ABSTRACT: We report on the magnetic properties of Dy atoms adsorbed on the (001) surface of SrTiO$_3$. X-ray magnetic circular dichroism reveals slow relaxation of the Dy magnetization on a time scale of about 800 s at 2.5 K, unusually associated with an easy-plane magnetic anisotropy. We attribute these properties to Dy atoms occupying hollow adsorption sites on the TiO$_2$-terminated surface. Conversely, Ho atoms adsorbed on the same surface show paramagnetic behavior down to 2.5 K. With the help of atomic multiplet simulations and first-principles calculations, we establish that Dy populates also the top-O and bridge sites on the coexisting SrO-terminated surface. A simple magnetization relaxation model predicts these two sites to have an even longer magnetization lifetime than the hollow site. Moreover, the adsorption of Dy on the insulating SrTiO$_3$ crystal leads, regardless of the surface termination, to the formation of a spin-polarized two-dimensional electron gas of Ti 3d$_{xy}$ character, together with an antiferromagnetic Dy–Ti coupling. Our findings support the feasibility of tuning the magnetic properties of the rare-earth atoms by acting on the substrate electronic gas with electric fields.

KEYWORDS: slow magnetic relaxation, single atom magnets, X-ray magnetic circular dichroism, density functional theory, perovskite oxides
In Ho/MgO/Ag(100), direct manipulation of the spin of the Ho atoms (i.e., read and write) with a scanning tunneling microscope (STM) tip was demonstrated, highlighting the potential of these systems for information storage. Alternative routes to the control of the magnetic state of the lanthanide atoms may be achieved through their interaction with the substrate. These span from structural modifications that can lead to local variations of the crystal field potential impacting the charge and magnetic anisotropy of the rare-earth atoms, to electronic modifications, such as variations of the surface electron density influencing the spin reversal rate of the lanthanide atoms.

A potential candidate as a support for rare-earth SAMs, allowing for the active control of both their structural and electronic properties, is the cubic perovskite dielectric oxide SrTiO$_3$ (STO). This is a paradigmatic example of a quantum paraelectric material, where paraelectricity down to temperatures in the mK range is the result of the competition between ferroelectricity, quantum fluctuations, and structural distortions. Paraelectricity in STO is intimately coupled with the giant piezoelectric effect observed at cryogenic temperatures. These properties make STO a rich playground to study the effect of electric-field-induced changes of the local crystalline environment on the magnetic properties of the lanthanide atoms. Moreover, whereas bulk STO has a large band gap of 3.25 eV, its surface can host a high-mobility two-dimensional electron gas (2DEG). The density of carriers within this surface can be controlled either via the application of a gate voltage or through exposure to intense ultraviolet radiation. Both methods can be effective in controlling the scattering rate between the conduction electrons of the substrate and the localized magnetic moments of the lanthanide atom, thus offering a potential way to control the reversal of the rare-earth spins.

In this context, we have studied the structural, electronic, and magnetic properties of Dy atoms adsorbed onto STO(001) surfaces. We have found that Dy impurities are preferentially located at four-fold hollow sites of the TiO$_2$-terminated surface, with a 4f configuration and a strong in-plane magnetic anisotropy. However, under the experimental conditions of this study, a significant minority of Dy adatoms adsorb at sites of the coexisting SrO termination. Dy atoms at the TiO$_2$-terminated surface are found to be SAMs, characterized by an open magnetization cycle and spin relaxation times of the order of at least 800 s at 2.5 K. This was unexpected since this atomic species is characterized by an easy-plane magnetic anisotropy (i.e., there is no unique magnetic quantization axis in the STO(001) plane). Finally, we find a significantly long-ranged antiferromagnetic coupling between Dy and Ti, related to the formation of a 2DEG at the STO surface upon Dy adsorption.

Figure 1. (a) Experimental magnetization cycle recorded by following the magnetic field dependence of the XMCD peak at the Dy $M_5$ edge (see black arrow in panel (c)), at $T = 2.5$ K, $dB/dt = 33.3$ mT/s, $\theta = 60^\circ$, $\Theta_{Dy} = 0.004$ ML (corresponding to a surface density of 0.026 Dy atoms/nm$^2$). (b) Experimental magnetization relaxation curve (dots) and corresponding exponential fit (line), recorded at $B = 0.375$ T (see black arrow in panel (a)) after saturation at $B = 5$ T (Dy $M_5$ edge, $\theta = 60^\circ$, $T = 2.5$ K, $\Theta_{Dy} = 0.029$ ML). (c) Normalized XMCD spectra measured for magnetic field applied in the out-of-plane direction ($\theta = 0^\circ$) and predominantly in the STO(001) plane ($\theta = 60^\circ$), at the Dy $M_5$ edge with $T = 2.5$ K, $B = 5$ T, $\Theta_{Dy} = 0.004$ ML. (d,e) Sketches of the atomic structures and (e,g) corresponding electronic band structures for: (d,e) the plain STO substrate and (e,g) Dy adatoms ($\Theta_{Dy} = 0.25$ ML) at the hollow site on the TiO$_2$ terminated surface (spin up channel only). Although in the latter case only the top two STO atomic layers are visualized in the sketch for space reasons, the bands were calculated using the same $2 \times 2$ STO slab sketched in panel (d). In panels (e) and (g), the orbital projection on the Ti-$d_{xy}$ character is highlighted, for the surface Ti layer only, by filled red circles whose size is proportional to its contribution at each eigenvalue. Note that the experimental data were acquired on Dy adsorbed on Nb:STO(001), while calculations are for a pure STO(001) cell.
RESULTS AND DISCUSSION

The electronic and magnetic properties of Dy adatoms on the STO(001) surface were studied experimentally by polarization-dependent X-ray absorption spectroscopy (XAS) at the M_{4,5} edges, in particular by making use of X-ray magnetic circular dichroism (XMCD) and X-ray linear dichroism (XLD). The high sensitivity of these spatially averaging techniques allows measuring the properties of surface spins down to the noninteracting limit. Such a high magnetic dilution is achieved by depositing minute amounts of magnetic atoms at cryogenic temperatures, thus preventing their diffusion and consequent aggregation, and ensures that the magnetic properties are those of individual atoms, as demonstrated by comparison with single-atom scanning probe investigations on similar systems.\(^{14,21,24,30,31,49}\) The experimental investigations were complemented by atomic multiplet simulations and first-principles calculations based on the density functional theory (DFT) (see Methods for a description of experimental and theoretical techniques). As depicted in Figure 1a, Dy atoms adsorbed with very low density on the clean and ordered Nb:STO(001) surface (see Methods for the sample preparation procedure) show slow relaxation of the Dy magnetization, resulting in an open magnetization cycle at a temperature \(T = 2.5 \text{ K}\) for magnetic fields up to \(B \approx \pm 3 \text{ T}\). We observe a similar opening of the magnetization cycle in a wide range of Dy surface concentrations, up to \(\Theta_{\text{Dy}} = 0.037 \text{ ML}\), and temperatures up to \(T = 6 \text{ K}\), while the opening is considerably reduced starting at \(\Theta_{\text{Dy}} = 0.145 \text{ ML}\) (see Supporting Information for the coverage dependence of the Dy magnetic properties). By following the decay of the XMCD amplitude as a function of time at a given magnetic field, after saturation at \(B = 5 \text{ T}\), we find the largest value of the magnetic lifetime \(\tau\) of the Dy atoms at \(B = 0.375 \text{ T}\), where \(\tau = 800 \pm 200 \text{ s}\), as shown in Figure 1b. Moreover (see Figure 1c), dilute Dy atoms show an in-plane magnetic anisotropy, as indicated by the larger XMCD amplitude (relative to the XAS peak) at the \(M_s\) absorption edge when the magnetic field is applied close to the STO(001) plane (\(\theta = 60^\circ\)), as compared to the out-of-plane direction (\(\theta = 0^\circ\)). Very similar results are obtained for Dy adsorbed on the (001) surface of pure (i.e., without Nb doping) STO (see Supporting Information for a comparison between pure and Nb-doped STO), indicating that the extra conductivity achieved through Nb doping does not shorten the magnetization relaxation times. Dy/STO(001) can therefore be classified as a SAM, but unlike the previously reported cases of RE SAMs,\(^{14,21,22,50}\) all showing strong out-of-plane magnetic anisotropy, here the Dy atoms have in-plane magnetic anisotropy. Contrary to Dy, Ho single atoms show purely paramagnetic behavior down to \(T = 2.5 \text{ K}\), despite a magnetic anisotropy similar to that of Dy (see Supporting Information for the Ho/STO magnetic properties).

