

Correlation between Electronic Configuration and Magnetic Stability in Dysprosium Single Atom Magnets

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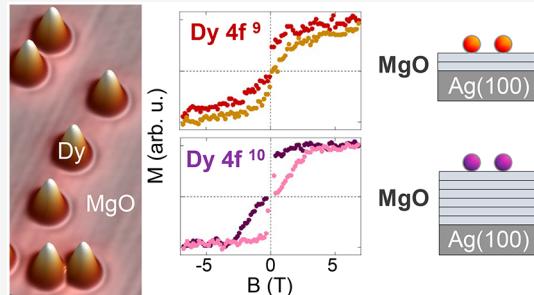
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ABSTRACT: Single atom magnets offer the possibility of magnetic information storage in the most fundamental unit of matter. Identifying the parameters that control the stability of their magnetic states is crucial to design novel quantum magnets with tailored properties. Here, we use X-ray absorption spectroscopy to show that the electronic configuration of dysprosium atoms on MgO(100) thin films can be tuned by the proximity of the metal Ag(100) substrate onto which the MgO films are grown. Increasing the MgO thickness from 2.5 to 9 monolayers induces a change in the dysprosium electronic configuration from $4f^9$ to $4f^{10}$. Hysteresis loops indicate long magnetic lifetimes for both configurations, however, with a different field-dependent magnetic stability. Combining these measurements with scanning tunneling microscopy, density functional theory, and multiplet calculations unveils the role of the adsorption site and charge transfer to the substrate in determining the stability of quantum states in dysprosium single atom magnets.

KEYWORDS: Single atom magnets, lanthanides, X-ray magnetic circular dichroism, scanning tunneling microscopy, density functional theory, multiplet calculations



Lanthanide-based quantum magnets are model systems for atomic scale memory^{1–8} and quantum logic devices.^{9,10} Because of their strong localization, their 4f electrons generally show a very limited degree of covalency and preserve an atomic-like character with well-defined integer orbital occupation. Depending on the ligand environment, lanthanide complexes and surface-adsorbed atoms can be mostly found in either atomlike ($4f^n$)^{4,11–15} or bulklike configuration ($4f^{n-1}$).^{1–3,16–23} Not only does the 4f occupation determine the magnetic moment and stability of the atom, but it also has an impact on the population of the 6s5d valence orbitals^{15,22,24,25} determining the behavior in spin transport measurements.^{8,26–28} Hence, understanding how to control the lanthanide atom's electronic configuration is a crucial step to develop novel approaches to design quantum magnets with tailored stability and accessibility of their magnetic states.^{22,29}

Atom adsorption on suitable surfaces is a viable pathway for creating such quantum magnets^{3,4,8} and allowing individual access to their spin states using transport techniques.^{8,26–28,30} However, despite the relatively simple atom-support coordination structure, it remains challenging to theoretically predict how the substrate and adsorption geometry impact their multiorbital spin configuration, calling for experiments to shed light on these mechanisms.

Among the lanthanide series, dysprosium (Dy) has been employed to realize molecular magnets with record-high

blocking temperature^{1,2,19} and surface-supported single atom magnets with long spin lifetime.^{4,8} Moreover, recent theoretical calculations on DyO complexes predict large magnetic anisotropy for Dy in both $4f^9$ and $4f^{10}$ electronic configurations.^{31,32} Here, we focus on O-coordinated Dy atoms resulting from low-temperature adsorption on MgO thin films grown on Ag(100). We show that the electronic configuration and, consequently, the magnetic properties of the Dy atoms depend on the thickness of the supporting MgO layer. For MgO layers with an average thickness $t_{\text{MgO}} < 5$ monolayers (ML), X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) at 2.5 K reveal a predominance of bulklike Dy $4f^9$ configuration, displaying magnetic hysteresis indicative of long lifetimes. By increasing the thickness of the MgO layer, Dy atoms with $4f^{10}$ configuration progressively increase in abundance and become the dominant species for $t_{\text{MgO}} > 6–7$ ML. Remarkably, Dy atoms show magnetic hysteresis also in this configuration, however, with a character-

