

EXPERIMENTAL REALISATION OF SINGLE-ATOM MAGNETS

The existence of single-atom magnets has been proven by X-ray magnetic circular dichroism. Monodisperse holmium atoms adsorbed on a nonmagnetic MgO thin film display magnetic hysteresis up to a temperature of 30 K and with a magnetic relaxation time of the order of 1500 s. This stability is exceptional for such tiny structures. This study unveils key factors to improve the stability of atom-sized magnets in a solid state environment.

Magnets possess both strength and memory. These two properties make them useful for a broad variety of applications, which involve action at a distance or retention of magnetic information. Yet, as a magnet is reduced in size, thermal fluctuations overcome the anisotropy barrier that keeps the magnetic axis stable, leading to the loss of permanent magnetisation.

Scientists have been working for a long time to define and reduce the size of permanent magnets down to the smallest possible limit. A recent study that we have carried out at the ESRF and SLS may have brought us to the end of this quest. Exceptional magnetic stability can be achieved by combining the properties

of rare earth atoms, such as holmium, with that of a weakly-interacting but mechanically-stiff supporting thin film, such as a 1 nm thick MgO layer. **Figure 1** shows the adsorption geometry of individual Ho atoms on the O sites of the MgO(001) lattice calculated by density functional theory (DFT) and probed by scanning tunnelling microscopy (STM).

X-ray magnetic circular dichroism measurements at the $M_{4,5}$ absorption edges of Ho (**Figure 2a**), carried out at beamline ID32, indicate that the Ho atoms possess a high magnetic moment in a magnetic field of 8.5 T and at 6 K. Surprisingly, hysteretic behaviour appears as the magnetisation is measured as a function of applied field (**Figure 2b**), revealing that the Ho atoms display magnetic remanence, just like a permanent magnet. Additional measurements, carried out at the SLS, show that magnetic hysteresis persists up to 30 K and correlates with the thickness of the MgO film. The magnetic relaxation time was found to be of the order of 1500 s or possibly larger, being limited by the X-ray photon flux used to probe the atoms. For comparison, the magnetic relaxation time in the most stable single molecule magnets reported to date is of the order of 1 ms at such temperatures.

Ligand field multiplet calculations and density functional theory show that, due to the symmetry of the ligand field, the electronic ground state of the Ho atoms is a superposition of angular momentum states that is immune to quantum tunnelling and first order spin reversal processes. Furthermore, MgO is a stiff insulating material that provides insulation from both electrons and thermal vibrations, which are responsible for inducing spin-flips and destroying magnetic remanence in small structures. The combination of these features enables the realisation of long-lived magnetic states in atomic scale structures.

This work is the culmination of a long-standing project that began 15 years ago at the ESRF, where the upgrade of beamline ID12 to ID08 and then to ID32 has led to the first experiments able to probe the magnetic ground state of monodispersed single atom arrays on surfaces [1-3]. Identifying the conditions that allow the stabilisation of the magnetic moment of

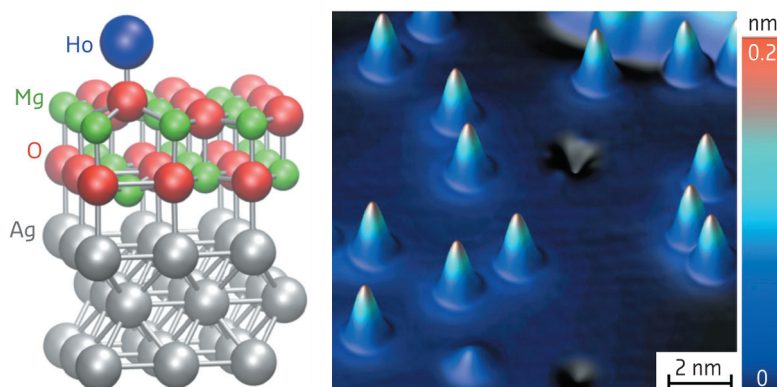


Fig. 1: Adsorption geometry of Ho atoms on a two-monolayer-thick MgO film deposited on Ag(100) as calculated by density functional theory (left) and measured by scanning tunnelling microscopy (right).

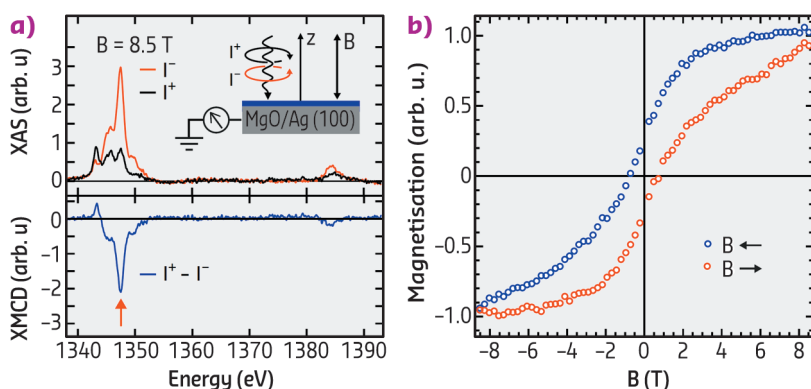


Fig. 2: a) X-ray absorption spectra and circular magnetic dichroism of an ensemble of individual Ho atoms adsorbed on MgO measured at the $M_{4,5}$ Ho edges at 6 K in a magnetic field of 8.5 T. b) Magnetic hysteresis curve measured at 6 K. The dots represent the maximum of the XMCD signal indicated by the arrow in (a) recorded as a function of magnetic field.

an atom coupled to a solid state environment permits the manipulation of atomic spins using microwave fields and even dc electric currents,

which is paramount for the development of model classical and quantum memory devices based on single atom magnet arrays.

