well as a small crystallite of neutral $Tb(Pc)_2$ that shows little but significant preferrential orientation of the molecules. As a back-up experiment we also did XMCD measurements on Ru impurities on a Ag(100) surface. The latter results have been published, full reference to the article as well as the title and abstract are given in reference 3. A summary of the measurements obtained on the $Tb(Pc)_2$ powder is presented in figure 1. The lineshape of the XAS spectra of the Terbium $M_{5,4}$-edge, shown in figure 1 (a), is compatible with a Tb(3+) ion with an J=6 ground state [4]. This is in agreement with the analysis of SQUID measurements [1]. Furthermore, the sizable XMCD signal and the $M_{5,4}$ XMCD branching ratio signify a large orbital moment at the Terbium ion. The N-edge spectrum reveals the signature of H_2Pc molecules [5], see figure 1 (b). The neutral $Tb(Pc)_2$ has an unpaired electron delocalized over the two Pc planes, however, no magnetic dichroism has been observed at the N-edge in magnetic fields up to 5T. This could indicate that the involved molecular orbital has only little electron

density at the nitrogen atoms. Figure 1 (c) shows the magnetization curve obtained with the normalized M_5 XMCD intensity at the Terbium edge at 8K (only one sweep shown). Although, the lowest available temperature of 8K is well below the blocking temperature no hysteresis has been observed. Sweeping the magnetic field from 5T to 0T is in the order of a few minutes, which might be still too long for the expected slow relaxation of the magnetic moment at 8K. Furthermore, the XMCD signal tends to saturate above 5T. The analysis of the magnetic moments employing the sum rules is not straight forward for the spin moment due to the unknown contribution of the spin dipolar term *T*, which could be large in such anisotropic systems. The orbital moment can be easily obtained and yields $1.2\mu_B$ for the f^8 shell. This value represents, however, a mean value due to the angular average in the powder sample.

Figure 2 summarizes the results obtained for the small crystallite of neutral $Tb(Pc)_2$ molecules. AFM measurements on the crystallite performed after the XAS experiments show that the crystallite has many facets at the surface. However, the N-edge spectra shown in figure 2 (a) are indicative of a preferrential orientation of the $Tb(Pc)_2$ molecules. The π^*-resonances below 403 eV exhibit a stronger intensity with x-rays polarized out-of-plane whereas the σ^*-resonances above 403 eV are enhanced with in-plane polarization. Hence, we conclude that the Pc planes are preferrentially aligned parallel to the crystallite surface plane. The magnetization curve presented in figure 2 (b) has been measured with magnetic field normal to the sample surface (0°) and almost parallel to the surface (70° to surface normal) at a temperature of 8K. The normalized Tb M_5 XMCD signal is stronger at magnetic fields normal to the sample surface. This indicates that the magnetization easy axis is along the symmetry axis of the $Tb(Pc)_2$ molecule, i.e., perpendicular to the Pc planes. The anisotropy is rather weak, however, the molecules are not fully aligned in the crystallite. Furthermore, the magnetization curves suggest that the saturation magnetization is different parallel and perpendicular to the molecule axis. It is worth to note, that the XMCD lineshape does not depend on the x-ray incidence angle (not shown).

In conclusion, we have measured for the first time the magnetic properties of neutral $Tb(Pc)_2$ molecules in powder and polycrystalline samples. The Tb $M_{5,4}$ XAS spectra are in agreement with Terbium(III) ions in J=6 ground state. There is a sizable magnetic moment and anisotropy with the easy axis perpendicular to the Pc units. However, there is no XMCD signal detectable at the N-edge. Furthermore, results obtained for Ru impurities on a Ag(100) surface have been published in reference 3.

References:

[1] N. Ishikawa et al., *J. Am. Chem. Soc.* **125**, 8694 (2003); *J. Phys. Chem. B* **108**, 11265 (2004).
[2] L. Vitali et al., *Nano Letters* **8**, 3364 (2008).
[3] J. Honolka et al., *Phys. Rev. B* **76**, 144412 (2007).

Absence of local magnetic moments in Ru and Rh impurities and clusters on Ag(100) and Pt(997)

The magnetism of quench-condensed Ru and Rh impurities and metal films on Ag(100) and Pt(997) has been studied using x-ray magnetic circular dichroism. In the coverage range between 0.22 and 2.0 ML, no dichroic signal was detected at the $M_{3,2}$ absorption edges of Ru on Ag(100) at a temperature of 5 K in the presence of an applied magnetic field. The same was found for coverages between 0.12 and 0.5 ML of Rh on Ag(100) and Pt(997). It is concluded that the magnetic moments of single impurities, small clusters of various shape, and monolayers of the 4*d* metals are below the detection limit of 0.04 μ_B per atom. These results provide an unambiguous determination of the local magnetic moment of Ru and Rh deposited on nonmagnetic transition-metal surfaces, which are in contrast with theoretical predictions.