The recorded value of \(\Theta\) for Dy/STO(001) is comparable to that previously reported for Dy/graphene/Ir(111).\(^{14}\) Indeed, our DFT calculations indicate that the STO substrate, whose atomic structure is depicted in Figure 1d, shares some features with such graphene/metal substrates. The (001) surface of bare, stoichiometric STO is an insulator as depicted in Figure...
Oxygen atoms at the TiO$_2$ terminated surface layer are responsible for the inverted parabolic band that reaches the Fermi level at the $\Gamma$ point. On the other hand, it is well-known that oxygen vacancies act as charge donors and lead to the formation of a 2DEG at the STO surface. Here, we show that also the presence of Dy adatoms on the stoichiometric STO(001) surface, sketched in Figure 1f, leads to an electron doping, resulting in the partial filling of conduction bands. This effect is shown in Figure 1g, which depicts the spin up/majority channel bands (similar bands and projections are found in the spin down/minority channel) for a calculation based on a $2 \times 2$ cell, corresponding to a Dy concentration $\Theta_{Dy} = 0.25$ ML. However, comparable results were obtained for a $4 \times 4$ cell (discussed later in Figure 6d), corresponding to $\Theta_{Dy} = 0.06$ ML, very close to the coverage range used during the XMCD experiments. Moreover, although we depict here the case of the hollow adsorption site on the TiO$_2$ termination (the different sites/terminations will be discussed at a later stage), the surface metallization occurs regardless of the crystal termination. It involves bands with predominant Ti 3d$_{xy}$ character, related to surface Ti atoms in the case of a TiO$_2$ termination, as shown in Figure 1g, and to subsurface Ti atoms in the case of a SrO-terminated crystal (see Supporting Information for the depth-dependence of this metallic state). Thus, our calculations show that, independently of the adsorption site, Dy deposition will lead to the formation of a 2DEG, reminiscent of what was previously observed at the oxygen-deficient STO surface.

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In order to rationalize our findings, we first analyze the XAS, XMCD, and XLD spectra of Dy adatoms deposited on the (001) surface of Nb:STO. Figure 2a displays the $M_{4,5}$ XAS (top panel) characteristic for the Dy coverage range up to $\Theta_{Dy} = 0.037$ ML. At the $M_{4,5}$ edges, transitions from a 3d$^{10}$ 4f$^9$ state to a 3d$^9$ 4f$^{10}$ state are mainly excited, allowing one to probe the electronic and magnetic configuration of the rare-earth 4f shell. The spectral line shape of the XAS and XMCD (middle panel) is typical for a 4f shell occupation $n = 9$. Thus, adsorption at the STO(001) leads to a decrease of one electron in the occupation of this shell, characterized by $n = 10$ for Dy atoms in the gas phase. The in-plane magnetic anisotropy, related to the larger XMCD amplitude at grazing than at normal incidence, suggests that the ground state of individual Dy atoms on STO(001) is characterized by a low value of the projection of the total angular momentum $J = 15/2$ along the $z$-axis [corresponding to the (001) axis of the STO lattice]. The spectral shape of the XLD (bottom panel of Figure 2a) at the $M_4$ edge is characterized by a large positive feature (blue arrow in the graph) followed, at higher energy, by a negative feature (red arrow). Such an XLD is characteristic for Dy when the 4f charge distribution is mostly pointing in the direction perpendicular to the STO surface. Due to the oblate character of the Dy(4f$^9$) free-ion electron density, this charge distribution corresponds to a 4f magnetic moment pointing within the STO surface plane, consistently with the XMCD result.
Table 1. Total Energies (in eV) and Occupations (\( n \)) of the 4f Orbitals of the Six Stable Adsorption Sites for Dy on TiO\(_2\) and SrO Terminations

<table>
<thead>
<tr>
<th>Termination</th>
<th>Adsorption Site</th>
<th>Energy (eV)</th>
<th>( n ) (e(^{-}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>hollow</td>
<td>+0.00</td>
<td>9.00</td>
</tr>
<tr>
<td></td>
<td>top-O</td>
<td>+2.61</td>
<td>9.39</td>
</tr>
<tr>
<td></td>
<td>top-Ti</td>
<td>+3.22</td>
<td>9.71</td>
</tr>
<tr>
<td>SrO</td>
<td>top-O</td>
<td>+2.34 (+0.00)</td>
<td>9.38</td>
</tr>
<tr>
<td></td>
<td>bridge</td>
<td>+2.95 (+0.61)</td>
<td>9.04</td>
</tr>
<tr>
<td></td>
<td>top-Sr</td>
<td>+4.87 (+2.53)</td>
<td>9.37</td>
</tr>
</tbody>
</table>

*The values are relative to the energy of the TiO\(_2\)/hollow site. In the case of the SrO termination, the energies in brackets are relative to the SrO/top-O site.*

In view of the quantitative interpretation of the experimental XAS, XMCD and XLD, we have established by DFT the most stable adsorption configurations on both TiO\(_2\) and SrO crystal terminations and the corresponding occupation of 4f and valence (6s, 6p, and 5d) orbitals. Since our simulation cell (see Figure 1c) hosts both terminations simultaneously, we can compare the total energies of all six high-symmetry adsorption sites, sketched in Figure 3a. The total energies are tabulated in Table 1. The most stable adsorption configuration is found to be the hollow site of the TiO\(_2\) termination (Dy\(_{\text{hollow}}\) atoms), where Dy has a four-fold coordination to its O nearest neighbors. This is followed in energy by the top-O site at the SrO termination (Dy\(_{\text{top}}\) atoms), where Dy is axially coordinated to the underlying O atom, and its Sr next nearest neighbors lead to a four-fold symmetry. Since the method used for the preparation of clean STO(001) surfaces in vacuum is known to yield coexisting TiO\(_2\) and SrO terminations,\(^{52}\) it is instructive to analyze the relative stability of the different sites on the two terminations separately. Based on the results of Table 1, on the TiO\(_2\) surface, the energy differences between hollow and top-O/top-Ti sites are so big (more than 2.5 eV) that we expect the Dy adatoms to easily diffuse to the most stable four-fold hollow site, irrespective of where the atoms land at deposition. Therefore, a single site is expected on this termination. On SrO terraces, top-O and bridge sites are close in energy (the difference is only 0.6 eV), whereas the top-Sr site is significantly higher in energy (2.5 eV), compared to the top-O site. In such a case, there might be diffusion barriers between the top-O and the bridge sites, which cannot be overcome at our low deposition temperature, whereas diffusion from top-Sr to the other sites is likely to have no barrier. On this termination, we thus expect occupation of both top-O and bridge sites. On the bridge site, Dy has a two-fold coordination with its O nearest neighbors and Sr next nearest neighbors. In each SrO unit cell, there are two bridge sites with perpendicular projections in the \( xy \) plane of the O−Dy−O bond, as sketched in Figure 3a. This projection is aligned along \( x \) for one bridge site and along \( y \) for the other bridge site. In our experiments, the external magnetic field is always applied in the \( xz \) plane, thus making Dy atoms at the two bridge sites inequivalent. We thus label as Dy\(_{\text{br-Ox}}\) Dy atoms at bridge sites with \( O \)−Dy−O bond projection along \( x \) and Dy\(_{\text{br-Oy}}\) those at sites with \( O \)−Dy−O bond projection along \( y \). Concerning the electronic configuration, Dy atoms at TiO\(_2\)/hollow sites are found to have \( n = 9 \) electrons in the 4f shell. The same holds for the SrO/bridge site, while a small departure from the 4f\(^{9}\) configuration is observed for all other sites, except for TiO\(_2\)/top-Ti, where the occupation is closer to 4f\(^{10}\). We find that for all adsorption sites the occupation of the valence orbitals of spd character is sizable. However, the magnetic polarization of each of these shells is very low, with spin moments below 0.1 \( \mu_B \). Figure 3b shows the contributions to the band structure close to the Fermi level of majority spin sp and d Dy orbitals, while in Figure 3c,d, the spin-dependent local density of states (LDOS) is plotted for spd Dy orbitals, for the case of the TiO\(_2\)/hollow site (for p and d orbitals, the symmetry dependence is also given). The spatial localization of spd electrons on the Dy atoms is clearly evidenced by the nondispersive character of the partially occupied band close to \( E_F \). Indeed, inspection of the projected electronic density of states shown in Figure 3c,d reveals the presence of a localized band at the Fermi level, with high spin polarization and mixed 6s−6p−5d\(^z\) character. This can be nicely visualized in real space by plotting the spin-density isosurface around the Dy ion, as shown in the inset of Figure 3c. Its anisotropic shape with a vertically elongated spatial extension, going well beyond the Dy atomic position, cannot be accounted for only by the anisotropy of the well localized 4f shell. The larger spatial extension of 5d\(^z\) and especially of 6p\(_{x,y}\) orbitals in the \( z \) direction, compared to that of the 4f shell, suggests assigning the spin cloud above the Dy atom to these orbitals. An anisotropic contribution from the 6s shell may also arise, due to the hybridization between this and the other valence orbitals.

