Sachse T, Neel N, Meierott S, Berndt R, Hofer WA, Kroger J. **Electronic and magnetic states of Mn\textsubscript{2} and Mn\textsubscript{2}H on Ag(111).** *New Journal of Physics* 2014, 16, 063012.

Copyright:

©2014 IOP Publishing

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

**DOI link to article:**

http://dx.doi.org/10.1088/1367-2630/16/6/063021

**Date deposited:** 30-10-2014

This work is licensed under a [Creative Commons Attribution 3.0 Unported License](http://creativecommons.org/licenses/by/3.0/)

ePrints – Newcastle University ePrints

http://eprint.ncl.ac.uk
Electronic and magnetic states of Mn$_2$ and Mn$_2$H on Ag(111)

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 New J. Phys. 16 063021

(http://iopscience.iop.org/1367-2630/16/6/063021)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 128.240.229.69
This content was downloaded on 30/10/2014 at 11:27

Please note that terms and conditions apply.
Electronic and magnetic states of Mn$_2$ and Mn$_2$H on Ag(111)

T Sachse$^{1,2}$, N Néel$^1$, S Meierott$^1$, R Berndt$^3$, W A Hofer$^2$ and J Kröger$^1$

$^1$Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany
$^2$Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool L69 3BX, UK
$^3$Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
E-mail: joerg.kroeger@tu-ilmenau.de

Received 10 February 2014, revised 23 April 2014
Accepted for publication 28 April 2014
Published 12 June 2014
New Journal of Physics 16 (2014) 063021
doi:10.1088/1367-2630/16/6/063021

Abstract
Manganese dimers on Ag(111) are investigated with scanning tunneling microscopy and density functional calculations. Two species of dimers coexist that differ in their apparent heights and the absence or presence of submolecular structure. These species can be interconverted by electron and hole injection from the microscope tip. Calculations identify the two kinds of dimers as pristine Mn$_2$ and Mn$_2$H and show that hydrogen attachment to Mn$_2$ leads to marked changes in the dimer electronic and magnetic structure. Antiferromagnetic coupling between Mn magnetic moments in Mn$_2$H leaves its spectroscopic signature in the electronic structure of the monohydride compound.

Keywords: magnetism at the nanometre scale, atomic-scale clusters on surfaces, scanning tunnelling microscopy, density functional theory

1. Introduction

The ongoing miniaturization of electrical circuitry renders supported clusters of magnetic atoms promising building blocks for magnetic storage devices. Recent experiments showed that the magnetization of atomic-scale clusters may be controlled by spin-torque transfer [1] or the excitation of spin–flip processes induced by inelastic electron tunneling [2]. Further, electron
transport through magnetic clusters [3–6] as well as magnetoresistive effects at atomic [7, 8] and molecular [9] levels have been reported.

Manganese plays an exceptional role among the magnetic elements since the atomic magnetic moment of $\mu_B (\mu_B$: Bohr magneton) is only marginally quenched in free, i.e., non-supported, clusters [10] as well as upon adsorption to noble metal surfaces [11–13]. According to previous calculations, the free dimer exhibits an antiferromagnetic (↑↓) coupling of the Mn magnetic moments at a bond distance of 0.289 nm [14]. Exceeding a mutual Mn distance of $\approx 0.3$ nm the coupling turns ferromagnetic (↑↑) [14]. Manganese on surfaces exhibits peculiar magnetic properties [15]. For instance, in single Mn layers on Ag(100) a phase transition from an antiferromagnetically ordered c(2 × 2) superstructure to a paramagnetic p(1 × 1) phase has been reported [16]. Further, ultrathin Mn films on Cu3Au(100) have been shown to exhibit ferromagnetic and antiferromagnetic ordering depending on the crystal growth [17]. On Ag(111) a single layer of Mn shows the 120° antiferromagnetic Néel structure, independent of the stacking with respect to the substrate [17]. Chiral magnetic order in single layers of Mn on W(110) [18] and transverse conical spin states of a double-layer Mn film on W(110) [19] reflect the subtle balance between Heisenberg exchange and Dzyaloshinskii–Moriya interactions in combination with magnetic anisotropy. Experimental studies on atomic-scale Mn clusters on surfaces are rather scarce. On Cu2N/Cu(100) Mn dimers show an antiferromagnetic coupling of the Mn magnetic moments [20, 21]. A previous theoretical work revealed that on Ag(111) ↑↑ and ↑↓ states of Mn2 are nearly degenerate [13]. On Ag(100) the energetically favored Mn2 ↑↑ clusters may be converted into Mn2 ↑↓ by a sufficiently high electric field [22].

