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# Magnetic and structural properties of Mn adatoms on copper nitride over Cu(100)

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Magnetic and structural properties of Mn adatoms and dimers adsorbed on a single atomic layer of copper nitride ($Cu_3N$) over a Cu(100) substrate are explored by first-principles calculations based on the density-functional theory. In all cases investigated here, the adsorption of the Mn atoms and dimers causes significant local structural changes and charge transfer between the ions, in comparison with the clean surface. However, some important properties depend strongly on Mn atoms and dimers local environments. When Mn atoms of the dimer are positioned atop N atoms, the direct coupling between the Mn atoms is antiferromagnetic. On the other hand, when the Mn atoms are positioned atop Cu atoms, which is the energetically favorable configuration, the antiferromagnetic coupling connecting the Mn spins has a superexchange character which is established through the N anions laying between them.

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## I. INTRODUCTION

The possibility of using the scanning tunneling microscopy (STM) spectroscopy to probe spin excitations of a single atom on a surface has been theoretically explored recently.[1] The basic idea behind the proposition was the prospect of the tunneling electrons coupling to magnetic degrees of freedom thereby allowing tunneling induced spin-flip processes. In a very beautiful experiment, it was subsequently demonstrated that the spin excitation spectra of individual Mn atoms on a surface may indeed be measured by the inelastic electron-tunneling spectroscopy (IETS) with a STM.[2] Significant changes in the spin-flip spectra were observed for Mn atoms in different local environments. Later, STM was used to build chains of Mn atoms on a single insulating $Cu_3N$ layer deposited atop a Cu(100) surface. Their spin excitations were probed with IETS (Ref. 3) and again it was noticed that the spectra depend strongly on the binding sites upon which the chains are built. The measurements indicate that the atomic Mn moments in those chains are antiferromagnetically coupled and the exchange coupling for a Mn dimer, with the Mn atoms placed atop Cu atoms in the $Cu_3N$ surface, was estimated to be $J=6.2$ meV, with a $\pm 5\%$ variation depending on where the dimer sits on different $Cu_3N$ islands. For Mn dimers built atop N atoms in the $Cu_3N$ layer, the observed coupling strength reduces by a factor of approximately 2.

The properties of Mn adatoms[4] and dimers[5] placed on top of Cu atoms adsorbed on $Cu_3N/Cu(100)$ have been investigated by means of first-principles calculations. Here we show that the structural, electronic, and magnetic properties of Mn adatoms and dimers depend strongly on the local environment where they are placed. For instance, the magnetic couplings between the Mn adatoms are very much influenced by how their atomic states bond to the underlying $Cu_3N$ surface. When the dimer is placed over the Cu ions, the interaction between the Mn cations is primarily mediated by an interposing N anion. Here, a direct hopping between *d* orbitals of the two Mn cations is unlikely to occur, and the strong antiferromagnetic coupling presents typical superexchange-like characteristics. On the other hand, when the dimer is placed upon N ions, a direct interaction between the two Mn ions clearly takes place.

## II. METHODOLOGY

We have performed *ab initio* calculations for Mn atoms adsorbed on distinct sites of a single atomic layer of $Cu_3N$ over Cu(100). Our calculations are based on spin-polarized density-functional theory (DFT) within the generalized gradient approximation (GGA) for the exchange and correlation potential of Perdew, Burke, and Ernzerhof[6] and norm conserving pseudopotentials,[7] as implemented in the SIESTA code.[8] A slab model containing four atomic layers of Cu(100) and one monolayer of $Cu_3N$ was used to represent the substrate. We consider Mn atoms originally placed on top of either Cu or N atoms in the $Cu_3N$ surface. Then, we allowed the structure to relax until all interatomic forces became smaller than 0.05 eV/Å. In the structural optimizations, we have included the Mn atoms and the first three subjacent layers, i.e., the $Cu_3N$ monolayer and two Cu layers beneath it.