Having established the most likely occupied adsorption sites and the presence of a charge and spin cloud localized above the Dy atoms on hollow sites, we have simulated the XAS, XMCD, and XLD of Dy adatoms on the STO(001) surface by atomic multiplet calculations performed with the Quanty code\(^{53}\) (see Methods and Supporting Information for details about the atomic multiplet calculations). The system Hamiltonian includes Coulomb, spin−orbit, Zeeman, and crystal-field (CF) interactions acting on the 4f shell only. Figure 2b shows our best simulations, which reproduce very well the experimental data shown in the corresponding panels of Figure 2a. Our simulations, based on the combination of spectra characteristic for different adsorption sites, indicate that (66 ± 5)% of the Dy adatoms occupy Dy\(_{\text{hollow}}\) sites, (20 ± 2)% occupy bridge sites, equally distributed among Dy\(_{\text{br-Ox}}\) and Dy\(_{\text{br-Oy}}\) species, and (14 ± 2)% are in Dy\(_{\text{top}}\) sites. Thus, we confirm that TiO\(_2\) and SrO terminations coexist, with relative abundances of (66 ± 5)% and (34 ± 5)%, respectively. The relative abundances of Dy atoms at top-O and bridge sites on the SrO termination, (41 ± 6)% and (59 ± 6)%, respectively, suggest that atoms landing on top-Sr sites diffuse with approximately the same probability to either of those sites. Indeed, from the statistics of impact sites (there are two bridge sites, one top-O and one top-Sr site per SrO unit cell) and in the case of equal diffusion probability from top-Sr to top-O and bridge, we infer relative abundances for these sites of 37.5% and 62.5%, respectively, in agreement with the experimental values. The coexistence of Dy atoms at top-O and bridge sites of the SrO termination is similar to the case of rare-earth adatoms on the MgO surface (which is isostructural to the SrO termination discussed here), where adsorption at both top-O and bridge sites was experimentally observed by STM.\(^{52,53,54}\) The equilibrium magnetization cycles calculated by atomic multiplet calculations capture very well both the angular dependence of the experimental magnetization cycles, as shown in Figure 2c, and their temperature dependence up to \( T = 15 \) K, as depicted in Figure 2d. At 15 K, the cycle is closed, indicating that, at this temperature, magnetic relaxation is faster than the measurement time, which is of the order of 10 s.
Based on the atomic multiplet calculations, we can establish the quantum level schemes and the ground-state wave functions for Dy in the three adsorption configurations used in our simulations, which are depicted in Figure 4a. Dy\textsuperscript{top} has a strong out-of-plane anisotropy, with a ground-state characterized by the maximum value of the total angular momentum \( J \) along the \( z \) direction, perpendicular to the STO(001) surface (see top panel of Figure 4b). The ground state wave function is

\[
\Psi_{\text{Dy}^{\text{top}}} = \pm 1.000 \, |J_z = \mp 15/2\rangle
\]

corresponding to a pure doublet, extremely well isolated from the first excited state (\( \Delta E = 84.2 \) meV), and with a total barrier height of 270 meV. On the other hand, the two-fold \( C_{2v} \) symmetry of the bridge site leads to a strong in-plane uniaxial anisotropy. The maximum projection of \( J \) for Dy\textsuperscript{br-Ox} atoms is along the \( x \) direction (see middle panel of Figure 4b), while it is along the \( y \) direction for Dy\textsuperscript{br-Oy} atoms (not shown). Along the respective easy axes, the ground state wave function for these two species is

\[
\begin{align*}
\Psi_{\text{Dy}^{\text{br-Ox}}} &= \pm 0.778 \, |J_x = \mp 15/2\rangle \\
&\pm 0.550 \, |J_y = \mp 11/2\rangle \\
&\pm 0.262 \, |J_y = \mp 7/2\rangle \\
&\pm 0.099 \, |J_y = \mp 3/2\rangle \\
&\pm 0.044 \, |J_y = \mp 1/2\rangle \\
&-0.029 \, |J_y = \pm 5/2\rangle \\
&-0.030 \, |J_y = \pm 9/2\rangle \\
&\pm 0.030 \, |J_y = \pm 13/2\rangle
\end{align*}
\]

with a first excited state at \( \Delta E = 11.3 \) meV and a total barrier height of 266 meV. Finally, on the hollow site of the TiO\textsubscript{2} termination, the maximum projection of \( J \) lies within the STO(001) plane, independent of the direction (bottom panel of Figure 4b). This suggests an easy-plane type anisotropy, with the hard axis perpendicular to the STO surface. In the plane, the ground state of the Dy 4f\textsuperscript{9} configuration is
Even in this case, the ground doublet is well isolated from the first excited state ($\Delta E = 11.9$ meV), while the total barrier height amounts to 109 meV.

Figure 5a shows the magnetic field dependence of the magnetization relaxation time $\tau_{\text{exp}}$ as recorded under low photon flux conditions (see Methods for the procedure used to measure $\tau_{\text{exp}}$ and for the definition of "low flux" conditions). As $B$ is decreased from 1 to 0.375 T, $\tau_{\text{exp}}$ more than doubles, reaching a maximum value of 800 ± 200 s. At lower magnetic fields, however, $\tau_{\text{exp}}$ falls rapidly reaching a value of about 200 s at $B = 125$ mT. In order to determine which Dy species are responsible for the observed field dependence of $\tau_{\text{exp}}$ we note that, as shown in Figure 1b, at $B = 0.375$ T, the decrease of the magnetization over time from its initial to its equilibrium value is of the order of 20%. In our grazing incidence geometry, Dy$^{\text{hollow}}$ atoms account for (69 ± 5)% of the total magnetization, while Dy$^{\text{br-Ox}}$ for (16 ± 2)% Dy$^{\text{top}}$ for (14 ± 2)% and Dy$^{\text{br-Oy}}$ for only about 1%. Assuming that a Dy species retains its saturation magnetization, while the magnetic field is quickly ramped from 5 T down to 0.375 T without exposing the sample to the X-ray beam and based on the equilibrium magnetization curves calculated for each species (see Supporting Information), we expect a maximum decrease over time at 0.375 T of $l = M(0.375 \text{ T}) - M(5 \text{ T})/M(5 \text{ T}) = 42$% if the decay of $M$ is due to Dy$^{\text{hollow}}$ atoms, 8% in the case of Dy$^{\text{br}}$, 6% for Dy$^{\text{br-Ox}}$, and about 1% in the case of Dy$^{\text{br-Oy}}$. In reality, due to its intrinsic finite lifetime, the magnetization partially relaxes already during the field ramp, so that the actual decrease of the magnetization over time at $B = 0.375$ T will be lower than the above estimate. We can thus conclude that the observed magnetization relaxation at $\theta = 60^\circ$ is likely related to the Dy$^{\text{hollow}}$ atoms.

Based on the magnetic field dependence of the electronic levels obtained by our multiplet simulations, we have calculated the magnetic field dependence of the intrinsic relaxation time $\tau$ with a spin–lattice relaxation model, including direct and Orbach-type scattering mechanisms, based on Fermi’s golden rule and the Hamiltonian proposed by Fort et al., which involves transitions with $\Delta J = \pm 1, \pm 2$. A Debye model was used for the low-energy phonon spectrum. Spin-electron scattering was included based on the theory by Delgado and Fernández-Rossier, involving transitions between states with $\Delta J = 0, \pm 1$ (see Supporting Information for a detailed description of the magnetic relaxation model). We neglected the coupling with the spin of the Dy spd shells, due to their vanishing spin polarization. The spin–lattice and spin–electron scattering cross sections were adjusted so as to match the values of $\tau_{\text{exp}}$ in the magnetic field range $0.375 \leq B \leq 1$ T, taking into account that $\tau_{\text{exp}}$ is related to $\tau$ by the expression $\tau_{\text{exp}} = \tau^{-1} + \tau_{\text{exp}}^{-1}$, where $\tau_{\text{exp}}$ is a contribution to the experimental relaxation time arising from secondary electrons generated in the X-ray absorption process (see Supporting Information for an evaluation of $\tau_{\text{exp}}$). The calculation for Dy$^{\text{hollow}}$, shown as a continuous blue line in Figure 5b, relates the decay of $\tau$ with increasing field beyond 0.3 T with an enhanced probability of spin–phonon scattering (see Figure S8a of the Supporting Information for the decomposition of $\tau$ into a spin–phonon and a spin–electron contribution). The field dependence of the lifetime for magnetic fields $B < 0.3$ T is not captured by our simplified model, which does not include Raman scattering mechanisms and local phonon modes. The drop of $\tau_{\text{exp}}$ at small fields may in fact originate in a two-phonon Raman mechanism similar to that found for Ho/MgO. We estimate that quantum tunneling due to the coupling of the 4f magnetic moment with the nuclear spin may be significant only for selected values of the magnetic field, in the range $B \leq 40$ mT, thus it cannot explain the field dependence of $\tau$ in our investigated field range (see Figure S8b of the Supporting Information for the effect of the coupling between 4f moment and nuclear spin in the field range of the experiment). For comparison, assuming identical spin–lattice and spin–electron cross sections for all adsorption sites, we can estimate the magnetic field dependence of $\tau$ for Dy$^{\text{br-Ox}}$ and Dy$^{\text{br}}$. These are also shown in Figure 5b. Dy$^{\text{br}}$ shows values of $\tau$ which are orders of magnitude greater than those of Dy$^{\text{hollow}}$. Indeed, the ground state of Dy$^{\text{br}}$, an almost pure doublet with $J \geq 15/2$, is expected to be particularly stable against spin–electron and spin–phonon scattering, even
colors are associated with an excess of spin up and down electrons, respectively. (d) Spin-resolved electronic band structures (top: spin-up, bottom: spin-down) for Dy adatoms ($^{152}$Dy).

