Electronic structure of atomic manganese chains supported on Cu$_2$N / Cu (100)

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Abstract. Scanning tunnelling microscopy and density functional theory studies of manganese chains adsorbed on Cu$_2$N/Cu (100) reveal an unsuspected electronic edge state at $\sim$ 1 eV above the Fermi energy. This Tamm-like state is strongly localised to the last Mn atom of the chain and fully spin polarised. However, no equivalence is found for occupied states, and the electronic structure at $\sim$ −1 eV is mainly spin unpolarised due to the extended p-states of the N atoms that mediate the coupling between the Mn atoms in the chain. Odd-numbered Mn chains present an exponentially decreasing direct coupling with distance between the two edges, leading to a vanishing bonding/anti-bonding splitting of states while even-numbered Mn chains present perfect decoupling of both edges due to the the antiferromagnetic ordering of Mn chains.

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1. Introduction

Magnetic nanochains are experiencing a lot of interest due to their quasi 1-D character that confers them with extraordinary properties [1]. Atomic magnetic nanochains are the best examples of what magnetic nanodevices can achieve and how they can be instrumental for spintronics [2]. These chains are assembled using the atom manipulation capabilities of the scanning tunnelling microscope (STM). Magnetic atoms have been positioned one by one at different distances and with different arrangements on a variety of substrates [3, 4, 5, 6, 7, 8]. The STM has permitted to characterize the chains by their spin signature using spin-polarised tips [9] and by their inelastic electron tunnelling spectra (IETS) [10, 11]. These measurements give unprecedented insight into the atomic mechanisms leading to magnetic ordering in nanostructures that can be compared with state-of-the-art theoretical results.

Theoretical works are generally based on density functional theory (DFT) studies. These works evaluate the actual atomic arrangements of the atoms on the surface, the local and global magnetic moments, as well as the magnetic anisotropy energies, the exchange couplings among the chain constituents and the possibility of canting due to the Dzyaloshinskii-Moriya interaction. For the case of Mn chains on Ni (100), Lounis and co-workers [12] showed that the competition of the different exchange couplings in the system led to an even/odd effect with the number of Mn atoms; even-numbered chains presenting a non-collinear arrangement of their spins and chains with an odd number of atoms a collinear antiferromagnetic ordering. Rudenko and collaborators [13] performed thorough calculations of Mn chains on a Cu$_2$N/Cu (100) substrate. They reproduced the exchange couplings between atoms that lead to magnetic excitation spectra in good agreement with the experimental ones [3]. Furthermore, they included spin-orbit interactions with different methods to study the non-collinearity of the magnetic-moment distributions, and they obtained that the Mn atoms had an out-of-plane easy axis, and that the canting of spins due to anisotropic exchange interactions was very small. Another complete study of Mn and Co chains on Cu$_2$N/Cu (100) was performed by Lin and Jones [14] where they extended their previous results [15] and confirmed that the atoms maintain their nominal spins on the surface, $S=5/2$ for Mn. Nicklas and co-workers [16] studied Fe chains on Cu$_2$N/Cu (100) showing that as for Mn, [13] N-mediated superexchange leads to antiferromagnetic coupling of the Fe atoms, in good agreement with later experimental measurements [5]. The interpretation of these experiments has shown the importance of correlation and entanglement in these antiferromagnetic chains [17]. Urdaniz et al. [18] performed a thorough study of Cr, Fe, Mn and Co chains on Cu$_2$N/Cu (100) using DFT calculations showing that the adsorption site determines to a great extent the type of magnetic coupling of the chain. This is presently used to generate atomic chains with different coupling schemes [19]. DFT calculations show how important it is to take into account the actual geometries of the chain, because this can completely change their electronic and magnetic behaviour [20, 21].
All these works focus in the low-energy structure tunnelling conductance spectra that has a direct link to the magnetic properties of the crafted nano-objects. Surprisingly, no work has been studied on the larger energy scale that actually has influences on the magnetic properties of these systems. In the present work, we report on the electronic structure with a special attention to states originating in orbitals more extended than pure $d$-electrons. We show that there are long-lived edge states that maintain strict localisation. These edge states are Tamm states due to the unsaturated bond of the edge Mn atom caused by the tilting of the last N–Mn bond together with the different nature of the last N atom. This last N atom presents a different environment (lack of Mn atom on one side, and a closer N-substrate distance) breaking the symmetry of the chain. The case of even-numbered Mn chains is particularly relevant for the link between the edge state and the particular magnetic properties of the chains. These edge states are at $\sim 1$ eV above the Fermi level. A broader resonance is also found for occupied states at about $\sim -1$ eV. However, there are no specific magnetic features associated with this state and it is rather a state originating in the covalent bonding of the Mn atoms with the N atoms glueing the Mn chain together. The magnetic structure of the Mn chains are due to the spin polarization of the $d$-electrons, much lower in energy than the $\sim -1$ eV structure of the N-Mn bonds.