## III. RESULTS AND DISCUSSIONS

We start by exploring the electronic structure of a single Mn atom adsorbed on the $Cu_3N$ surface. Here we employed a supercell with 53 atoms and $4\times4\times1$ Monkhorst-Pack $\vec{k}$ points were used to sample the Brillouin zone. Before presenting our results, it is worth remarking that in a clean $Cu_3N$ surface the Cu and N atoms form a polar covalent network wherein the electronic charge is transferred from the Cu to the N atoms.[4]

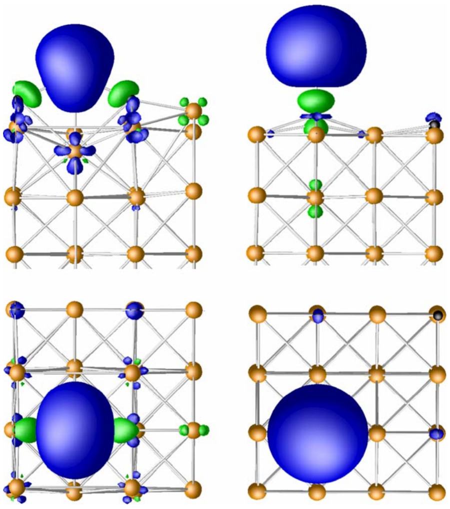

FIG. 1. (Color online) Calculated magnetization densities $m = \rho_{\uparrow} - \rho_{\downarrow}$ in units of Bohr magnetons for Mn atoms adsorbed on a single layer of $Cu_3N$ over Cu(100). The left and right panels show results for a Mn atom adsorbed atop a Cu and a N atom in the $Cu_3N$ surface, respectively. Front and top views of the atomic structure are depicted in the up and low panels. Contours of constant magnetization density ($0.005\mu_B/\text{Å}^3$) are shown for ↑ (blue) and ↓ (green) spin directions. The Cu and N atoms are represented by small orange and black balls, respectively.

As shown in Fig. 1, the adsorbed Mn atom modifies the local atomic structure around it substantially. In accordance with previous calculations,[4] we also see that when the Mn atom is placed on top of a Cu atom in the $Cu_3N$ surface (Fig. 1, left panel) it pushes the Cu atom underneath it toward the Cu(100) substrate, and it establishes polar covalent bonds with the two nearest-neighbor N ions which are pulled in its direction. The Mn adatom almost takes the place of the dislodged Cu ion in the Cu-N polar network, becoming positively charged and making the two nearest-neighbor N ions even more negatively charged than they were in the originally pure $Cu_3N$ surface. Constant magnetization density isosurfaces $m(r) = \rho_{\uparrow}(r) - \rho_{\downarrow}(r)$ in units of Bohr magnetons ($\mu_B$) are also plotted in Fig. 1, for majority (↑—blue) and minority (↓—green) spins, to reveal the characteristics of the local spin polarizations. The presence of the Mn atom clearly induces appreciable local spin polarizations in the nearby N and Cu atoms; however, the dominant contribution to the total magnetization definitely comes from the $d$ orbitals of the Mn ion, as expected. It is noteworthy that the asymmetries in the electronic spin-density distributions around the two nearest-neighbor N ions and the local magnetization densities are antiparallely aligned to the Mn magnetic moment in the regions facing the Mn ion and exhibit a reverse orientation in the opposite regions. This is expected from the Pauli's exclusion principle and the overlap between the N and Mn atomic orbitals establishing the bond. Small induced magnetization densities oriented mainly parallel to the Mn magnetic moment are also visible around the nearby Cu atoms, but the next-nearest-neighbor Cu atoms in the $Cu_3N$ surface (located along the direction defined by the two nearest-neighbor N atoms) clearly exhibit magnetization densities aligned in the opposite direction.