Thus, we barely see an opening of the magnetization loop at 60° when projected at the top site of MgO. These show stable magnetization over time scales of at least a few hundreds of seconds. It is interesting that, although the Dy$_{0.035}$ML site with its out-of-plane magnetic anisotropy appears to be by far the most stable, the easy-plane configuration of Dy$_{0.06}$ML on the TiO$_2$ terminated surface. The orbital projection on the Ti-d$_{xy}$ character is highlighted by filled red circles (whose size is proportional to its contribution at each eigenvalue) for the surface Ti layer and by filled blue circles for the first subsurface Ti layer. The spin splitting at the top-O site with its out-of-plane anisotropy of this species. However, our magnetization cycles are recorded under X-ray flux conditions which may also lead to slow magnetic relaxation.

Stimulated by the finding of a Dy-adsorption-induced metallization of the STO substrate, we have investigated the influence of the Dy deposition on the magnetic properties of the STO surface. Figure 6a shows the XAS (top panel) and the corresponding XMCD (middle panel) recorded at the clean Nb:STO(001) surface. (b) Comparison between the magnetic field dependence of the Ti 3d orbital magnetic moment $m_{3d}$ (red dots) and the Dy total 4f moment (blue squares and line), both normalized at their corresponding values at $B = 5$ T. (c) Spin density isosurface of Dy/STO (Dy$_{0.06}$ML) at the hollow site of the TiO$_2$ terminated surface. The orbital projection on the Ti-d$_{xy}$ character is highlighted by filled red circles (whose size is proportional to its contribution at each eigenvalue) for the surface Ti layer and by filled blue circles for the first subsurface Ti layer. The spin splitting at the top-O site amounts to 22 meV.

when projected at $\theta = 60°$. In fact, the adsorption geometry of Dy$_{0.06}$ML is identical to that of both Dy and Ho on the top-O site of MgO. These show stable magnetization over time scales of hours or days (only limited by the time scales of the measurements), in a wide range of fields (up to at least 7 T for Dy and 8 T for Ho) and temperatures (up to at least 15 K for Dy and 40 K for Ho). The influence of the Dy deposition on the magnetic properties of the STO surface. The orbital projection on the Ti-d$_{xy}$ character is highlighted by filled red circles (whose size is proportional to its contribution at each eigenvalue) for the surface Ti layer and by filled blue circles for the first subsurface Ti layer. The spin splitting at the top-O site amounts to 22 meV.
concentration of oxygen vacancies which may form at the surface during the sample preparation procedure or by irradiation with the X-rays. Although the magneto-optical sum rules cannot be applied to determine the spin magnetic moment at the Ti L$_2$,3 edges, due to mixing of the L$_2$ with the L$_1$ intensity, we can extract an orbital magnetic moment $m_\text{orb} = - (L_{2,3}) = -0.003 \pm 0.001 \mu_B$ (assuming a vanishing $\delta$ and thus 10 holes in the 3d shell). Its negative sign suggests that, according to Hund’s rules, the Ti spin magnetic moment is aligned parallel to the applied magnetic field. The extremely small magnitude of the orbital moment supports that $\delta \ll 1$.

After Dy deposition, the Ti XAS shows only minor variations, with a small decrease of the intensity of the sharp peaks and a consequent increase of the valleys between them. This indicates that, at least locally around the Dy impurities, the Ti 3d orbital occupation $\delta$ slightly increases, thus confirming that the Dy deposition actually dopes the STO(001) surface even in the case of Nb-doped STO crystals. The XMCD, on the other hand, shows no significant change of magnitude, but its sign and that of its integral are reversed. This implies that the Ti spin moment aligns antiparallel to the Dy spin moment, suggesting the onset of an antiferromagnetic coupling between the two. Indeed, Figure 6b shows that the magnitude of the Ti XMCD integral (proportional to the Ti orbital moment), normalized at its value at $B = 5$ T follows closely the normalized Dy magnetization curve. Thus, our experimental results are fully consistent with the first-principles calculated spin-density isosurface sketched in Figure 6c. Here, the opposite spin polarization of Ti with respect to Dy extends for several atomic distances, especially across Ti layers, and is maximal within the Ti subsurface layer, where Ti exhibits the highest spin magnetic moment $m_\text{Ti} = -0.06 \mu_B$/Ti atom, as compared to $m_\text{Dy} = -0.03 \mu_B$/Ti atom in the surface layer (note that these are the moments of the Ti atoms which, in each layer, are closest to the Dy atom). This finding correlates with the fact that the largest electron doping is found for the Ti-d$_{xy}$ orbitals of the subsurface layer, whose bands are shown as blue circles in Figure 6d, while the Ti-d$_{yz}$ bands of the surface layer (red circles) remain well above the Fermi level. We conclude that Dy induces a sizable spin polarization of the Ti atoms, which extends beyond the nearest-neighbor positions, suggesting that long-range Ti–Ti correlations may be active even at the extremely low Dy surface densities under study, likely due to the formation of the 2DEG within a couple of atomic layers at the Dy/STO interface.

CONCLUSIONS

In conclusion, we have observed that Dy atoms adsorbed on the SrTiO$_3$(001) surface show slow relaxation of the magnetization at temperatures $T \leq 6$ K in an extended range of magnetic fields up to about 3 T. A careful comparison between experimental results, first-principles calculations, and a simple spin–lattice relaxation model allows us to attribute our observations to Dy atoms adsorbed at the hollow site of the TiO$_2$ termination. These are characterized by an occupation of the 4f shell with 9 electrons and a strong easy-plane magnetic anisotropy, which results from the combined effect of the equatorial O and Ti ligands and a top charge due to strongly anisotropic, partially occupied Dy spd orbitals. The lifetime of the magnetic state, of the order of a few hundred seconds, is mainly limited by transitions between the two states of the ground-state doublet. In this geometry, Dy atoms induce a sizable spin polarization at the Ti atoms, whose magnetic moments couple antiferromagnetically with those of Dy. The formation of a spin-polarized 2DEG of Ti 3d$_{xy}$ character at the Dy/STO interface offers promising ways for the electrical manipulation of the Dy magnetism. Besides tuning the density of carriers of the 2DEG, modifying the STO lattice through its piezoelectricity or exploiting the substrate magnetic moments induced by the fluctuating charge dipoles near the STO ferroelectric quantum critical point, one can envisage injecting/extracting a spin-polarized electrical current in/from the surface or subsurface TiO$_2$ layer to “write/read” the Dy magnetization.

METHODS

Clean and ordered SrTiO$_3$(001) surfaces were prepared by cycles of Ar$^+$ sputtering and annealing in O$_2$ atmosphere (partial pressure of $p = 2–5 \times 10^{-6}$mbar) at a temperature of 923 K on commercial SrTiO$_3$ single crystals, either pure or doped with 1% at. Nb (the latter are referred to as Nb:STO in the manuscript). Nb:STO crystals were preferentially used, as their enhanced electrical conductivity compared to that of pure STO led to a higher signal-to-noise ratio of the XMCD measurements in the surface-sensitive total-electron-yield mode. The ordered surfaces exhibited sharp 1 × 1 LEED patterns (see Supporting Information), i.e., they were unreconstructed. Dy was evaporated, from thoroughly degassed rods or lamps in tungsten crucibles, onto SrTiO$_3$(001) kept at $T \leq 6$K in order to prevent surface diffusion, and $\leq 5 \times 10^{-12}$mbar. The Dy coverage is expressed in monolayers (ML) relative to the SrTiO$_3$(001) surface, where 1 ML is defined as 1 Dy atom per SrTiO$_3$(001) unit cell (lattice parameter $a = 0.3905$ nm), corresponding to a surface density of 6.56 atoms/nm$^2$. The coverage calibration based on the Dy XAS integral is obtained by comparison with previous investigations on Sm/graphene/Cu(111) (where STM and XAS were combined on the same sample) after proper rescaling of the different absorption coefficients and lattice parameters of the substrates and the number of holes of the rare-earth atoms.