2. Experimental method

Experiments were performed in an ultrahigh-vacuum low-temperature STM at a base temperature of 1.15 K. The differential conductance was directly measured using lock-in detection with a 2-mV rms modulation at 938 Hz of the sample bias $V$.

The Cu(100) surface was cleaned by Ar sputtering and then annealed up to 650 K. After having big terraces of the Cu(100) crystal, a monolayer of Cu$_2$N was formed as a decoupling layer by N irradiation. Single Mn atoms were deposited onto the cold surface. By capturing the Mn atom with the tip and dropping it onto the substrate via bias pulses, the single atoms were arranged into closed-packed Mn chains along the [010]-direction of the Cu$_2$N surface. This leads to mono-atomic chains of Mn atoms ontop of Cu atoms that are aligned along a nitrogen row, identical to the structures reported in Ref. [3].

3. Theoretical method

Ab initio calculations were performed within the density-functional theory (DFT) framework as implemented in the VASP code [22]. We have expanded the wave functions using a plane-wave basis set with a cutoff energy of 300 eV. Core electrons were treated within the projector augmented wave method [23, 24]. The PBE form of the generalized gradient approximation was used as exchange and correlation functional [25]. To model the surface we have used a slab geometry with four Cu layers plus the Cu$_2$N layer. We have used an optimized theoretically lattice constant for Cu of 3.65 Å.
Following the above experimental procedure, the transition-metal atoms are positioned on Cu atoms, forming a chain in the [010] direction. We have used a unit cell that increases its size along this direction with the number of atoms of the chain as $[3 \times (n+3)]$, where $n$ is the number of Mn atoms. In this way we keep the distance between chain images constant for all sizes, being of 3 lattice constants in the unrelaxed configuration. The bottom Cu layer was kept fixed and the remaining atoms were allowed to relax until forces were smaller than 0.01 eV/Å. The $k$-point sample was varied accordingly to the unit cell, and tests were performed to assure its convergence.

In order to account for the atomic magnetic moments of the Mn atoms on the surface, the GGA+U method of Dudarev et al. [26] was employed, with a $U_{\text{eff}} = U - J$ of 4 eV. The chosen values correspond to roughly subtracting $J \approx 1$ to $U = 4.9$ eV as computed by Lin and Jones [14] for Mn ontop a Cu atom.

4. Results

4.1. Scanning tunneling spectroscopy of electronic states

Constant current STM images obtained for sample biases above 1V show that the Mn chains develop a “dumbell” shape and present enhanced states at the edges. Figure 1 (a) shows the image obtained at $V_s = 2$ V. Here the distortion is evident for Mn$_5$ and Mn$_6$. Mapping the conductance at a fixed bias of 1V gives direct evidence of the localisation of the contributing electronic states. Indeed, Fig. 1 (b) shows that most of the conductance is located on the borders of the corresponding protrusions of Fig. 1 (a). However, no spatial feature can be appreciated at negative bias. Figure 1 (c) depicts the constant current image at -1V and a featureless protrusion straddles the atoms of the chain. Consequently, the corresponding dI/dV map (not shown) does not reveal any localisation inside the chain.