[4] J. B. Goedkoop et al., *Phys. Rev. B* **37**, 2086 (1988).
[5] S. Kera et al., *Surf.Sci.* **600**, 1077 (2006).

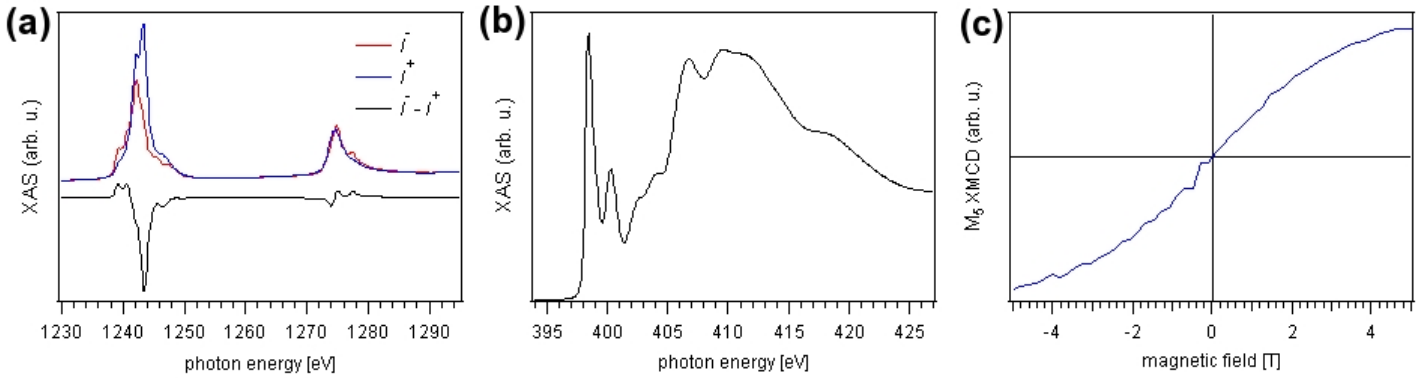

Figure 1: XAS and XMCD characterization of neutral $Tb(Pc)_2$ powder sample. (a) Tb-edge XAS and XMCD spectra taken in total electron yield at 8K and 5T. (b) N-edge XAS taken in total electron yield at 300K. (c) Magnetization measured with the normalized M_5 XMCD intensity at 8K.

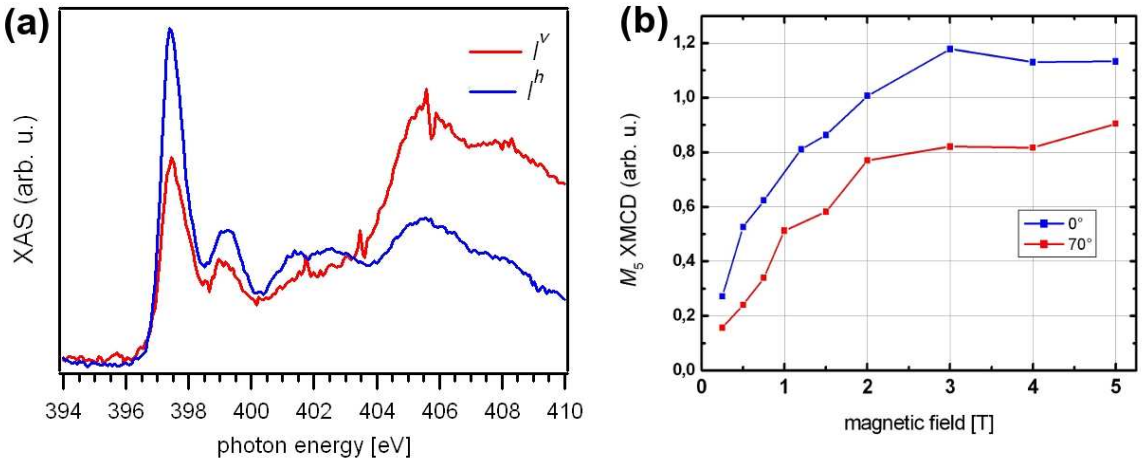

Figure 2: (a) XAS at Nitrogen *K*-edge with linear polarized light in total electron yield mode. I^v corresponds to electric field vector of incident x-rays in the surface plane and I^h to almost out-of-plane (20° to surface normal). (b) Normalized Terbium M_5 XMCD intensity taken at normal (0°) and grazing (70°) x-ray incidence at a temperature of 8K. There is no dichroism at zero magnetic field.