The role of H in low-temperature experiments is closely related to exploring magnetism at the nanometer scale [23–28]. Transition-metal and rare-earth atoms, which have interesting magnetic properties, tend to form metal-hydride compounds by spontaneous dissociation of H2 at the metal atom site. The hydrogenated compounds are readily discernible from their pristine counterparts in scanning tunneling microscopy (STM) images and spectra of the differential conductance (dI/dV) [23–26]. On Ag(100) Cr, La, Ce atoms were shown to form CrH, LaH, CeH compounds, which appear with upright and tilted adsorption configurations [23, 24]. Ti atoms on hexagonal boron nitride on Rh(111) and Ni(111) are likewise subject to H uptake [25]. Both TiH and TiH2 complexes are likely to coexist on these surfaces [25]. Spectroscopy of the differential conductance performed for TiH on hexagonal boron nitride on Rh(111) leads to a zero-bias resonance that has been interpreted as the signature of the TiH Kondo effect [25]. This result shows that also magnetic properties may be considerably changed by H attachment. Magnetic properties have been thoroughly investigated for single Co atoms adsorbed to graphene on Pt(111) [26]. On this surface, aside from clean Co atoms, CoHn (n = 1, 2, 3) compounds coexist and exhibit magnetic properties that are different from clean Co atoms [26]. Single H atoms attached to the apex of Cr-coated W tips were shown to considerably increase the spin polarization of the tip close to the Fermi energy ($E_F$), which led to high magnetic contrast in spin-resolved STM [27]. Recently, the spin state of a Mn-phthalocyanine molecule adsorbed to Au(111) has been reversibly changed by adding a H atom to the metal core and removing it [28].

Here, we present investigations into the electronic and magnetic structure of Mn dimers adsorbed to Ag(111). Two types of dimers were identified with STM from their different apparent heights and the absence or presence of submolecular structure. Both species can be
reversibly converted into each other by injection of electrons or holes from the microscope tip. Density functional calculations assign the observed species to pristine Mn$_2$ and Mn$_n$H. Simulated STM images are in good agreement with experimental data. Due to the hybridization of Mn with the metal substrate density functional methods rather than the Heisenberg model [20] have been used to unravel the coupling between Mn magnetic moments. For pristine Mn$_2$, STM images and calculations are compatible with degenerate ferromagnetic and antiferromagnetic couplings, while for Mn$_n$H an antiferromagnetic coupling is indicated. The calculated energies for H removal from Mn$_n$H and H attachment to Mn$_2$ are compatible with electron and hole energies that lead to the experimentally observed interconversions.

2. Experiment

Experiments were performed with a home-made scanning tunneling microscope operated at 7 K and in ultrahigh vacuum ($10^{-9}$ Pa). Ag(111) surfaces were cleaned by Ar$^+$ bombardment and subsequent annealing. Single Mn atoms were deposited onto the substrate at $\approx 10$ K by heating a Mn wire of 99.99% purity. Prior to deposition the Mn wire had been thoroughly degassed to reduce the amount of concomitantly adsorbed hydrogen [23, 25]. All STM images were acquired in the constant-current mode with the voltage applied to the sample.