The XMCD experiments were carried out at the EPFL/PSI X-Treme beamline$^{63}$ of the Swiss Light Source (data taken at 2.5 and 15 K), at the BOREAS beamline$^{64}$ of the ALBA synchrotron radiation facility (data taken at 5 K), and at the ID32 beamline$^{65}$ of the European Synchrotron Radiation Facility (data not shown in the manuscript). The measurements were performed in the total-electron-yield mode at temperatures in the range 2.5–15 K, and magnetic fields up to 9 T, applied parallel to the X-ray beam. The energy resolution of the X-ray beam at the Dy M$_{4,5}$ edges was of the order of at least 250 meV, the photon flux was of the order of $2 \times 10^{30}$ photons/s, and both linear and circular X-rays were polarized to a degree close to 100%. The background-subtracted Dy M$_{4,5}$ edge XAS ($I^+ - I^-$)/2, where $I^+$ and $I^-$ are the XAS spectra recorded with and left circularly polarized X-rays, respectively, as shown in Figure 2a, is obtained by subtracting the X-ray absorption spectra of the bare SrTiO$_3$(001) crystals, taken prior to Dy evaporation, from those of Dy/SrTiO$_3$(001) recorded under identical conditions, and then subtracting step functions at the two edges. The XMCD is then calculated as $I^+ - I^-$.

The XLD is defined as $I^+ - I^-$, where $I^+$ and $I^-$ are the XAS spectra recorded with vertically and horizontally linearly polarized X-rays. With reference to the sample orientation, as shown in Figures 3 and 4, the vertical linear polarization lies along the vertical axis, and thus the horizontal linear polarization lies within the $xz$ plane. The magnetic field dependence of the magnetization relaxation time $\tau$ was recorded by saturating the Dy magnetization at a field of +5 T, then ramping the field to its target value at a speed of 33.3 mT/s and without X-rays on the sample, and finally recording the time dependence of the XMCD magnitude, which is fitted by a single exponential function.

DFT calculations were performed by means of the augmented-plane wave + local orbitals method, as implemented in the Wien2K code,$^{66,67}$ without including spin–orbit coupling. The in-plane STO lattice constant was fixed to the experimental value at $T = 300$ K, $a = 0.3905$ nm. The generalized-gradient approximation (GGA) of the exchange and correlation functional was considered for the structural characterization. Atomic relaxations of the coordinates of the Dy adatom and of...
the upper substrate layer atoms, carried out within the GGA functional, were allowed until residual forces were <1 meV/au. The electronic structure analysis reported in the main text was obtained by using an on-site version of the hybrid B3LYP functional, while, for testing purposes, an on-site Hubbard correction term (as implemented in the DFT+U method) on the f orbitals of Dy (U = 7 eV, J = 0.82 eV) was also considered. The former approach was found to describe the valence configuration of the Dy ions better, and a comparison between the two methods is given in the Supporting Information. Within the on-site B3LYP approach, a calculated electronic gap for STO bulk of 2.3 eV was found, to be compared with an experimental value of 3.25 eV. Further details on the simulation cell are given in the Supporting Information.

Atomic multiplet calculations were performed with the Quanty multielectron code, partially using the Crispy graphical interface, and used to simulate the temperature and magnetic field dependence of XAS, XMCD, XLD, and magnetization cycles. The Hamiltonian for the multiplet calculations includes electron–electron interactions, spin–orbit coupling, Zeeman energy due to the external magnetic field, and the crystal field potential acting on the Dy 4f shell. The electron–electron interactions (in terms of Slater–Condon integrals) as well as the spin–orbit coupling values were computed using Cowan’s atomic structure code. The Slater integrals were reduced to 66% of their atomic value in order to account for the screening due to surface electrons. The crystal field potential was calculated, for each adsorption site, by using an electrostatic point charge model, based on the optimized adsorption geometry and the Bader charges of the Dy neighbors, as obtained by our first-principles calculations (see Supporting Information for charge values and positions and the corresponding crystal field parameters in Wybourne notation). The final state Hamiltonian includes the presence of the core hole.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsnano.2c04048](https://pubs.acs.org/doi/10.1021/acsnano.2c04048).

Complementary experimental data: STO(001) crystals characterization; Comparison between Nb-doped and pure SrTiO$_3$; Coverage dependence of XAS, XMCD and magnetization cycles; XAS, XMCD, XLD and magnetization cycles of Ho/STO(001). DFT calculations: further details on the DFT simulation cell and the methodology; Comparison GGA+U vs on-site B3LYP; Spin and orbital projected band structures: 2DEG at the STO surface; Details about the atomic multiplet calculations: Point charges and crystal field parameters; Simulated XAS, XMCD, and magnetization cycles for each adsorption site; Details about the calculation of the magnetization relaxation time $\tau$: theoretical model; Estimate of the secondary electrons contribution to the value of the relaxation time ($PDF$)

**AUTHOR INFORMATION**

**Corresponding Author**

Alessandro Barla — Istituto di Struttura della Materia (ISM), Consiglio Nazionale delle Ricerche (CNR), I-34149 Trieste, Italy; orcid.org/0000-0002-5632-4915; Email: alessandro.barla@trieste.ism.cnr.it

**Authors**

Valerio Bellini — S3-Istituto di Nanoscienze-CNR, I-41125 Modena, Italy
Stefano Rupsoni — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0002-8494-5532

Jindřich Koleněc — Institute of Physics (FZU), Czech Academy of Sciences, CZ-182 21 Prague, Czech Republic
Sanjoy K. Mahatha — Istituto di Struttura della Materia (ISM), Consiglio Nazionale delle Ricerche (CNR), I-34149 Trieste, Italy; School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala 147004, India; orcid.org/0000-0002-5394-6911
Miguel Angel Valbuena — Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, E-08193 Barcelona, Spain; Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanoscience), E-28049 Madrid, Spain; orcid.org/0000-0002-0585-5636
Luca Persichetti — Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland; Dipartimento di Fisica, Università di Roma “Tor Vergata”, I-00133 Roma, Italy; orcid.org/0000-0001-6578-254X
Marina Pivetta — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0001-5330-8648
Boris V. Sorokin — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0002-4950-5654
Darius Merk — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
Sébastien Reynaud — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
Dante Sblendorio — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
Sebastian Stepanow — Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland; orcid.org/0000-0002-4090-6574
Corneliu Nistor — Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland
Pierluigi Gargiani — ALBA Synchrotron Light Source, E-08290 Cerdanyola del Vallès, Spain; orcid.org/0000-0002-6649-0538
Davide Betto — European Synchrotron Radiation Facility, F-38043 Grenoble, France
Aitor Mugarza — Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, E-08193 Barcelona, Spain; Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona E-08010, Spain; orcid.org/0000-0002-2698-885X
Pietro Gambardella — Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland
Harald Brune — Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0003-4459-3111
Carlo Carbone — Istituto di Struttura della Materia (ISM), Consiglio Nazionale delle Ricerche (CNR), I-34149 Trieste, Italy

Complete contact information is available at: [https://pubs.acs.org/10.1021/acsnano.2c04048](https://pubs.acs.org/10.1021/acsnano.2c04048)

**Notes**

The authors declare no competing financial interest.
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REFERENCES


Supporting Information for: Slow magnetic relaxation of Dy adatoms with in-plane magnetic anisotropy on a two-dimensional electron gas

Valerio Bellini,† Stefano Rusponi,‡ Jindřich Kolorenč,§ Sanjoy K. Mahatha,¶ Miguel Angel Valbuena,⊥# Luca Persichetti,@@ Marina Pivotta,† Boris V. Sorokin,† Darius Merk,‡ Sébastien Reynaud,† Dante Sblendorio,† Sebastian Stepanow,† CorNELiu Nistor,® Pierluigi Gargiani,∇ Davide Betto,†† Aitor Mugarza,⊥‡‡ Pietro Gambardella,@@ Harald Brune,‡ Carlo Carbone,§ and Alessandro Barla*§

†S3-Istituto di Nanoscienze-CNR, Via Campi 213/A, I-41125 Modena, Italy
‡Institute of Physics, EPFL, Station 3, CH-1015 Lausanne, Switzerland
¶Institute of Physics (FZU), Czech Academy of Sciences, Na Slovance 2, CZ-182 21 Prague, Czech Republic
§Istituto di Struttura della Materia (ISM), CNR, I-34149 Trieste, Italy
∥School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala - 147004, India
⊥Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, E-08193 Barcelona, Spain
#Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanoscience), E-28049 Madrid, Spain
@@Department of Materials, ETH Zurich, CH-8093 Zurich, Switzerland
△Dipartimento di Fisica, Università di Roma “Tor Vergata”, I-00133 Roma, Italy
∇ALBA Synchrotron Light Source, E-08290 Cerdanyola del Vallès, Spain
††European Synchrotron Radiation Facility, F-38043 Grenoble Cedex, France
‡‡Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona E-08010, Spain

E-mail: alessandro.barla@trieste.ism.cnr.it
Complementary experimental data

STO(001) crystals characterization

Figure S1: (a) LEED pattern of the clean and ordered Nb:SrTiO$_3$(001) surface taken at an electron beam energy of 90 eV. (b,c) XAS (top) and XLD (bottom) spectra of the STO(001) surface, measured at the (b) Ti $L_{2,3}$ edges and (c) O $K$ edge, at a temperature $T = 2.5$ K and a magnetic field $B = 0.1$ T, at grazing incidence ($\theta = 60^\circ$). (d) LEED pattern of the reconstructed Nb:SrTiO$_3$(001) surface taken at an electron beam energy of 94 eV.