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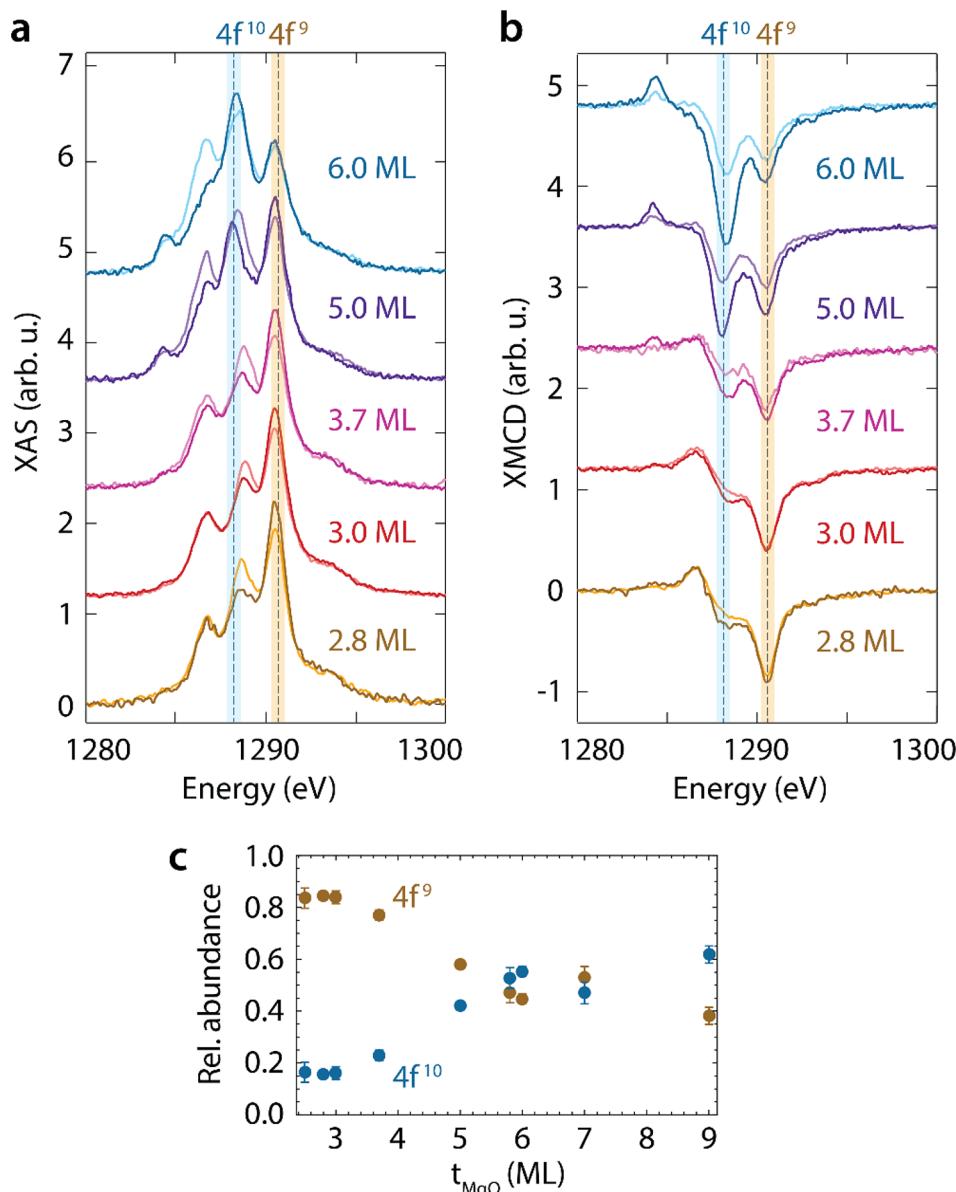


Figure 1. 4f occupation versus MgO thickness for Dy atoms on MgO/Ag(100). (a) XAS and (b) XMCD at the Dy M₅ edge as a function of the average MgO thickness t_{MgO} . Fractional values of t_{MgO} indicate incomplete filling of the MgO atomic layers. Darker/lighter lines show the measurement at normal/grazing incidence, respectively. The position of the 4f⁹ and 4f¹⁰ main peaks of XAS and XMCD measurements are indicated with light blue and brown bands, respectively. (Dy coverage $\Theta_{\text{Dy}} = 0.004\text{--}0.014 \text{ ML}$, $B = 6.8 \text{ T}$, $T = 2.5 \text{ K}$). (c) Relative abundance of the 4f⁹ and 4f¹⁰ species obtained by fitting the experimental data with simulated spectra from multiplet calculations (see SI for details). Standard deviations from the fit are displayed as error bars.

istic butterfly loop indicating quantum tunneling of the magnetization (QTM) in the absence of an external field. Magnetic relaxation measurements reveal that the lifetime of magnetic states can be controlled using the external field, with a maximum of about 200 s for 0.25–0.40 T. Density functional theory (DFT) and multiplet calculations reveal how charge transfer to the substrate and adsorption geometry determine the electronic configuration of Dy and the stability of its magnetic states.