3. Results and discussion

Deposition of Mn onto the cold Ag(111) surface leads to Mn monomers, which are indicated as Mn$_1$ in figure 1(a). Monomers appear as protrusions with circular circumferences. At a sample voltage of 100 mV their apparent height and full width at half maximum (FWHM) are $\approx 102$ pm and $\approx 0.95$ nm, respectively, as determined from cross-sectional profiles (figure 1(b)). These values are in good agreement with a previous report where single Mn atoms were used to build artificial atom arrays on Ag(111) [29, 30]. In addition to Mn monomers, adsorption species that exhibit an appreciably lower apparent height are present on the surface (labeled Mn$_1$H in the inset to figure 1(a)). The latter species are assigned to hydrogenated Mn compounds, which is in agreement with observations from Ti on hexagonal boron nitride [25] and Co on graphene [26], where hydrogenated Ti and Co atoms appeared lower than their clean counterparts. We assign the hydrogenated Mn atoms to Mn$_1$H$_x$ with $x > 1$, which will be further discussed below. Clean Mn monomers can be readily manipulated with the STM tip [29, 30]. Typical feedback loop parameters for manipulation were 100 mV and 50–100 nA. Approaching two Mn atoms to within a Ag(111) nearest-neighbor distance leads to the spontaneous formation of a Mn species that appears as a double-protrusion feature in constant-current STM images (Mn$_2^*$ in figure 1(a)). The long axis of Mn$_2^*$ is oriented along one of $\langle\overline{1}10\rangle$ directions, which is indicated by the arrow in figure 1(a). The protrusions are separated by $\approx 0.49$ nm (figure 1(b)). The apparent height of Mn$_2^*$ is $\approx 71$ pm (figure 1(b)), which is even lower than the Mn monomer apparent height. The Mn$_2^*$ FWHM along $\langle\overline{1}10\rangle$ is $\approx 1.30$ nm. Applying voltages $0.2 \, V < |V| < 2.5 \, V$ with the tip positioned above the center of Mn$_2^*$ at a tunneling current of 50 pA induces rotations of Mn$_2^*$ about the surface normal (not shown). All rotated Mn$_2^*$ were aligned along $\langle1\overline{1}0\rangle$ directions. Placing the tip above the center of Mn$_2^*$ and
injecting holes or electrons from the STM tip at bias voltages $|V| > 2.5$ V converts $\text{Mn}_2^*$ into another species that appears as a single protrusion in constant-current STM images ($\text{Mn}_2$ in figure 1(a)). The apparent height (FWHM along $\langle 1\bar{1}0 \rangle$) of $\text{Mn}_2$ at 100 mV is $\approx 141$ pm (1.05 nm)
Conversion of Mn$_2^*$ into Mn$_2^*$ has been achieved by pulsing the bias voltage to $|V| = 1$ V after setting the tunneling gap atop the Mn$_2$ center at $|V| = 0.1$ V and 50 pA.

Based on previous reports on $d$ metal atoms on $sp$ metal surfaces, e.g., Mn on Ag(111) [29, 30], Co [31], Cr [32], Ni [33] on Au(111), the experimental data suggest the assignment of Mn$_1$ and Mn$_2$ features to Mn monomers and dimers, respectively. However, identification of Mn$_2^*$ with STM investigations alone is difficult. Due to the inevitable presence of H in low-temperature experiments (inset to figure 1(a)) [23–27, 34] Mn$_2^*$ may be a hydrogenated Mn complex, e.g., Mn$_2$H. Mn$_2^*$ may likewise represent another pristine Mn dimer whose electronic and geometric ground states have so far eluded experimental and theoretical studies. Further, the tip apex may be contaminated with a single Mn atom thus giving rise to the anomalously low apparent height and double-protrusion structure of Mn$_2^*$. To determine which scenario applies, density functional calculations and simulations of STM images were performed.

Geometry relaxations were performed by means of Kohn–Sham density functional theory (DFT) as implemented in the Vienna $ab initio$ simulation package (VASP) [35–37] using the quasi-Newtonian relaxation scheme included therein so that in the relaxed geometry all forces were lower than 100 meV nm$^{-1}$. The projector augmented wave pseudopotential as parametrized by Perdrew, Burke and Ernzerhof [38–40] was used with a plane-wave basis-set curtailed at 202.4 eV. All relaxations were carried out in 6 × 6 unit cells in order to keep interactions between adjacent adsorbates at an acceptable level [41] whilst using at least 1.2 nm of vacuum between neighboring slabs of three Ag layers for the same reason [13]. Considering the unit cell size, a fine Monkhorst–Pack [42] grid of $3 \times 3 \times 1$ k-points was employed. Constant-current STM images were simulated within the Tersoff–Hamann approximation [43, 44] using bSKAN [45–47] and keeping the tip at realistic tunneling distances [48], i.e., at least 0.5 nm above the sample. All calculations were performed without symmetry constraints.