When the Mn adatom is placed on top of a N ion in the $Cu_3N$ surface (Fig. 1, right panel) rather distinct binding and magnetic aspects show up. The Mn atom also transfers electrons to the $Cu_3N$ surface; it pulls the subjacent N ion in its direction and establishes a polar covalent bond with it. The induced spin-polarization density now appears mostly along the direction perpendicular to $Cu_3N$ surface. Both the N and Cu atoms situated below the Mn adatom develop two lobes of induced magnetization densities aligned antiparallel to the Mn moment. Very small pockets of magnetization density parallel to the Mn moment are also visible close to the next-nearest-neighbor N atoms. Our calculations show that among the two possible locations for the Mn adatom on the $Cu_3N$ surface, the position atop the Cu site is the more stable, in agreement with what has been observed in Ref. 3; we find that the energy difference between the two atomic configurations is 1.24 eV.

We next inquire into the electronic structure properties of a Mn dimer adsorbed onto a monolayer of $Cu_3N$ over Cu(100). Once again we consider two possible locations for the Mn atoms: either they are positioned atop Cu ions in the $Cu_3N$ surface so that a N atom lays between them or placed atop N ions with a Cu atom amid them. In both cases, we have examined the likelihood of the Mn magnetic moments being aligned either ferromagnetically (FM) or antiferromagnetically (AFM). In all cases, the structures were allowed to relax until all interatomic forces became smaller than 0.05 eV/Å; the Mn atoms and the first three subjacent atomic layers were included in our structural optimizations. For the dimer calculations, we used a supercell with 90 atoms (2 Mn, 8 N, and 80 Cu) and $2 \times 4 \times 1$ Monkhorst-Pack $\vec{k}$ points to sample the Brillouin zone.

Among the four possibilities we have considered, the AFM state with the Mn positioned atop Cu ions is the one with the lowest energy. The structural rearrangements caused by the adsorbed dimer, as well as the local spin-polarization densities calculated for all examined cases, are depicted in Figs. 2 and 3. The induced structural changes have similar features to the ones produced by a single Mn atom. When the dimer is placed over the Cu ions, for instance, the Mn atoms push them down toward the Cu substrate, transfer electrons to the $Cu_3N$ surface, and establish polar covalent bonds with the nearest-neighbor N anions, which turn even more negatively charged than in the pure surface. It is noteworthy that the interaction between the Mn cations in this case is primarily mediated by the interposing N anion, even though the other closest N and Cu ions also intervene to a lesser extent. Here, a direct hopping between $d$ orbitals of the two Mn cations is unlikely to occur, and the strong antiferromagnetic coupling between the positive Mn ions presents typical superexchange-like characteristics, with the two lobes of the ligand $2p$ N orbital becoming spin polarized with local magnetization densities aligned opposite to each other and antiparallel to the magnetic moment of the nearest-neighbor Mn atoms. Our calculations reveal that the Mn chains investigated in Ref. 3 are, in fact, intercalated by N anions of the $Cu_3N$ surface, which intermediate to a great extent the exchange coupling between the Mn cations. Presently, it may be hard to observe those N anions by spin-polarized STM due to insufficient contrast in such a length scale. We remark

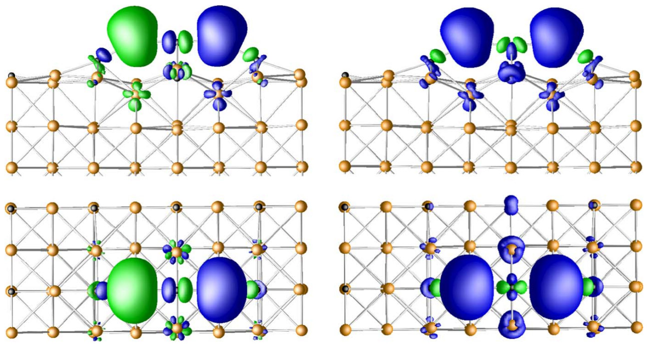

FIG. 2. (Color online) Calculated magnetization density $m=\rho_{\uparrow}-\rho_{\downarrow}$ in units of Bohr magnetons for a Mn dimer adsorbed atop Cu atoms in the $Cu_3N$ surface. Left and right panels show results for the AFM and FM configurations of the Mn dimer, respectively. Front and top views of the atomic structure are depicted in the up and low panels for the AFM and FM configurations. Contours of constant magnetization density ($0.005\mu_B/Å^3$) are shown for ↑ (blue) and ↓ (green) spin directions. The Cu and N atoms are represented by small orange and black balls, respectively.