In order to gain more insight, we plot in Fig. 1 (d) the conductance as a function of bias for three different positions over the Mn$_6$ chain. When the tip is above a chain’s edge, a distinct peak is detected at 1V. This is in good correspondence with the previous Figs. 1 (a) and (b), and strongly suggests that there is an electronic state localised at the edges of the Mn chains. When the bias is shifted to negative biases, there is a broader peak at $\sim -1$ V with larger intensity at the centre of the chain. From these data, we conclude that an electronic edge state appears at $\sim 1$ V, while for occupied states an electronic state appears at $\sim -1$ V with an broader line shape, and extended along the chain.

Figure 2 displays the tunnelling conductance as a function of bias for Mn$_2$, Mn$_3$, Mn$_4$, and Mn$_5$. As the size of the Mn chains is reduced, the occupied states evolve becoming very broadened and undistinguishable from the conductance background, Fig. 2. On the contrary, the spectral intensity for the unoccupied state at the edges increases as the chain is reduced. Moreover, the state stays at the same energy position, independently of the chain’s length, supporting its localised character.
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4.2. Density functional theory characterisation of the electronic states

Structural relaxation of the Mn atomic chains reproduce the geometry and bonding configuration from previous theoretical results [13, 16, 18]: Mn atoms induce an important reconstruction of the supporting substrate by incorporating N atoms to form a Mn-N-Mn-N-⋯ chain. This has important consequences both for the electronic structure and the magnetic ordering of the atoms. Figure 3(a) shows isosurfaces of spin density. In agreement with previous experimental studies [3], this corroborate that Mn atoms interact antiferromagnetically with their neighbours, as discussed by Rudenko et al.
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Figure 2. Tunnelling conductance over the edge (red), and clean surface (black) for Mn$_2$, Mn$_3$, Mn$_4$, and Mn$_5$, upper row (feed back opened at $V_s = -2$ V, $I_t = 1.5$ nA). Plots of conductance (color scale) as a function of bias (x-axis) and position along the chain (y-axis), the plots extend slightly more than the chain sizes. All chains show the distinct feature of the edge states at the edges of each chain.

The joining N atoms serve both to stabilise the chain via covalent bonding with the Mn atoms, and to induce the antiferromagnetic order through a superexchange interaction, clearly seen by the equal coexistence of the two spins on the N atoms in Fig. 3(a). These results imply that the actual arrangement of Mn and N atoms does matter and different magnetic orderings can be achieved [18]. These results also show that the occupied electronic structure associated with N atoms must be spin unpolarised.

As previously mentioned [13, 14, 16, 18], the $d$ electrons maintain the free-atom configuration of Mn in the chains with all majority spin $d$-orbitals occupied and the minority one empty. Figure 3(b) also shows that the PDOS on $d$-electrons is mainly independent of the size of the Mn chains, indicating that their $d$-electron states are fairly localised and not perturbed by neighbouring Mn atoms.

A consequence of the finite size of the chains is the apparition of additional localised states at the terminations due to the change of geometry. In strong correspondence with the experimental results, we find at $V_s \sim 1$ eV above the Fermi energy a state purely localised at the edges. This state, depicted in Fig. 3(c) for the case of a Mn$_3$ trimer, is strictly spin-polarised, and has very little weight on atoms other than the two edge Mn atoms. It thus has a small intrinsic width.

The projected density of states gives us more information on the two states found in the STM studies (Figs. 1 and 2). The edge states only have contributions from $s$ and $d_{z^2}$ orbitals (where $z$ is the direction along the Mn chain). This leads to a sharp peak in the density of states projected onto the 4$s$ orbital of the edge Mn atom, centred at $\sim 1$ V, Fig. 3(d). These data allow us to characterize the edge state as a Tamm state due to...
the unsaturated $s - dz^2$ hybrid orbital formed by the twisting of the chain at the edge.