As a first step pristine Mn monomers and dimers on Ag(111) were simulated. According to the calculations hexagonal close-packed (hcp) and face-centered cubic (fcc) Ag(111) lattice sites are virtually degenerate adsorption sites for single Mn atoms, in agreement with a previous report [13]. The obtained binding energy of 1.88 eV for Mn residing on hcp and fcc sites is higher than obtained for top (1.42 eV) and bridge (1.85 eV) sites. For the following calculations the hcp site has been chosen. At this site a single Mn atom exhibits a calculated magnetic moment of $4.59 \mu_B$, which is close to the previously reported value of $4.72 \mu_B$ [13]. Next, constant-current STM images of Mn residing at Ag(111) hcp lattice sites were simulated within the Tersoff–Hamann approximation [43, 44]. To this end a minimum tip–surface distance of 0.5 nm and a sample voltage of 0.4 V were chosen$^4$. The results are presented in the top row of figure 2(a). Due to the absence of temperature effects in DFT such as phonons and diffusion processes the perfect threefold symmetry of Mn adsorbed to the center of an hcp site is retained in simulated STM images. The apparent heights of Mn with magnetic moments parallel ($\uparrow$) and antiparallel ($\downarrow$) to the surface normal are virtually identical (table 1).

$^4$ In the calculations sample voltages between $-0.4$ and 0.4 V with increments of 0.1 V were tested. The best agreement with experimental data was obtained for 0.4 V, which differs from the bias voltage of 0.1 V used in the experiments. We assign this deviation to the difficult definition of the Fermi energy in density functional calculations.
Figure 2. (a) Calculated (second and third columns) and measured (right column) constant-current STM images of a Mn monomer (top row), a Mn dimer (middle row) and a Mn$_2$H compound (bottom row) on Ag(111). All image sizes are 3.5 nm × 3.5 nm. The gray scale ranges from 0 (black) to 250 pm (white). Adsorbates on the topmost Ag (111) layer are sketched in the first column. The out-of-plane orientations of Mn magnetic moments and their coupling in the dimer and the monohydride compound are indicated as arrows. Calculations were performed on a 6 × 6 unit cell, with a bias voltage of 0.4 V and a minimum tip–surface distance of 0.5 nm. Bright spots in the corners of the simulated images represent structures from adjacent unit cells. Experimental data were acquired with 0.1 V and 30 pA. (b) Calculated cross-sectional profiles of Mn$_1$, pristine Mn$_2$ ↑↑ and Mn$_2$H ↑↓ on Ag(111) extracted from constant-current STM images in (a) along a crystallographic direction. Calculated height ratios, $h_{\text{Mn}_1}: h_{\text{Mn}_2}: h_{\text{Mn}_2\text{H}} = 1.26: 1: 0.78$, are in good agreement with experimental data, 1.38: 1: 0.70.
To simulate STM images of Mn$_2$ on Ag(111) neighboring hcp sites were considered as adsorption sites since they are energetically favored by $\approx 10$ meV over other site combinations. In accordance with a previous report [13] ↑↑ and ↑↓ couplings of the Mn magnetic moments represent virtually degenerate states. Indeed, both magnetic configurations differ in binding energy by no more than 1 meV. The middle row of figure 2(a) compares calculated and experimental constant-current STM images of Mn$_2$. The calculated apparent height and FWHM of Mn$_2$ ↑↑ and of Mn$_2$ ↑↓ are summarized in table 1. Simulations of STM images were likewise performed for Mn$_2$ ↑↑ and Mn$_2$ ↑↓ at less favorable adsorption sites (not shown). However, in all cases the apparent heights of dimers exceeded the apparent height of the monomer and, in addition, submolecular structure was not observed. Therefore, while these findings support the assignment of experimentally observed Mn$_2$ features to Mn dimers we exclude pristine Mn dimers as the origin of the experimentally observed Mn$_2^*$. In a next step Mn$_2$H compounds were analyzed in the calculations. The presence of H$_2$ on Ag(111) and its spontaneous dissociation at the Mn atom site is likely in the light of previous publications [23–26] and due to the overview STM image in the inset to figure 1(a). The resulting H atom can easily diffuse even at low temperatures owing to similar binding energies on different Ag(111) adsorption sites [49]. Therefore, Mn monomers and dimers are likely to be visited by diffusing H atoms. The calculations showed that for ↑↑ as well as for ↑↓ interactions between Mn magnetic moments a Mn–H–Mn structure is favored, i.e., the H atom bridges the Mn atoms on top of the dimer (sketch in the bottom row of figure 2(a)). The calculated binding energy is $\approx 1.2$ eV, which is more than 0.5 eV higher than binding energies of all other considered structures$^5$. The bottom row of figure 2(a) clearly shows that exclusively the calculated STM image of the Mn$_2$H ↑↓ compound matches experimental data. The double-protrusion feature as well as the anomalously low apparent height are reproduced (figure 2(b) and table 1). The protrusions are separated by $\approx 0.43$ nm, which is close to the experimental value ($\approx 0.49$ nm). In contrast, the Mn$_2$H ↑↑ molecule does not exhibit submolecular structure and appears slightly higher than Mn$_2$. As an important result we obtain that in favorable cases magnetic order leaves its fingerprint in the electronic structure that is routinely accessible by conventional STM.