Fig. S1a shows the $1 \times 1$ Low Energy Electron Diffraction (LEED) pattern of the clean Nb:SrTiO$_3$(001) surface, following the preparation discussed in the Methods section. The sharp squared pattern, with the edges of the square aligned along the $x$ and $y$ axes, indicates that the surface is well ordered following the cubic structure of bulk STO, with no reconstruction. The crystals used in the XAS experiments were all oriented like in Fig. S1a, with x-ray beam and magnetic field aligned along the $z$ axis (i.e. perpendicular to the plane of the figure) at normal incidence ($\theta = 0^\circ$), and within the $xz$ plane at grazing incidence ($\theta = 60^\circ$). As shown in Figs. S1b and c, we observe sizable XLD both at the Ti $L_{2,3}$ and at
the O K edge, at $T = 2.5 \text{ K}$, respectively. This arises from the anisotropy of the Ti 3d and of the O 2p orbitals within the almost cubic structure of STO at low temperatures.

An alternative preparation method was tested, which was reported to lead to a fully TiO$_2$-terminated surface.$^1$ Following this procedure, the as-received STO(001) crystals were first etched in a buffered solution of hydrofluoric acid (HF) for 30 s, then annealed in air at 1223 K for 1 hour. The samples were successively inserted in our UHV surface preparation chamber, where residual surface contamination was removed by annealing in O$_2$ atmosphere (partial pressure of $p = 2 \times 10^{-6} \text{ mbar}$) in two steps: first at 1023 K for 30 minutes and then at 1108 K for further 30 minutes. After cooldown to room temperature, LEED patterns were recorded at several electron beam energies, resulting in a reconstructed surface, with a coexistence of the previously reported p(2×1) and c(6×2) reconstructions,$^2$ as shown in Fig. S1d. As the coexistence of two reconstructions and the lack of knowledge of the precise atomic arrangement within the reconstructed surface would prevent us from determining the possible adsorption sites and the corresponding crystal field acting on the rare-earth adatoms, required to simulate the XAS, XMCD and XLD spectra, we did not investigate the magnetic properties of rare-earths on these samples.

**Comparison between Nb-doped and pure SrTiO$_3$**

Figure S2 shows a comparison between the XAS, XMCD, XLD and magnetization cycles of Dy adatoms adsorbed on Nb-doped (left column) and pure (right column) STO(001). Although the main spectral features are almost identical between the two cases, one observes a small reduction of the in-plane anisotropy for Dy on pure STO, with a corresponding increase of the XMCD at $\theta = 0^\circ$, and a reduction of the XLD amplitude. This is very likely due to a slightly different distribution of the Dy adatoms among the various adsorption sites, with a larger population of the top-O site of the SrO termination, characterized by an out-of-plane magnetic anisotropy, in the case of the pure STO(001) crystal. Despite these differences, the two magnetization cycles are almost identical, showing a clear hysteresis with
approximately the same area in both cases. This indicates that, under the same experimental conditions, Dy has nearly identical magnetization relaxation time on both single crystals, thus ruling out any significant role of the Nb doping in the magnetic stability of the Dy adatoms.
Coverage dependence of XAS, XMCD and magnetization cycles

Figure S3: X-ray absorption spectra and magnetization curves of Dy on the Nb:STO(001) surface, for Dy coverages in the range between $\Theta_{\text{Dy}}=0.004\,\text{ML}$ and $\Theta_{\text{Dy}}=0.145\,\text{ML}$. The XAS and XMCD spectra are measured at the Dy $M_{4,5}$ edges at a temperature $T=2.5\,\text{K}$ and a magnetic field $B=5\,\text{T}$, both at normal ($\theta=0^\circ$) and at grazing incidence ($\theta=60^\circ$). All spectra at each coverage are normalized to the total integral of the XAS recorded at normal incidence. The red and blue arrows in each XMCD panel indicate the magnitude of the XMCD at the smallest coverage of $\Theta_{\text{Dy}}=0.004\,\text{ML}$ for grazing and normal incidence, respectively. The magnetization curves are recorded at $T=2.5\,\text{K}$ and $\frac{dB}{dt}=12.5\,\text{mT/s}$, at grazing ($\theta=60^\circ$) incidence.

We have characterized the magnetic properties of Dy/Nb:STO(001) in a wide range of Dy surface concentrations. Figure S3 shows the XAS, XMCD and magnetization curves in the range of coverages from $\Theta_{\text{Dy}}=0.004\,\text{ML}$ to $\Theta_{\text{Dy}}=0.145\,\text{ML}$. Across the whole series, the XAS does not show any appreciable lineshape variation. The XMCD is barely affected by the increase of Dy concentration. It decreases by less than 4% for a coverage increase from 0.004 to 0.036 ML, corresponding to a reduction of Dy monomers from 98% to 86% for a statistical distribution of adatoms on a square lattice. At a coverage $\Theta_{\text{Dy}}=0.145\,\text{ML}$, where small clusters of a few atoms are formed, the XMCD is decreased by 10% with respect
to $\Theta_{\text{Dy}} = 0.004$ ML. Correspondingly, the opening of the magnetization cycles progressively reduces with increasing Dy coverage, suggesting that the magnetization of dimers and larger clusters is considerably less stable than that of Dy individual atoms on the SrTiO$_3$(001) surface.

**XAS, XMCD, XLD and magnetization cycles of Ho/Nb:STO(001)**

Fig. S4a displays the $M_{4,5}$ XAS, XMCD, and XLD for Ho atoms on the Nb:STO(001) surface. As for Dy, we do not observe changes of the XAS and XMCD for Ho coverages up to $\Theta_{\text{Ho}} = 0.036$ ML. The spectral lineshape is typical for a 4f shell occupation $n = 10$. Thus, similar to the case of Dy, adsorption of Ho on the STO(001) surface leads to a decrease of one electron in the occupation of this shell, which is characterized by $n = 11$ for Ho atoms in the gas phase. The larger XMCD amplitude at grazing incidence than at normal incidence indicates an in-plane magnetic anisotropy, as found for Dy. This is confirmed by the spectral shape of the XLD at the $M_5$ edge. Contrary to the case of Dy, however, the magnetization cycles are paramagnetic at both normal and grazing incidence, for $T = 5$ K (see Fig. S4b), and they remain closed even at a lower temperature of $T = 2.5$ K, as shown in Fig. S4c.
Figure S4: X-ray absorption spectra and magnetization curves of Ho individual atoms on a Nb:STO(001) surface, for a Ho coverage Θ_{Ho} = 0.036 ML. (a) XAS, XMCD and XLD spectra measured at the Ho M_{4,5} edges and a temperature T = 5 K; the XAS and XMCD were recorded at a magnetic field B = 6 T; the XLD was recorded at grazing incidence (θ = 70°), for B = 6 T. (b) Magnetization curves recorded at T = 5 K and dB/dt = 33.3 mT/s, at normal (θ = 0°) and grazing (θ = 70°) incidence. The curves are normalized to the corresponding XMCD. Dark symbols are used for the downward magnetic field ramps (i.e. from positive to negative field), while light symbols are used for the upward field ramps. (c) Magnetization curves recorded at grazing incidence (θ = 60°) and dB/dt = 33.3 mT/s at T = 2.5 K and a Ho coverage Θ_{Ho} = 0.018 ML.

DFT calculations

Further details on the simulation cell and the methodology

In order to compare the properties of the different Dy adsorption sites on the two possible STO surface terminations, we considered an asymmetric slab, as depicted in Fig. 1d, placing
Dy ions either on top or below the slab. A 2×2 in-plane cell, in terms of the STO lattice constant (0.3905 nm), was used to simulate the properties of the isolated adatoms. The slab is composed of three and a half repetitions of the STO bulk cell in the direction perpendicular to the surface. For the analysis of the magnetic polarization of the substrate, a 4×4 in-plane cell was used, since the aim was to check the extension of the polarization given by a single Dy adatom. Vacuum space of 15 Å was considered in all the supercells in order to avoid slab replica spurious interactions. The RKmax parameter, that in the Wien2K code determines the size of the plane wave basis set, was chosen such as to ensure the number of APW’s per atom ranged from 100 to 150 depending on the size of the simulation cell (equivalent in terms of cut-off energy to a 150-220 eV range). Concerning k-point integration in the Brillouin zone, we considered for the structural relaxation a 6×6 k-points grid for the 2×2 cell, and a 3×3 k-points grid for the 4×4 cell, shifted from Γ. A finer k mesh was used for the electronic properties (band structure, LDOS, orbital occupations). The convergence of the results as a function of the above parameters was checked. Moreover, local orbitals were added to the basis set, in order to describe more accurately s and p semi-core states within 80 eV from the Fermi level. For Dy, Ti, Sr and O atoms, muffin tin radii of 2.40, 1.74, 2.48, and 1.50 a.u. were used, respectively.