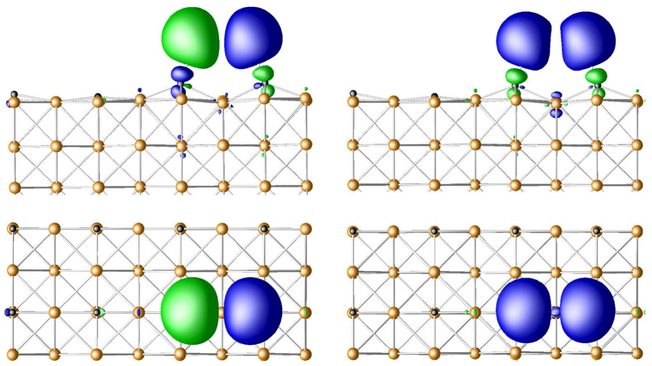

FIG. 3. (Color online) Calculated magnetization density $m=\rho_{\uparrow}-\rho_{\downarrow}$ in units of Bohr magnetons for a Mn dimer adsorbed atop N atoms in the $Cu_3N$ surface. Left and right panels show results for the AFM and FM configurations of the Mn dimer, respectively. Front and top views of the atomic structure are depicted in the up and low panels for the AFM and FM configurations. Contours of constant magnetization density ($0.005\mu_B/Å^3$) are shown for ↑ (blue) and ↓ (green) spin directions. The Cu and N atoms are represented by small orange and black balls, respectively.

that in the FM state, the N anion between the two Mn atoms acquires a significant net magnetic moment of approximately $0.2\mu_B$, which is oriented antiparallel to the Mn magnetic moments.[9,10]

When the dimer is placed upon N ions (Fig. 3), each Mn atom attracts the supporting nitrogen and also sets up a polar covalent bond with it. In this situation, however, a direct interaction between the two Mn ions clearly takes place though supplemented by a smaller indirect one intermediated by the substrate. Contrary to what has been presumed,[3] the equilibrium interatomic distance of the dimer in this case is significantly smaller than the corresponding one when it is built atop Cu atoms in the $Cu_3N$ surface. The actual difference may be appraised from Table I where other results of our calculations are also presented. Among them, we find the energy difference between the FM and AFM states for the Mn dimer sitting atop Cu atoms is nearly a factor of 2 larger than the corresponding energy difference when it lies upon N atoms in the $Cu_3N$ surface. This is in excellent agreement with what has been observed.[3] However, if we employ a Heisenberg model to describe such energy differences, we obtain values for the exchange couplings $J$ twice as large as those measured.[3] It is worth noting that Rudenko *et al.*[5] reported even a much larger calculated value of the exchange coupling with the use of the local spin density approximation (LSDA). However, they were able to achieve very good agreement with experiment by employing an LDA+$U$ approach with on-site Coulomb and Hunds interactions $U=6$ eV and $J_H=0.9$ eV, respectively. The improvement is attributed to the different atomic relaxations obtained with the two approaches. More specifically to the distinct Mn-N-Mn bond angles, which they find equals to 171° using the LSDA, and 143° within LDA+$U$. Our GGA calculations, on the other hand, lead to a Mn-N-Mn bond angle equals to 173°, and yet we find an exchange coupling which is substantially smaller than what they have obtained with the LSDA. Atomic relaxations clearly depend on how one treats the exchange and correlation potential in DFT, but the exchange coupling between the Mn ions is also directly affected by the choice of the on-site Coulomb interaction used in an LDA+$U$ approach, even if atomic relaxations are entirely neglected. From the results in Ref. 5, it is nevertheless clear that to improve the agreement with experiment one needs to include effective on-site interactions to obtain a better description of electronic correlations in this system.