---

$^5$ Other Mn$_2$H compounds consisted of H atoms attached to a single Mn atom in on-top or side positions. H bridging Mn atoms at the sides of the dimer were also investigated.

**Table 1.** Calculated apparent heights and full widths at half maximum (FWHM) of Mn, Mn$_2$ and Mn$_2$H. Magnetic moments are oriented parallel (↑) and antiparallel (↓) to the surface normal. For the dimer and the monohydride compound ferromagnetic (↑↑) and antiferromagnetic (↑↓) couplings between Mn magnetic moments were considered.

<table>
<thead>
<tr>
<th></th>
<th>Height (pm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn↑</td>
<td>195</td>
<td>0.82</td>
</tr>
<tr>
<td>Mn↓</td>
<td>195</td>
<td>0.82</td>
</tr>
<tr>
<td>Mn$_2$ ↑↑</td>
<td>245</td>
<td>0.86</td>
</tr>
<tr>
<td>Mn$_2$ ↑↓</td>
<td>230</td>
<td>0.89</td>
</tr>
<tr>
<td>Mn$_2$H ↑↑</td>
<td>205</td>
<td>0.82</td>
</tr>
<tr>
<td>Mn$_2$H ↑↓</td>
<td>153</td>
<td>0.97</td>
</tr>
</tbody>
</table>
The absolute values of the calculated apparent heights and the FWHM differ from their experimental counterparts. Due to the simplifications of the Tersoff–Hamann approximation quantitative agreement between calculated and experimental data is not expected [43, 44]. However, the ratio between calculated apparent heights for $M_n^2$, $M_n^{\uparrow \downarrow}$, $M_nH^\uparrow \downarrow$, $M_nH^\uparrow \uparrow$, and $M_nH^\downarrow \downarrow$, i.e., $h_{M_n^2}: h_{M_n}: h_{M_nH} = 1.26: 1: 0.78$, matches the experimental ratio ($1.38: 1: 0.70$) very well. According to the calculations, $\uparrow \uparrow$ and $\uparrow \downarrow$ couplings represent degenerate magnetic states of $M_n^2$. Both dimers appear with similar heights in simulated STM images. The experimental STM images may therefore show a time average of $M_n^2$, $M_n^{\uparrow \downarrow}$, and $M_nH^{\uparrow \downarrow}$ clusters. For $M_nH$ the calculations likewise reveal a $\uparrow \uparrow$–$\uparrow \downarrow$ degeneracy. However, the calculated STM images of $M_nH^{\uparrow \uparrow}$ and $M_nH^{\downarrow \downarrow}$ differ strongly (figure 2(a)). Experimental STM images exclusively show data that are compatible with simulations of $M_nH^{\downarrow \downarrow}$, which hints at a mechanism that lifts the calculated $\uparrow \uparrow$–$\uparrow \downarrow$ degeneracy of $M_nH$. This mechanism is unclear at present (see discussion below) and additional calculations are required to explore whether non-collinear spin structures of $M_nH$ may give rise to non-degenerate $\uparrow \uparrow$ and $\uparrow \downarrow$ states.