We perform XAS/XMCD measurements at the M_{4,5} edges (3d → 4f transitions) of Dy at 6.8 T and 2.5 K at the EPFL/PSI X-Treme beamline at the Swiss Light Source³³ to determine the 4f orbital occupation and magnetic properties. To avoid measurements on exposed Ag(100) regions, we use MgO films with $t_{\text{MgO}} > 2 \text{ ML}$. XAS/XMCD spectra are

acquired in two different geometries, that is, with the photon beam and magnetic field oriented along the surface normal (normal incidence) and 60° off-normal (grazing incidence, see SI for details), to determine the magnetization easy axis of the Dy atoms.^{4,11,12,34}

The XAS and XMCD spectra as a function of the average MgO thickness are displayed in Figure 1a,b, respectively. The energy of the maximum at the M₅ edge, both in XAS and XMCD, changes from 1290.5 to 1288.3 eV going from ultrathin to thicker MgO layers. These two energies are characteristic of 4f⁹ and 4f¹⁰ electronic configurations, respectively, as deduced by comparison with previous data of Dy atoms on metals¹¹ and supported graphene.^{4,12} The continuous evolution implies the coexistence of 4f⁹ and 4f¹⁰ Dy atoms, whose proportions depend on the MgO thickness.

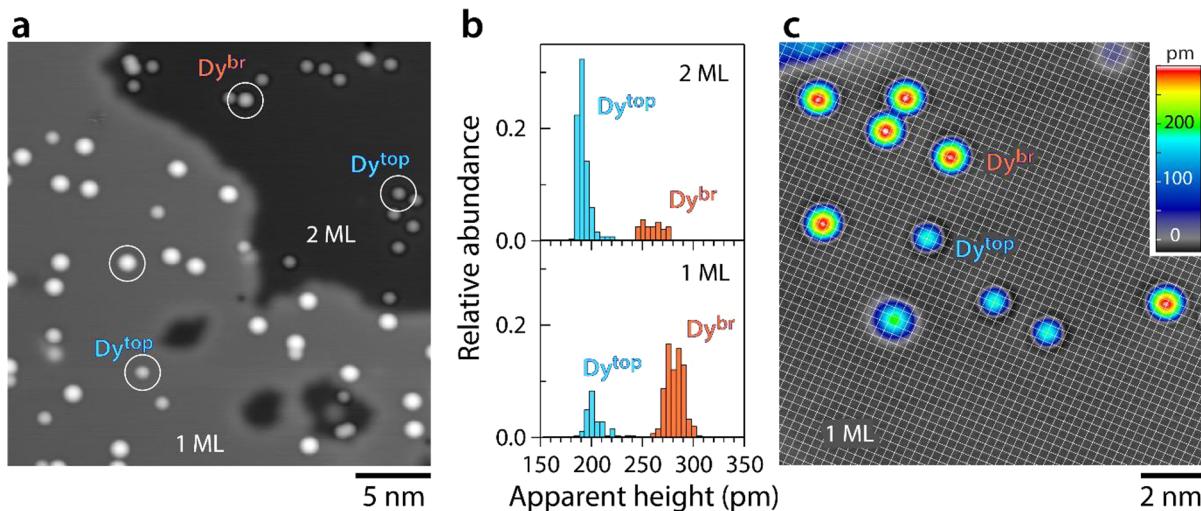


Figure 2. Scanning tunneling microscopy of Dy atoms on MgO/Ag(100). (a) After deposition on the MgO surface kept at around 10 K, two Dy species with different apparent heights are observed in STM images. (b) Apparent height distributions of the two Dy species for 1 and 2 ML MgO. (c) By overlapping a grid representative of the O sublattice, corresponding to the crossings of the grid, we identify the two species as Dy atoms adsorbed on O-top (Dy^{top}) and on bridge (Dy^{br}), respectively. The grid is obtained from an atomically resolved image of the MgO surface in a spot without Dy atoms. The species with elongated shape on the bottom-left side of the image is tentatively identified as a Dy dimer ($\Theta_{\text{Dy}} = 0.007 \text{ ML}$, $V_t = -100 \text{ mV}$, $I_t = 20 \text{ pA}$, $T = 5 \text{ K}$).