**GGA+U vs. on-site B3LYP**

We present here the results obtained by the DFT+U method in its Around Mean Field version, and rotationally invariant implementation. An on-site Hubbard correction term on the f orbital of Dy was added, choosing a value of $U = 7$ eV and $J = 0.82$ eV, as previously used for Dy adatoms on metal substrates. Tests were carried out increasing the value of $U$ up to 10 eV and only minor modifications were observed. In Table S1 we compare the results obtained by the GGA+U method with the ones obtained using the on-site B3LYP method already presented in the main text. The total energy of Dy at different adsorption sites is given, following the same definition as in Table 1 of the main text, together with
Table S1: Comparison between the GGA+U and on-site B3LYP calculations for the different adsorption sites at the two possible TiO$_2$ and SrO terminations. Total energy values (in eV) are referred to the most stable solution. In the case of the SrO termination, energies (in brackets) are referred to the most stable solution among the ones on the same termination. Electronic occupations of the 4f Dy adatom orbital are also reported.

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the occupation of the Dy 4f orbitals. We observe that the GGA+U method predicts the same trend as the on-site B3LYP for the relative stability of the different adsorption sites, although some variations are found in the absolute values. As anticipated in the main text, the on-site B3LYP method leads to results which are generally in better agreement with the experimental observation of a 4f$^9$ configuration for the Dy 4f shell. An occupation closer to 4f$^{10}$ is always associated with a reduction of the occupation of the 6s, 6p and 5d orbitals composing the valence shell, leading to a different distribution of the electrons within the spdf shell, while charge transfer to the surface is similar for both valences.

**Spin and orbital projected band structures: 2DEG at the STO surface**

As discussed in the main text, the presence of Dy adatoms on both TiO$_2$ and SrO terminations of the STO(001) surface induces a metallization of the substrate and the appearance of parabolic conduction bands with Ti-d$_{xy}$ character as depicted in Fig. 1g of the main text. In Fig. S5 we present the depth dependence of such bands for the TiO$_2$/hollow (panels from a to d) and SrO/top-O adsorption sites (panels e and f), in the case of the majority spin
Figure S5: Majority spin ($\uparrow$) orbitally-projected electronic band structure in the $[-3\,\text{eV},+3\,\text{eV}]$ energy range around the Fermi level. The size of the red circles is proportional to the Ti-$d_{xy}$ orbital contribution in the case of a Dy adatom (a-d) at the hollow site on the TiO$_2$ terminated surface, and (e,f) for a Dy adatom at the top-O position on the SrO terminated surface. The contribution of Ti atoms at increasing depth within the substrate is shown moving from (a) to (d) and from (e) to (f), as evidenced by the structural sketches in the insets of the various panels.

band structure. We note that the metallic states are mainly localized in the surface or subsurface TiO$_2$ planes, similarly to what was previously observed by DFT calculations for the 2DEG states induced by intrinsic O-vacancies in STO interfaces and surfaces.$^{9,10}$ Moreover the predominant Ti-$d_{xy}$ character of the metallic bands is observed independently of the termination on top of which the Dy adatoms are adsorbed. This means that the 2DEG bands will exist on the entire STO(001) surface, not just at islands of a particular termination.
Details about the atomic multiplet calculations

Point charges and crystal field parameters

Table S2: Point charges used to calculate the crystal field parameters at the different adsorption sites (hollow, top-O and top-Ti) of the TiO$_2$ termination. The Dy atom position is the origin of the coordinate system.

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The crystal field parameters used in atomic multiplet calculations for the 4f orbitals were obtained by using a point charge model based, for each adsorption site, on the DFT optimized adsorption geometry and the corresponding Bader charges of the ligands surrounding the
Table S3: Point charges used to calculate the crystal field parameters at the different adsorption sites (top-O, bridge and top-Sr) of the SrO$_2$ termination. The Dy atom position is the origin of the coordinate system.

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Table S4: Rescaled (see text) crystal field Wybourne parameters (in units of meV) for the six Dy adsorption sites on the two surface terminations of STO(001).

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Dy atoms. In the case of Dy on the TiO$_2$/hollow site, we have explicitly included a small negative charge above the Dy atom, in order to reproduce the anisotropic charge density associated with the Dy spd electrons. Tables S2 and S3 show the point charges used in the case of the TiO$_2$ and the SrO terminations, respectively. With these, we calculated the crystal field parameters, in Wybourne notation, using the “pointc” module$^{11}$ within the software McPhase.$^{12}$ In order to compensate for the well-known underestimation of the crystal field parameters of order 4 and 6 with respect to those of order 2 by the point charge model, we have rescaled the crystal field by factors $\kappa_l$ ($l = 2, 4, 6$) following the procedure outlined by Singha et al.$^{13}$ ($\kappa_2 = \sqrt{2}$, $\kappa_4 = 2\sqrt{2}$, $\kappa_6 = 4$), thus obtaining the modified Wybourne parameters used in Quanty for the atomic multiplet calculations, indicated as $A_l^m$ in Table S4 (with $m = 0, 2, 4, 6$).
Simulated XAS, XMCD and magnetization cycles for each adsorption site

Figure S6: XAS and XMCD spectra at the Dy $M_{4,5}$ edges and magnetization loops simulated by means of atomic multiplet calculations for each Dy adsorption site on the TiO$_2$ termination of the STO(001) surface. The simulations are performed for a temperature $T = 2.5$ K. A magnetic field $B = 5$ T is applied at $\theta = 0^\circ$ and $\theta = 60^\circ$ for the XAS and XMCD, while the XLD was calculated for $\theta = 60^\circ$.

Figures S6 and S7 show the XAS and XMCD spectra calculated by atomic multiplet calculations at the Dy $M_{4,5}$ edges for each adsorption site at the TiO$_2$ and SrO terminations, respectively. The simulations are for a temperature $T = 2.5$ K and a magnetic field $B = 5$ T. The bottom graphs in each column show the corresponding magnetization cycle at thermodynamical equilibrium. The magnetic field and the X-ray beam rotate in the $xz$-plane when
Figure S7: XAS and XMCD spectra at the Dy $M_{4,5}$ edges and magnetization loops simulated by means of atomic multiplet calculations for each Dy adsorption site on the SrO termination of the STO(001) surface. The simulations are performed for a temperature $T = 2.5 \text{ K}$. A magnetic field $B = 5 \text{ T}$ is applied at $\theta = 0^\circ$ and $\theta = 60^\circ$ for the XAS and XMCD, while the XLD was calculated for $\theta = 60^\circ$.

going from normal ($\theta = 0^\circ$) to grazing ($\theta = 60^\circ$) incidence. The two-fold symmetry of the top-O site on the TiO$_2$ termination and of the bridge site on the SrO termination leads to the coexistence of two Dy species on each site. In fact, the two Ti next-nearest neighbours for the top-O site, and the two O nearest neighbours for the bridge site may either be aligned along the $x$ direction (sites indicated as ”top-Ox” and ”bridge-Ox”) or along the $y$ direction (sites indicated as ”top-Oy” and ”bridge-Oy”). While in the top-O case both orientations correspond to a magnetic hard axis, for the bridge site the ”bridge-Ox”, with the Dy magnetic moments aligned towards the neighbour O atoms, is the magnetic easy axis. Among
the other sites, all showing four-fold symmetry, the hollow and top-Ti on the TiO$_2$ termination and the top-Sr on the SrO termination exhibit in-plane magnetic anisotropy, while the top-O site on the SrO termination has a strong out-of-plane anisotropy.

**Details about the calculation of the magnetization relaxation time $\tau$**

**Theoretical model**

The spin-phonon scattering probability between an initial $|i\rangle$ and a final $|j\rangle$ eigenstate of the Dy/STO(001) atomic system, following the model proposed by Fort et al.,\textsuperscript{14} can be written as:

$$G^{ij}_{\text{ph}} = \begin{cases} 
C_{\text{ph}} M^{ij}_{\text{ph}} |\Delta E_{ij}|^3 n_{ij} & \text{for } \Delta E_{ij} < 0 \text{ (phonon absorption)} \\
C_{\text{ph}} M^{ij}_{\text{ph}} |\Delta E_{ij}|^3 (n_{ij} + 1) & \text{for } \Delta E_{ij} > 0 \text{ (phonon emission)} 
\end{cases}, \quad (S1)$$

where $C_{\text{ph}}$ is a constant characteristic for the spin-phonon scattering cross-section in Dy/STO(001), $\Delta E_{ij} = E_i - E_j$ is the difference of the energies of eigenstates $|i\rangle$ and $|j\rangle$, $n_{ij} = \{\exp[|\Delta E_{ij}|/(k_B T)] - 1\}^{-1}$ is the Bose-Einstein distribution of phonon population, $k_B$ is Boltzmann’s constant, and $T$ is the temperature. The spin-phonon scattering matrix elements, following the notation by Cervetti et al.,\textsuperscript{15} are defined as:

$$M^{ij}_{\text{ph}} = |\langle j | J_2^- | i \rangle|^2 + |\langle j | J_2^+ | i \rangle|^2 + 2|\langle j | \{J_-, J_z\} | i \rangle|^2 + 2|\langle j | \{J_+, J_z\} | i \rangle|^2, \quad (S2)$$

with $J_{\pm} = J_x \pm i J_y$. The same matrix elements were previously used for Dy based molecular complexes.\textsuperscript{16}