To shed more light on the electronic structure of $M_nH$, charge density isosurfaces were calculated. Figure 3 shows results for $M_n^2$ dimers and $M_nH$ compounds with $\uparrow \uparrow$ and $\uparrow \downarrow$ interactions between the Mn magnetic moments. Partial charge density isosurfaces were calculated for those bands between $E_F$ and $E_F + 0.4$ eV that give the dominant contribution to the simulated STM images in figure 2(a). Close to Mn the charge density is mainly of $d$ character while in the vicinity of H the charge density preponderantly exhibits $s$ character. Obviously, only for $M_nH^{\uparrow \downarrow}$ the partial charge density exhibits a depletion at the H site, which leads to the central depression in constant-current STM images of $M_nH$. We are confident that the presented density functional calculations give the correct local density of states of the true

![Image of Mn and MnH charge density isosurfaces](image.png)

**Figure 3.** Mn$_2$ (left) and Mn$_2$H (right) charge density isosurfaces (blue) for those states that give the dominant contribution to the simulated STM images in figure 2(a). Isosurfaces were calculated at $k = 0$, between $E_F$ and $E_F + 0.4$ eV and for ferromagnetic ($\uparrow \uparrow$) and antiferromagnetic ($\uparrow \downarrow$) coupling of the Mn magnetic moments. H (green) and Mn (red) atoms are depicted as spheres whose radii are 60% of their respective Wigner–Seitz radii.

The superposition of calculated cross-sectional profiles of $M_nH^{\uparrow \uparrow}$ and $M_nH^{\downarrow \downarrow}$ results in the absence of submolecular resolution and an apparent height that is only slightly lower than the Mn$_1$ apparent height.

---

6 The superposition of calculated cross-sectional profiles of $M_nH^{\uparrow \uparrow}$ and $M_nH^{\downarrow \downarrow}$ results in the absence of submolecular resolution and an apparent height that is only slightly lower than the Mn$_1$ apparent height.
ferromagnetic and antiferromagnetic Mn\textsubscript{2}H states. In VASP incorrect ground state energies are expected when a magnetic easy axis that does not coincide with the surface normal is present. For Mn\textsubscript{2} calculations considering non-collinear magnetism were performed and revealed the absence of any easy axis. We had to refrain from similar calculations for Mn\textsubscript{2}H due to considerably increased computational cost. However, previous publications reveal that the magnetocrystalline anisotropy of Mn clusters on surfaces is small and the easy axis is normal to the surface. For this reason, the magnetic ground state predicted by our calculations is reliable. For instance, Mn on Cu\textsubscript{2}N/Cu(100) exhibits a weak magnetocrystalline anisotropy along the surface normal [50]. This observation is consistent with small anisotropy values for Mn in molecular magnetic clusters [51]. In addition, the antiferromagnetic ground state of Mn dimers on Cu\textsubscript{2}N/Cu(100) has been demonstrated to be independent of the Mn adsorption sites, i.e., Mn atop Cu or Mn atop N [52]. While the attachment of H to the Mn dimer may change the absolute value of the anisotropy constant, the direction of the easy axis is likely to be preserved. The attachment of H to Co on graphene led to a reduction of the anisotropy constant compared to clean Co and did not change the anisotropy direction [26].

The orbital character of the electron cloud around the atomic sites has been estimated by projecting the wave functions onto spherical harmonics around these sites. The radii of these harmonics have been chosen to the Wigner–Seitz radii of the respective elements. These results show for both ferromagnetic and antiferromagnetic states that, around the Mn sites, there is a small loss in \( s \) character and a small gain in \( p \) character parallel to the surface upon H attachment. The \( d \) character of both magnetic orientations remains virtually unchanged. The small increase in orbital momentum implies a slightly stronger magnetic moment, which may give rise to a magnetic anisotropy induced by H attachment. However, this increase in orbital momentum is observed for Mn\textsubscript{2}H \( \uparrow \uparrow \) and Mn\textsubscript{2}H \( \uparrow \downarrow \). We therefore conclude that the H-induced orbital changes are not at the origin of the experimentally observed lifting of the degeneracy of Mn\textsubscript{2} magnetic states.