The state at $\sim -1$ eV is also found in DFT if the full electronic structure is projected onto the $p$ orbitals of the central N-atoms of the chain. Figure 3(d) shows a sharp peak in the PDOS of the $p_z$ orbital of the third N atom in the Mn$_6$ chain. This allows us to characterize the experimental peak at $\sim -1$ V as a chain state originating in the N-atoms. The PDOS on the $p$ orbitals of the central N-atoms is identical for both spins, as we expected for electronic states with a strong N component. Hence, the experimental peak for occupied states corresponds to a state extended over the chain with a strong N character.

To explore the evolution the edge states with chain length we compare in Fig. 4 the density of states projected on an edge Mn atom for Mn$_n$ chains with $n = 3, 4, 5, 6$. In agreement with the experimental results in Fig. 2, the edge state is observed pinned at $\sim 1$ eV and having basically the same shape regardless of the length of the chain. This is due to the large localisation of the state at the edge Mn atoms, thus interacting very weakly with the state at the other end. Even-numbered chains (Mn$_{2n}$ with $n$ integer) are an interesting case because, in a broken-symmetry description, the two edge states are of opposite spin and localised to each edge atom due to the antiferromagnetic character of the chains. The localisation of the edge states due to their opposite magnetism holds even when preserving the full entanglement of the antiferromagnetic solution. As a consequence, even for the dimer, Mn$_2$, the two edge states are not interacting. However, in Fig. 2 we observe that the conductance peak associated to the edge states increases for Mn$_2$. For such a small chain, the STM tip can couple simultaneously to both edge states and, accordingly the conductance is expected to be larger.

In Fig. 4 we also observe that the edge state spin is anti-aligned with the spin of the edge atom (majority spin). However, previous studies [27, 28] showed that the electron transmission proceeded through the majority spin due to the prevailance of majority spin electrons at the Fermi energy. Figure 4 shows indeed that for all chains the majority spin density of states tends to be larger, leading us to conclude that as for the single Mn atom, electron transmission through the chains at low bias takes part mainly in the majority-spin channel, but at large positive biases the minority-spin components dominate the transmission. Let us notice that the electronic structure of the single Mn atoms and chains of Mn atoms are subject to different symmetry due to the clear axis of the Mn chains.

5. Conclusions

In summary, we have investigated the electronic structure of Mn atomic chains constructed on Cu$_2$N/Cu (100) by atomic manipulation. We have found two electronic states in the tunnelling spectra: an unoccupied Tamm state, very localised on the edge atoms and an occupied state extended along the chain. The unoccupied state presents a strict spin-polarisation, and is originated from the hybridization of Mn $d_{z^2}$ and $4s$ orbitals. The occupied state has weight on both N and Mn atoms and it is not spin
Figure 3. (a) Isosurface of spin density obtained as the difference of electronic density between the densities of majoritary (red) and minoritary (yellow) spins of a (broken-symmetry) DFT calculation. (b) Projected density of states (PDOS) over all Mn d-electrons of Mn$_6$ and Mn$_3$ showing minor differences, for the majority (↓) and minority (↑) spins. (c) Isosurface of wave-function amplitude of the edge state of an adsorbed Mn$_3$ chain. (d) PDOS of Mn$_6$ on the $p_z$ orbitals of N (where $z$ is the direction along the Mn$_6$ chain) and on the $s$ and $d_{z^2}$ electrons of a Mn edge atom.

polarised due to the absence of magnetism of the N atoms. We expect that in this model system, the parity of the number of atoms would have an effect in their spectral fingerprint. For even-numbered Mn chains, their antiferromagnetic character leads to a strict localisation of their edge states into a single Mn edge atom because of the opposite spin-polarisation of the states on each edge. This fact is independent of spin entanglement. However, for odd-numbered chains, there is no spin decoupling of the two edge states. Nevertheless, the small interaction between neighbouring Mn atoms leads to effectively decoupled edge states.

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Figure 4. Projected density of states (PDOS) over all atomic orbitals of an edge Mn atom for Mn$_3$, Mn$_4$, Mn$_5$, and Mn$_6$ for majority and minority spins. The edge state is pinned at the same energy and for the minority spin of each edge atom in the DFT broken-symmetry picture.

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