Analogously, following Delgado and Fernández-Rossier,\textsuperscript{17} we write the spin-electron scat-
tering probability as:

\[ G_{el}^{ij} = C_{el} M_{el}^{ij} \frac{\Delta E_{ij}}{e^{\frac{\Delta E_{ij}}{k_B T}} - 1}, \]  

(S3)

where \( C_{el} \) is a constant characteristic for the spin-electron scattering cross-section in Dy/STO(001), which in turn depends on the (unknown) electronic density of the STO(001) substrate, and the spin-electron scattering matrix elements are defined as:

\[ M_{el}^{ij} = |\langle j|J_-|i\rangle|^2 + |\langle j|J_+|i\rangle|^2 + 2|\langle j|J_z|i\rangle|^2, \]  

(S4)

which assumes that the exchange of the Dy 4f shell with the conduction-electron spins \( s \) is accurately approximated by the bilinear Heisenberg exchange in the form \( J \cdot s \), despite some deviations and/or extra terms due to the orbital component of the total moment \( J \) are to be expected.\(^{18}\)

With the knowledge of \( G_{ph}^{ij} \) and \( G_{el}^{ij} \), we can solve the set of \( N_{lev} \) differential rate equations (\( N_{lev} \) is the total number of eigenstates of the Dy/STO(001) system), relating the population \( P_i(t) \) of state \( |i\rangle \) at time \( t \) with the probability of phonon or electron related scattering to/from the other states \( |j\rangle \), with \( j \neq i \):

\[
\frac{\partial P_i(t)}{\partial t} = -P_i(t) \sum_{j=1}^{N_{lev}} \left( G_{ph}^{ij} + G_{el}^{ij} \right) + \sum_{j=1}^{N_{lev}} P_j(t) \left( G_{ph}^{ji} + G_{el}^{ji} \right),
\]  

(S5)

with the boundary conditions \( P_1(0) = 1 \) (where \( |1\rangle \) is the ground-state of the system) and \( P_j(0) = 0 \) for \( j = 2 \ldots N_{lev} \). The time evolution of the population of the ground state \( |1\rangle \), \( P_1(t) \), is then fitted with an exponential decay function of the type:

\[ P_1(t) = P_1(0)e^{-\frac{t}{\tau}}, \]

allowing us to determine \( \tau \).

In the case of the Dy\(^{hollow}\) species, the magnetic field dependence of \( \tau \) shown in Fig. 5b
of the main text is calculated based on the values $C_{\text{ph}} = 2.1 \times 10^{-2}$ and $C_{\text{el}} = 7.5 \times 10^{-5}$.

Figure S8: (a) Intrinsic magnetization relaxation time $\tau$ and its decomposition into a spin-phonon contribution ($\tau_{\text{ph}}$) and a spin-electron contribution ($\tau_{\text{el}}$) at $T = 2.5$ K and $\theta = 60^\circ$; (b) Comparison between the magnetic field dependence of $\tau$ calculating with and without including the coupling of the 4f magnetic moment with the nuclear spin $I = 5/2$.

Fig. S8a shows the decomposition of the intrinsic magnetization relaxation time $\tau$ into a spin-phonon contribution ($\tau_{\text{ph}}$) and a spin-electron contribution ($\tau_{\text{el}}$). The values for $\tau$ are those displayed in Fig. 5b of the main text. It is evident that for all three adsorption sites the calculated values of $\tau$ are dominated by the spin-electron scattering at low magnetic fields, while the spin-phonon scattering contribution prevails at high magnetic field. In Fig. S8b we compare the magnetic field dependence of $\tau$ as calculated including or neglecting the coupling of the 4f magnetic moment with the nuclear spin $I$. Such coupling is effective
only for Dy isotopes with $I \neq 0$: $^{161}\text{Dy}$ with relative abundance of 18.9% and $^{163}\text{Dy}$ with relative abundance of 24.9%, both having $I = 5/2$. As evident from the figure, there is negligible difference between the two cases in the magnetic field range of our experimental investigations of $\tau$ ($B > 0.1 \text{T}$).

**Estimate of the secondary electrons contribution to the value of the relaxation time**

The X-ray flux dependent contribution $\tau_{\text{sec}}(\Phi)$ of secondary electrons to the measured value of the relaxation time $\tau_{\text{exp}}(\Phi)$ can be estimated by noting that the latter may be expressed as $\tau_{\text{exp}}^{-1}(\Phi) = \tau^{-1} + \tau_{\text{sec}}^{-1}(\Phi)$, where $\tau$ is the intrinsic relaxation time of the Dy magnetization and $\Phi$ is the X-ray flux. Because of the limited magnetic field range (between 0.1 and 1 T) studied in our investigations of $\tau$, we assume that $\tau_{\text{sec}}(\Phi)$ does not depend on magnetic field, and we determine its X-ray flux dependence at $B = 0.375 \text{T}$. By measuring $\tau_{\text{exp}}$ at two X-ray fluxes $\Phi_{\text{lf}}$ and $\Phi_{\text{hf}} = 4 \times \Phi_{\text{lf}}$ (where the indices ”lf” and ”hf” stand for ”low flux” and ”high flux”, respectively), we obtain a system of two equations:

\[
\begin{align*}
\tau_{\text{exp}}^{-1}(\Phi_{\text{lf}}) &= \tau^{-1} + \tau_{\text{sec}}^{-1}(\Phi_{\text{lf}}) \\
\tau_{\text{exp}}^{-1}(\Phi_{\text{hf}}) &= \tau^{-1} + \tau_{\text{sec}}^{-1}(\Phi_{\text{hf}})
\end{align*}
\]  \hspace{1cm} (S6)

By combining the two equations above, we obtain:

\[
\tau_{\text{sec}}(\Phi_{\text{lf}}) = \frac{a \tau_{\text{sec}}(\Phi_{\text{hf}})}{a - \tau_{\text{sec}}(\Phi_{\text{hf}})},
\]

where $a = \frac{\tau_{\text{exp}}(\Phi_{\text{lf}}) \tau_{\text{exp}}(\Phi_{\text{hf}})}{\tau_{\text{exp}}(\Phi_{\text{lf}}) - \tau_{\text{exp}}(\Phi_{\text{hf}})}$. The obvious condition $\tau_{\text{sec}}(\Phi_{\text{lf}}) \geq 0$ imposes that $\tau_{\text{sec}}(\Phi_{\text{hf}}) \leq a$, setting an upper limit for the secondary electrons contribution to the relaxation time in our ”high flux” conditions, which correspond to the X-ray flux used for recording all the magnetization cycles presented in this manuscript. At $B = 0.375 \text{T}$, where we record $\tau_{\text{exp}}(\Phi_{\text{lf}}) = 800 \pm 200 \text{s}$
and \( \tau_{\text{exp}}(\Phi_{\text{hf}}) = 160 \pm 20 \text{ s} \), we then obtain \( \tau_{\text{sec}}(\Phi_{\text{hf}}) \leq 200 \pm 40 \text{ s} \). The lower limit for \( \tau_{\text{sec}}(\Phi_{\text{hf}}) \), on the other hand, is represented by the largest value of \( \tau_{\text{exp}}(\Phi_{\text{hf}}) \) in our magnetic-field dependent series, which is \( 190 \pm 30 \text{ s} \) at \( B = 0.1 \text{ T} \). Due to the large uncertainty in these values, we take \( \tau_{\text{sec}}(\Phi_{\text{hf}}) \) to lie in the middle of its allowed range, corresponding to \( \tau_{\text{sec}}(\Phi_{\text{hf}}) = 195 \pm 35 \text{ s} \).

With this value, we estimate the intrinsic value of the magnetization relaxation time at \( B = 0.375 \text{ T} \) by using the bottom equation in (S6), giving \( \tau = 900 \pm 40 \text{ s} \). This, in turn, allows us to estimate the secondary electrons contribution to the relaxation time in our "low flux" conditions (corresponding to the X-ray flux used for recording the values of \( \tau_{\text{exp}} \) shown in Fig. 5a of the main text), by using the top equation in (S6), resulting in \( \tau_{\text{sec}}(\Phi_{\text{lf}}) = 7100 \pm 200 \text{ s} \).

Taking into account the above estimated values of \( \tau_{\text{sec}} \), with the condition \( \tau_{\text{sec}}^{-1}(\Phi = 0) = 0 \), we find a quadratic dependence of the secondary electrons contribution to the relaxation time on the X-ray flux:

\[
\tau_{\text{sec}}^{-1}(\Phi) = b \left( \frac{\Phi}{\Phi_{\text{hf}}} \right)^2,
\]

(S7)

with \( b = (5 \pm 1) \times 10^{-3} \text{ s}^{-1} \).
References