PRINCIPAL PUBLICATION AND AUTHORS

Magnetic remanence in single atoms, F. Donati (a), S. Rusponi (a), S. Stepanow (b), C. Wackerlin (a), A. Singha (a), L. Persichetti (b), R. Baltic (a), K. Diller (a), F. Patthey (a), E. Fernandes (a), J. Dreiser (a,c), ˙Z. Šljivančanin (d,e), K. Kummer (f), C. Nistor (a), P. Gambardella (a) and H. Brune (a),

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REFERENCES

[1] P. Gambardella *et al.*, *Phys. Rev. Lett.* **88**, 047202 (2002).

[2] P. Gambardella *et al.*, *Science* **300**, 1130 (2003).

[3] P. Gambardella *et al.*, *Nature Mater.* **8**, 189 (2009).

UNDERSTANDING MAGNETIC COUPLING IN LANTHANIDE-BASED MOLECULES BY XMCD AND *ab initio* MODELLING

A comprehension of the mechanisms linking a molecular spin centre with its environment is crucial for the development of spintronics functionalities at the molecular scale. Here we combine X-ray magnetic circular dichroism (XMCD) with *ab initio* calculations to investigate the microscopic spin path in bis(phthalocyaninato)-lanthanide(III) single molecule magnets coupled to a Ni substrate.

Magnetic molecules of the family of bis(phthalocyaninato)-lanthanide(III) (LnPc_2 , so called “double decker”) are made by a single lanthanide ion as the magnetic centre, sandwiched between two phthalocyanines (Figure 1, inset). This specific structure, where the localised lanthanide f-orbitals are coupled with the delocalised π -type electrons of the organic ligands, allows the existence of a sizeable magnetic interaction with the environment, while at the same time the magnetic core is efficiently protected. The intramolecular spin communication channels are highlighted here by studying how the coupling between the molecules and a Ni substrate is varied upon the substitution of the central Ln-ion.

Our experiments were carried out at beamline ID08 (now ID32). The molecular units were sublimated *in situ* on a freshly prepared Ni(111) surface with sub-monolayer coverage. Our results show that they are isolated and lying flat, with the Pc plane parallel to the surface. The low-temperature ($T = 8$ K) XMCD-derived magnetisation curves of the three compounds (LnPc_2 , where Ln = Tb, Dy and Er) and of the Ni substrate are shown in Figure 1. The Ln-curves display a characteristic “N-shape” behaviour, in

particular for small magnetic fields the magnetisation is generally opposed to the field. These features reveal an antiferromagnetic coupling of the Ln-magnetic moment with the Ni substrate. The quantitative estimation of the coupling strength can be obtained by fitting the experimental data with a model spin-Hamiltonian, where the only fitting parameter is the Ln-Ni coupling and all the microscopic molecular

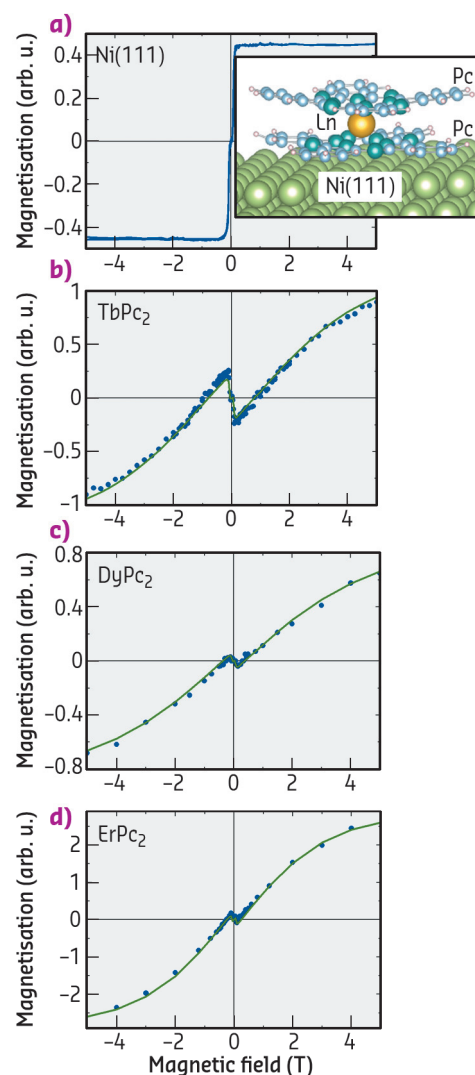


Fig. 1: Element resolved XMCD magnetisation measurements of Ni (a), Tb (b), Dy (c), Er (d) for the $\text{LnPc}_2/\text{Ni}(111)$ systems, taken at the incidence angle $\Theta = 70^\circ$ between the X-ray beam and the surface. Experimental data are shown as dots, while the theoretical fit are the continuous lines.