In order to simulate the XAS/XMCD spectra and to derive quantitative information on the abundance of the different electronic configurations, we investigate the adsorption sites of Dy atoms using STM for the MgO thickness range accessible to this technique. On ultrathin MgO layers on Ag(100), Dy atoms appear as protrusions with two distinct apparent heights, whose precise values depend on the MgO layer thickness (see Figure 2a,b). Overlaying the MgO lattice deduced from atomic-resolution images allows one to attribute the 2-fold bridge adsorption site to the species with the largest apparent height and a 4-fold symmetric site to the other ones, see Figure 2c. Further samples prepared by codepositing Co and Dy allow one to ascertain the 4-fold adsorption site as O-top (see Figure S1).^{3,35,36} The abundances of the two populations, hereafter being referred to as Dy^{br} and Dy^{top}, respectively, vary with the thickness of the MgO layer. On 1 ML MgO, Dy^{br} atoms ($79 \pm 4\%$) are more abundant than Dy^{top} ones ($21 \pm 4\%$), whereas on 2 ML thick regions the abundances are essentially reversed with $25 \pm 5\%$ Dy^{br} and $75 \pm 5\%$ Dy^{top}. A comparable ratio is also found on 3 ML MgO. This abrupt change of adsorption site abundances between 1 and 2 MgO layers seems dissociated from the smooth variation from 4f⁹ to 4f¹⁰ population occurring over a broader range of t_{MgO} , suggesting that the change in 4f occupation has a different origin. Similar variations in the relative population of O-top and bridge were also found for Ho atoms and ascribed to the layer-dependent transient mobility after surface adsorption.^{35,36} However, compared to Ho, for the same MgO thickness Dy atoms show a larger abundance of bridge species^{35,36} that need to be considered to interpret ensemble-averaged XAS/XMCD measurements.

To quantify the abundance of species with 4f⁹ and 4f¹⁰ configuration, we fit the angle-dependent XAS for each MgO thickness with simulated spectra from multiplet calculations using the MultiX code,³⁷ including the adsorption site specific C_{4v}- and C_{2v}-symmetric crystal field (CF) from a point charge model with the positions and values of the point charges deduced from DFT Born charges, as discussed in SI. Although

the STM measurements are carried out on ultrathin MgO films, we assume that both adsorption sites are present also on thicker ones with both 4f⁹ and 4f¹⁰ occupations. This procedure provides us with spectra characteristic of each of the four electronic configuration–adsorption site pairs, which we combine to reproduce the experiments (see Figures S2 and S3). Our fits reproduce the angle-dependent XAS very well and provide the abundance of each species as a function of the thickness of the MgO film (Table S5) with the overall 4f⁹ and 4f¹⁰ fractions shown in Figure 1c. The 4f⁹ fraction changes smoothly from 84% for the thinnest MgO layer to 38% for the thickest one with the crossover between the two electronic configurations occurring at around 6–7 ML of MgO. The continuous trend is a consequence of the roughness of the MgO films on Ag(100).³⁸

The ability to tune the electronic configuration by varying the MgO film thickness gives us the unique opportunity to characterize the magnetic properties of the Dy in 4f⁹ and 4f¹⁰ electronic states while keeping the same crystal field. Indeed, we observe a different magnetic behavior as highlighted by the angular and magnetic field dependence of the XMCD. The difference between normal and grazing incidence XMCD signals is almost negligible at the lowest MgO thickness where the 4f⁹ signal dominates, while it becomes more pronounced when the relative weight of the 4f¹⁰ configuration is larger, see Figure 1b.

Pronounced angular dependence of the XMCD with largest signal in normal incidence is the fingerprint of species with large perpendicular magnetic anisotropy.^{3,4,11,12,17,18,21,34,39–41} The absence of out-of-plane anisotropy for the 4f⁹ species is in apparent contrast with previous STM studies finding record-high values of uniaxial perpendicular anisotropy for Dy^{top} on 2 ML MgO/Ag(100),⁸ the largest among surface spins. However, due to 4f⁹ Dy^{br} atoms with a larger XMCD along the grazing orientation, the directional contribution of the two 4f⁹ species cancels out, resulting in a very small angular dependence of the overall 4f⁹ XMCD. On the other hand, the pronounced angular dependence at the 4f¹⁰ peak indicates that

both $4f^{10}$ Dy^{top} and Dy^{br} have perpendicular anisotropy, as also predicted by multiplet calculations (see Figure S2).