TABLE I. Calculated total-energy differences $\Delta E$ (in eV) between the AFM and FM states of the Mn dimer adsorbed atop Cu (Mn/Cu) and N (Mn/N) atoms in the $Cu_3N$ surface over Cu(100). The corresponding Mn magnetic moments $m$ (in $\mu_B$) (Ref. 9) and the Mn dimer equilibrium interatomic distances $d$ (in Å) calculated for the FM and AFM configurations are also shown.

| | $\Delta E$ | $m_{\mathrm{AFM}}$ | $m_{\mathrm{FM}}$ | $d_{\mathrm{AFM}}$ | $d_{\mathrm{FM}}$ |
|---|---|---|---|---|---|
| Mn/Cu | −0.167 | 4.7 | 4.8 | 3.77 | 3.85 |
| Mn/N | −0.073 | 5.3 | 4.9 | 2.57 | 2.66 |

Our calculations also demonstrate that the act of switching the dimer magnetic configuration from AFM to FM causes significant atomic structure relaxations and perceptible changes in the size of the Mn atomic spin magnetic moment. When the dimer is positioned atop Cu atoms, for instance, the interatomic distance between the Mn cations varies by approximately 2% as the magnetic state changes from AFM to FM, and the induced magnetic moment of the N anion amid them also alters considerably. The corresponding interatomic distance variation increases to 3.5% for dimers built atop N sites. This is a relatively large magnetoelastic effect which, perhaps, may be explored experimentally as a way of exciting vibrational modes using a magnetic pulse. The field needs to be sufficiently strong to saturate the magnetization of the Mn molecule and lasts long enough for atomic relaxations to take place.

## IV. CONCLUSIONS

In summary, we have performed DFT *ab initio* calculations of the electronic, magnetic, and structural properties of Mn isolated atoms and dimers adsorbed on a $Cu_3N$ monolayer over a Cu(100) substrate. In all cases, the adsorbates cause significant local structural changes and charge transfer that strongly affect their magnetic properties and depend very much on the local environment where they are placed.

The total energy of a single Mn adatom placed atop a Cu site is 1.24 eV smaller than when it sits over a N site, in agreement with what has been observed.[3] In the first case, as reported previously,[4] the Mn atom pushes the Cu atom underneath it toward the Cu(100) substrate and establishes polar covalent bonds with the two nearest-neighbor N ions which are pulled in its direction. The presence of the Mn atom clearly induces appreciable local spin polarization in the nearby N and Cu atoms; however, the dominant contribution to the total magnetization definitely comes from the *d* orbitals of the Mn ion, as expected. On the other hand, when the Mn adatom is placed on top of a N ion, distinct binding and magnetic properties are found. The Mn atom pulls the subjacent N ion in its direction and establishes a polar covalent bond with it. The induced spin-polarization density now appears mostly along the direction perpendicular to $Cu_3N$ surface.

For the Mn dimer with both atoms positioned atop Cu sites, the AFM configuration is 0.167 eV energetically more favorable than the FM one. In this case, the interaction between the Mn cations is mediated by the N anion between them and the AFM coupling has clear superexchangelike characteristics, with a substantial charge transfer taking place between the Mn cations and the N anion. Remarkably, in the FM state, the N anion between the two Mn atoms acquires a significant net magnetic moment of approximately $0.2\mu_B$, which is oriented antiparallel to the Mn magnetic moments. When both Mn atoms are positioned atop N sites, the effective exchange coupling is also AFM, but it is a factor of 2 smaller than in the previous case, as observed. However, contrary to what has been presumed,[3] the equilibrium interatomic distance of the dimer in this case is significantly smaller than when it is built atop Cu atoms in the $Cu_3N$ surface. Here, the underlying mechanism for the exchange coupling has a different character, since a direct interaction between the Mn ions takes place.

Finally, we have found that when the dimer magnetic configuration is switched from AFM to FM, the interatomic distance between the Mn ions changes considerably. Such a relatively large magnetoelastic effect suggests that magnetic pulses may be possibly used to excite vibration modes of a Mn dimer adsorbed onto a $Cu_3N$ surface.

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