Before discussing the interconversion of Mn\textsubscript{2} and Mn\textsubscript{2}\* species, we briefly comment on the adsorption species indicated MnH\(_x\) in the inset to figure 1(a). Simulations of constant-current STM images of Mn and MnH are virtually identical. Therefore, MnH\(_x\) complexes with \( x > 1 \) are most likely the origin of the additional adsorption species. This assignment is in agreement with previous results where TiH\(_x\) (\( x = 2 \)) on hexagonal boron nitride [25] and CoH\(_x\) (\( x = 2, 3 \)) on graphene [26] exhibit lower apparent heights than the pristine metal atoms.

Calculations were performed to explain the experimentally observed reproducible interconversion of Mn\textsubscript{2} and Mn\textsubscript{2}\*. Estimations of energies required for dissociating H from Mn\textsubscript{2}H show that H removal from Mn\textsubscript{2}H with Mn atoms adsorbed to Ag(111) hcp lattice sites costs an energy of slightly more than 1 eV\(^7\). This energy is in the same order of magnitude as the energy of tunneling electrons that induce a Mn\textsubscript{2}\* \( \rightarrow \) Mn\textsubscript{2} conversion. It suggests that the conversion is indeed caused by a removal and a change of the position of the adsorbed H atom. The calculations further reveal that approaching a H atom to Mn\textsubscript{2} requires surmounting a barrier.

\(^7\) Starting from the fully relaxed geometry, i.e., H bridging the Mn atoms, H has been moved perpendicular to the dimer axis in eight steps to one of the hcp sites which are nearest to the dimer. The chosen path avoids top positions. For each step, all atoms were fixed perpendicular to the surface normal but relaxed parallel to it. Total energies were calculated at every step.
of \( \approx 0.1 \text{ eV} \). This observation lends support to the idea that the presence of the tip is important for the formation of \( \text{Mn}_n\text{H} \) since the energy barrier would hamper the spontaneous attachment of \( \text{H} \) to \( \text{Mn}_n \) at 7 K. A systematic experimental study on whether the \( \text{Mn}_2 \rightarrow \text{Mn}_2^* \) conversion is induced by the electric field or by the tunneling current has not been performed here. Previous results [23–25, 53] where interactions between the tip electric field and \( \text{H} \) contaminants were demonstrated to lead to instabilities in STM imaging are in accordance with the present findings. Our calculations additionally support the experimental observation that \( \text{Mn}_2^* \) species occur as a result of Mn manipulation experiments and after applying a voltage pulse atop \( \text{Mn}_2 \).

In both cases the electric field between tip and surface is enhanced.

We have moreover considered the contamination of the tip apex with a single Mn atom. Occasional attachment of Mn to the tip may have occurred during adsorption or manipulation experiments. Mn at the tip may lead to a spin-polarized tunneling current and a corresponding magnetic contrast in images. However, the calculations revealed that STM images of \( \text{Mn}_2 \uparrow \uparrow \) and \( \text{Mn}_2 \uparrow \downarrow \) are similar to STM images acquired with a clean tip. Furthermore, in the simulations magnetic moments of Mn atoms are not stable at a temperature of 7 K, neither for the monomer attached to the tip apex nor for the dimer adsorbed to Ag(111). Total energy calculations were performed for non-collinear orientations of the magnetic moments, where the Mn magnetic moment was gradually rotated from 0° (parallel to the surface normal) to 180° and total energies were recorded at every step. The maximum difference between these energies is well below 20 µeV. Consequently, a Mn-contaminated tip can be safely excluded as an explanation for the experimentally observed \( \text{Mn}_2^* \) species.

In conclusion, \( \text{H} \) attachment to Mn dimers on Ag(111) leads to a monohydride compound with antiferromagnetically coupled Mn atomic moments. The magnetic coupling between the Mn atoms is imprinted on the \( \text{Mn}_2\text{H} \) electronic structure, which is readily probed by STM images. Our findings are important to unravelling magnetic structure even in the absence of thermally stable magnetic moments.

Acknowledgments

Funding by the Deutsche Forschungsgemeinschaft through KR 2912/7-1 and SFB 668 and discussions with T O Wehling, K Palotás, D Vogtenhuber, P Ferriani and S Heinze are acknowledged. We thank the Erasmus Programme of the European Commission for financial support. The processing of STM images was performed by WSxM [54].

References