In order to evaluate the magnetic stability of the individual species, we acquire hysteresis loops by measuring the intensity of the XMCD while sweeping the external magnetic field. The energy difference in the XMCD peak related to the two electronic configurations allows one to resolve the field-dependent magnetization separately for the $4f^9$ and $4f^{10}$ species. Figure 3 shows the out-of-plane magnetization loops

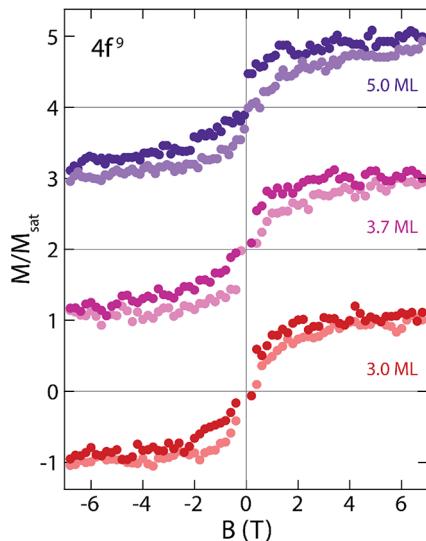


Figure 3. Out-of-plane hysteresis loops of Dy $4f^9$ species for different MgO thicknesses. The points represent the out-of-plane XMCD at the Dy $4f^9$ peak (1290.5 eV) acquired while sweeping the magnetic field at 33.3 mT/s ($\Theta_{\text{Dy}} = 0.009 - 0.014 \text{ ML}$, $T = 2.5 \text{ K}$).

of the Dy $4f^9$ species acquired by measuring the XMCD signal at 1290.5 eV as a function of the magnetic field sweeping from +6.8 T to -6.8 T and back to +6.8 T with a rate of 33.3 mT/s. In all samples, we observe a narrow opening, which extends up to the maximum available field. The area of the loop slightly increases with the thickness of the MgO film, possibly due to a larger decoupling from the hot electrons generated in the Ag substrate by X-ray photon absorption.⁴² The presence of magnetic hysteresis indicates that the magnetic relaxation to the ground state is slower than the time resolution of the experiment. According to previous STM results,⁸ Dy^{top} atoms exhibit a long magnetic lifetime up to 5 T, which should result in a wide hysteresis loop. Conversely, Dy^{br} atoms, being in a low symmetry CF, are expected to show reduced magnetic lifetime and to exhibit a fully paramagnetic loop. On the basis of the mixed composition of the ensemble, we interpret the narrow hysteresis as an average behavior between hysteretic Dy^{top} and paramagnetic Dy^{br} species.

The out-of-plane hysteresis curve acquired at the XMCD peak of the $4f^{10}$ species (1288.3 eV) reveals a very different shape and pronounced anisotropy; see Figures 4a and S4. The loop is wide open up to 3 T with a strong signature of QTM at zero external field. Similar signature of QTM was also observed for Dy(II) $4f^95d^1$ in single ion magnets²² and ascribed to the non-Kramers nature of the ion, which is more sensitive to deviations from a perfect axial environment.³¹ The low symmetry adsorption geometry of the $4f^{10}$ Dy^{br} is not expected to enable long magnetic lifetimes, similar to $4f^9$ Dy^{br} discussed

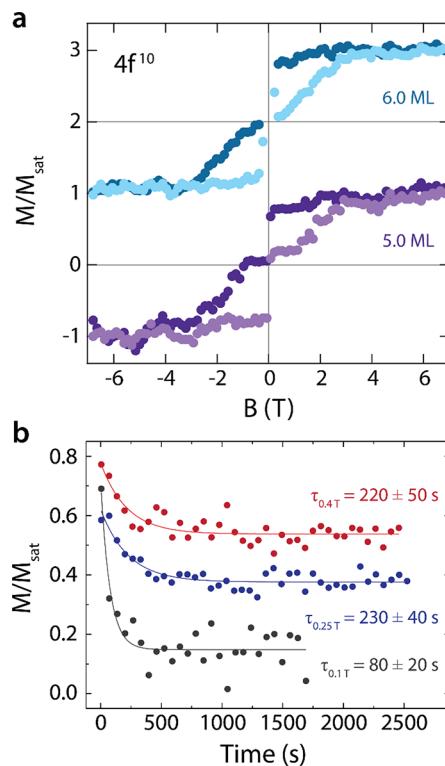


Figure 4. Out-of-plane hysteresis loops and magnetic relaxation of Dy $4f^{10}$ species. (a) The points represent the out-of-plane XMCD at the Dy $4f^{10}$ peak (1288.3 eV) acquired while sweeping the magnetic field at 33.3 mT/s for different MgO thicknesses. (b) Decay of the normal incidence XMCD signal as a function of time for $B = 0.4 \text{ T}$ (red dots), $B = 0.25 \text{ T}$ (blue dots), and $B = 0.1 \text{ T}$ (black dots) after saturating the ensemble at 3 T on a sample with 6.0 ML MgO. Lines are exponential fits to the data providing the magnetic lifetime τ at the related field ($\Theta_{\text{Dy}} = 0.009 - 0.012 \text{ ML}$, $T = 2.5 \text{ K}$).

above. Hence, we attribute the hysteretic behavior of the $4f^{10}$ species to the Dy^{top} atoms.

To quantify the lifetime of the $4f^{10}$ Dy^{top}, we record the time decay of the XMCD signal at constant external field after saturating the magnetization in a field of 3 T prior to switching the field to the indicated values and starting the acquisition.^{3,4,18,40,42,43} Figure 4b shows the magnetic relaxation at three different external fields with the asymptotic value of the XMCD signal indicating the corresponding equilibrium magnetization of the ensemble. The $4f^{10}$ species show a magnetic lifetime of about 200 s at both 0.25 and 0.4 T, while lowering the field to 0.1 T shortens the relaxation time to less than 100 s due to QTM becoming more effective in this field range, as observed for other non-Kramers single molecule magnets.²² Magnetic relaxation at lower fields becomes too fast to be detected with our setup. The lifetime of $4f^{10}$ Dy atoms on MgO is a few orders of magnitude shorter than that reported for $4f^9$ Dy^{top} on 2 ML MgO/Ag(100),⁸ and for other Ho and Dy single atom magnets with the same 4f occupation^{3,12,43} but similar to that of divalent Dy $4f^95d^1$ single molecule magnets in polycrystalline form.²²

In order to unravel the mechanism determining the variation of the Dy 4f orbital filling with the thickness of the supporting MgO layer, we perform DFT calculations using pseudopotentials and plane wave bases, as implemented in Quantum Espresso.⁴⁴⁻⁴⁹ To correct for the self-interaction of the exchange-correlation functional, we applied a Hubbard U

correction of 9 eV on both the 4f and 5d manifolds.^{50,51} To understand the role of the adsorption site and of the Ag(100) substrate, we simulate the Dy^{top} and Dy^{br} species on both free-standing 2 ML MgO(100) and 2 ML MgO/Ag(100). When adsorbed on O-top on MgO(100) (Figure 5a), the Dy atoms

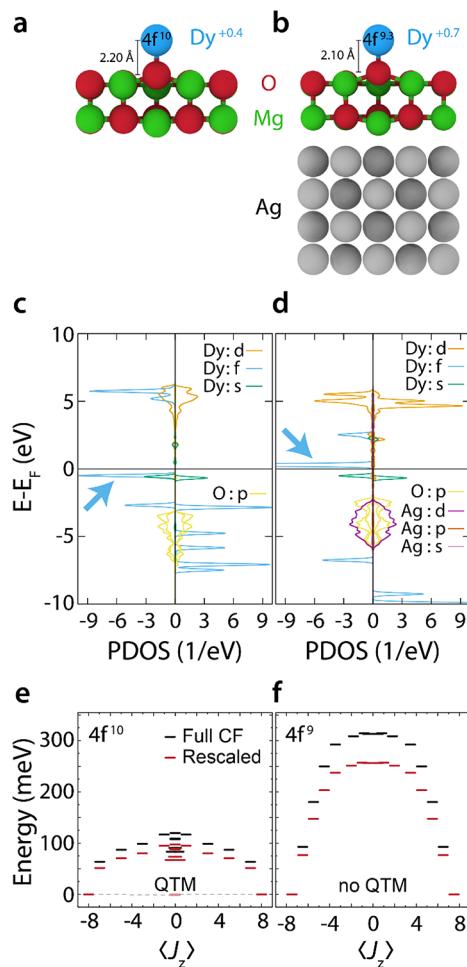


Figure 5. Calculated adsorption geometry, as well as electronic and magnetic configurations of Dy^{top} atoms. Cross section of the Dy/surface adsorption complex along the crystallographic (010) direction on (a) 2 ML free-standing MgO(100) and (b) 2 ML MgO/Ag(100), showing the charge state, 4f occupation, and Dy–O bond length. PDOS of Dy atoms on (c) MgO(100), and (d) MgO/Ag(100) obtained from DFT. The thick cyan arrows mark the 4f states that are mostly affected by the presence of the Ag(100) and determine the change of 4f occupation in Dy atoms. (e) Energy level scheme for the magnetic states of Dy atoms in the 4f¹⁰ configuration obtained from multiplet calculations using the structure calculated in (a). Dashed lines show the ground state mixing at zero field, producing two singlet states with no net magnetization (light red lines). (f) Energy level scheme for the magnetic states of the 4f⁹ configuration using the structure calculated in (b). In both (e,f), black lines are the result of the full CF potential, while red lines are obtained rescaling the CF by a factor 0.8 to match results of previous STM experiment.⁸

show an atomic-like 4f¹⁰ occupation, with a slight electron transfer of 0.4 e to the MgO, mostly from the outer 6s shell. Differently, on MgO/Ag(100) the presence of the Ag layer induces a reorganization of the electronic configuration to 4f⁹³ with almost one electron transferred from the 4f orbitals to the Ag substrate (Figure 5b). The corresponding orbital-projected density of states (PDOS) of the Dy^{top} species reveals a

different occupation of the 4f minority states close to the Fermi level, as highlighted in Figures 5c,d. When Dy is adsorbed on free-standing MgO, we observe a peak in the 4f PDOS below the Fermi level, which moves to the unoccupied states on MgO/Ag(100). Our calculations reveal that the reorganization of the 4f charge is driven by two factors: (i) more pronounced electron transfer from the Dy to the substrate when the Ag(100) is included (0.4 e for MgO, 0.7 e for MgO/Ag(100)), (ii) shortening of the bond length to the underneath O from 2.2 Å for MgO to 2.1 Å for MgO/Ag(100), as also indicated in Figure 5a,b, and Table S7. Remarkably, both the orbital occupation and bond length of Dy/MgO/Ag(100) are essentially identical to that of [Dy/MgO]⁺, where the total charge of the system is artificially reduced by one unit (see SI). Very similar behavior is also observed in the calculations for the bridge site (see SI). This similarity suggests a simplified picture with the Dy atoms on MgO/Ag(100) assuming a singly ionized configuration and those on free-standing MgO films keeping a close to neutral state. As also observed for pentacene on MgO/Ag(100), the gradual neutralization of the charged species with increasing MgO thickness can be attributed to the increase of electrostatic energy as in an equivalent charged-capacitor scheme,⁵² which progressively reduces the energy gain associated with the charging from the electron transfer. Using a plane capacitor model, we infer that an electrostatic energy of about 150 meV per Dy atom is required to overcome the configurational energy difference between 4f⁹ and 4f¹⁰ occupation, a value of comparable magnitude with respect to previous estimations for Dy divalent compounds.¹⁵

Changes in bond length and 4f occupation have a large impact on the adatom magnetic states and anisotropy barrier. For 4f¹⁰ Dy^{top}, multiplet calculations indicate a lowest manifold with total angular momentum $J = 8$ and relatively large level splitting of 120 meV, see Figure 5e. For these non-Kramers spins, the nonaxial crystal field terms generated by the nearest Mg neighbors mix the states of the lowest doublet with projected moment $J_z = \pm 8$ in a pair of nondegenerate singlets at zero magnetic field, resulting in QTM. Conversely, for the 4f⁹ Dy^{top} atoms we find a lowest manifold with $J = 15/2$ and giant anisotropy barrier of 314 meV, see Figure 5f. For these Kramers spins, the $J_z = \pm 15/2$ levels belonging to the lowest doublet cannot be mixed by crystal field terms due to time-reversal symmetry. Therefore, the ground state doublet is protected against QTM at zero magnetic field. The lack of QTM and the giant magnetic anisotropy identify the 4f⁹ Dy^{top} as an extremely stable quantum magnet, in agreement with previous findings.⁸ Conversely, Dy^{br} species show strong mixing of the magnetic states due to the absence of axial symmetry (see Figure S7), hence lacking the prerequisite for magnetic stability. The apparent contradictory observation of a smaller opening in the magnetization curve of 4f⁹ vs 4f¹⁰ species originates from the fact that the 4f⁹ Dy^{top} lifetime is so long and weakly affected by the magnetic field that the spin dynamics is basically negligible in the time lapse of a hysteresis. Even in the presence of secondary electrons that can accelerate the dynamics of the spin state,^{3,40,42} the 4f⁹ Dy^{top} population does not seem to attain a large imbalance between the two bistable spin orientations, hence the contribution to the 4f⁹ magnetization remains small. Consequently, the data on thin MgO films are dominated by the S-shaped curve of the paramagnetic 4f⁹ Dy^{br} atoms.

We finally note that the anisotropy barrier of 4f⁹ Dy^{top} predicted by our multiplet calculations is 25% larger than the

value of 258 meV (2081 cm^{-1} , 2994 K) inferred from STM experiments,⁸ possibly due to the well-known inaccuracy of point charge models based on physical charge distribution.⁵³ By rescaling the CF charges of all species to match the previously reported barrier for $4f^9$ Dy^{top}, we obtain a reduced anisotropy barrier of 97 meV (782 cm^{-1} , 1126 K) for the $4f^{10}$ Dy^{top} (red lines in Figures 5e,f). For the latter species, the rescaled barrier height results are smaller than the one estimated for $4f^{10}$ Ho atoms on MgO^{24,26} despite their identical 4f filling. The reason can be traced to the more extended Dy^{top}-O bond when Dy is in its neutral state, which reduces the uniaxial anisotropy component and hence the robustness of the magnetic states against QTM and spin-phonon scattering.³¹

Recent calculations for DyO linear complexes find anisotropy barriers of $4f^9$ and $4f^{10}$ electronic configurations comparable with our results.^{31,32} The lower magnetic stability at zero field observed for the $4f^{10}$ Dy^{top} with respect to the previously reported long lifetime of $4f^{10}$ Dy/gr/Ir(111) is a consequence of the crystal field symmetry.^{4,12} The adsorption on the graphene hollow site produces a C_{6v} symmetric CF resulting in a degenerate ground state doublet characterized by $J_z = 7$, and thus protected from QTM. On the contrary, in the present case, the C_{4v} symmetric CF produces a ground split-doublet exhibiting QTM in a vanishing magnetic field.

Electron transfer from metal supports through ultrathin MgO films has been observed for molecular adsorbates^{52,54} and Au atoms.^{36,54,55} The lower ionization potential of lanthanides offers the possibility to realize the opposite transfer mechanism, that is, from the adatom to the metal substrate. As shown in a previous study, such a mechanism occurs for Gd and Ho atoms, leaving the adsorbate in a singly ionized configuration.²⁴ Our findings reveal a very similar behavior for Dy: the charge transfer removes one electron from the 4f orbitals leading to a $4f^9$ occupation. In this configuration, adsorption on O-top gives rise to the highest magnetic anisotropy barrier observed for surface spins, and absence of QTM. Increasing the thickness of the oxide layer reduces the energy gain associated with this process,⁵² inducing the Dy atoms to gradually recover a neutral atomic-like configuration. Although characterized by a reduced perpendicular anisotropy compared with the $4f^9$ Dy^{top} case, the $4f^{10}$ Dy^{top} species also exhibit long magnetic lifetimes and open hysteresis. Our results prove the charge transfer to be a controllable mechanism to tune the magnetic behavior in surface-adsorbed spins.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c02744>.

Sample preparation, STM and XAS/XMCD measurements, and the related analysis, additional details on the DFT and multiplet calculations (PDF)

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Author Contributions

F.D., M.P., A.S., C.Wäckerlin, R.B., S.L.A., L.P., C.N., J.D., A.B., and S.R. performed the XAS/XMCD synchrotron experiments under the supervision of P.G. and H.B. The analysis of the XAS/XMCD data using multiplet calculations was performed by F.D. with the help of S.L.A. STM experiments were performed and analyzed by M.P., J.-G.de G., and E.F. DFT calculations were performed by C. Wolf. The

manuscript was written by F.D., M.P., C. Wolf, and S.R. and finalized through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

STM, scanning tunneling microscopy; XAS, X-ray absorption spectroscopy; XMCD, X-ray circular magnetic dichroism; t_{MgO} , average thickness of the MgO layer; Θ_{Dy} , Dy coverage; Dy^{op} , Dy atoms adsorbed on O-top site of MgO; Dy^{br} , Dy atoms adsorbed on bridge site of MgO; CF, crystal field; DFT, density functional theory; PDOS, projected density of states; QTM, quantum tunneling of the magnetization.

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