Spin structure of an atomic protrusion: Probing single atoms on cobalt nanoislands

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Single Ni, Co, and Cu atoms deposited in the center of cobalt nanoislands grown on Cu(111) are investigated by low-temperature scanning tunneling spectroscopy. The surface states of this model magnetic nanolead are unveiled and assigned to arise from atomiclike and surface-induced states by *ab initio* calculations. Contrary to the first, the second contribution is predicted by calculations to favor a change in sign of the spin polarization with respect to the pristine lead.

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Spin electronics has seen a considerable effort aimed at improving the structural quality of devices because there is a growing awareness that nanostructural details may substantially affect the magnetoresistive response. Devices include magnetic tunnel junctions (MTJs),[1] consisting of two ferromagnetic layers separated by a thin insulating tunnel barrier, as well as atomic-size constrictions formed by bringing into contact two magnetic protrusions[2] usually made of nickel or cobalt. To gain insight into the disruptive nature of these structural details, one possibility is to focus on the interplay between structure-related and spin-related properties in model magnetic systems. An individual atom adsorbed (adatom) on a magnetic surface, for example, can be regarded as an experimental realization of a magnetic protrusion,[3,4] readily accessible through scanning tunneling microscopy and spectroscopy (STM and STS). Additionally, in a STM setup, the interface between a magnetic surface and vacuum may be regarded as a well-characterized MTJ interface. Atoms on this surface can then mimic interface impurities or roughness, which are believed to decrease the magnetoresistance of MTJs from ideal values.[5,6]

In deep contrast with the profusion of STS studies on nonmagnetic surfaces, where subtle interactions among atoms and their environment have been revealed,[7–12] joint experimental and theoretical studies of atoms on magnetic surfaces remain limited.[13,14] Among magnetic surfaces, cobalt islands on Cu(111) [Fig. 1(a)] are particularly appealing because of their spin-polarized (SP) electronic states near the Fermi energy,[15–18] involving *d*-like localized states of minority character, as well as freelike *s*-*p* states of majority character. A recent experimental study revealed distinct SP electronic structures for Fe and Cr atoms residing on cobalt nanoislands[19] but was unable to shed light on their respective origin.

Motivated by this work, in this Brief Report, we combine low-temperature STS and *ab initio* calculations to study the SP electronic structure of isolated magnetic (Ni and Co) and weakly magnetic (Cu) atoms adsorbed in the center of the cobalt nanoislands. Two competing contributions are identified, namely, surface-induced states and atomiclike resonances. The large minority *d* contribution found for the pristine lead is reduced over the atoms, the surface-induced states favoring a change in sign of the spin polarization. Atomiclike resonances, on the contrary, reinforce the minority *d* contribution over finite-energy ranges. Similar contributions will be present in MTJs with weak interface roughness and impurity disorder.

A STM operating below 10^{-10} mbar and cooled to 2.8 K was employed for the measurements. Spectra of the differential conductance $dI/dV(V)$, where V is the sample bias measured with respect to the tip, were acquired via a lock-in amplifier with a bias modulation of 2 mV rms at frequencies of 0.5–5 kHz. The Cu(111) surface as well as chemically etched W or Ni tips was cleaned by argon-ion bombardment and annealing. Two atomic layers high cobalt nanoislands were obtained by evaporating 0.7 monolayers (MLs) of Co at 0.15 ML/min onto the Cu(111) surface at room temperature from a thoroughly outgassed Co rod. After deposition, the sample was immediately transferred in the precooled STM. Single nickel, cobalt, and copper atoms were then deposited onto the substrate by a controlled transfer of the tip-apex atom,[20] so that isolated atoms residing in the island center could be obtained [Fig. 1(b)]. The coating material for the tip apex was therefore chosen accordingly to the desired atom. For all tips, tip-structure artifacts were negligible in the dI/dV over the voltage range of interest, the steplike onset of the Cu(111) Shockley surface state appearing then as a sharp feature in the dI/dV [Fig. 3(a)]. No thermal diffusion of the atoms was observed within measurement times, although occasional tip-induced movements occurred during dI/dV acquisition (these dI/dV's were discarded).

A dI/dV acquired over a cobalt nanoisland is presented in

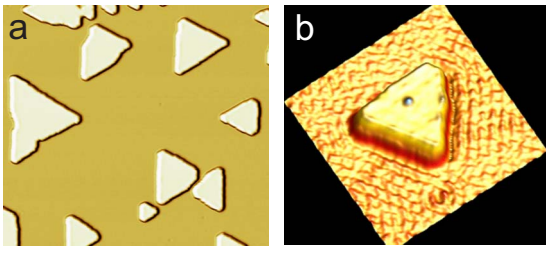

FIG. 1. (Color online) Constant-current STM image: (a) triangularlike cobalt nanoislands on Cu(111) (80×70 nm^2, 0.3 nA, and 0.80 V) and (b) hcp cobalt nanoisland after the transfer of a Cu atom from the tip apex to its center (24×24 nm^2, 0.3 nA, and −0.03 eV). The scattering of Shockley surface states produces the spatial oscillations on Cu(111).

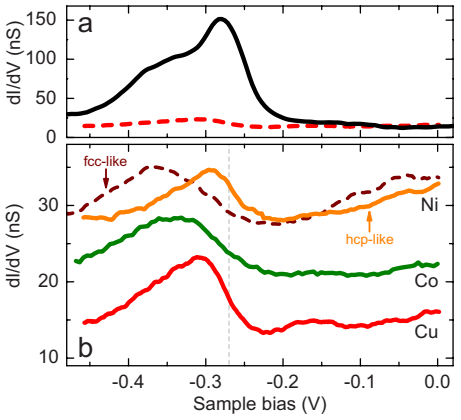

FIG. 2. (Color online) (a) dI/dV over a Co nanoisland (solid line) and over a Cu atom adsorbed on a hcp-like nanoisland (dashed line). Feedback loop opened at 0.4 nA and 0.03 V. (b) dI/dV over Ni, Co, and Cu atoms adsorbed near the center of a hcp-like cobalt nanoisland (feedback loop opened at 0.4 nA and 0.03 V.); the dashed curve is a dI/dV acquired over a Ni adatom on a fcc-like island. The Ni and Co spectra are shifted vertically by 14 and 7 nS, respectively. All spectra are averaged over various atoms of same nature. The dashed line gives the approximate position of the majority s-p surface-state onset.

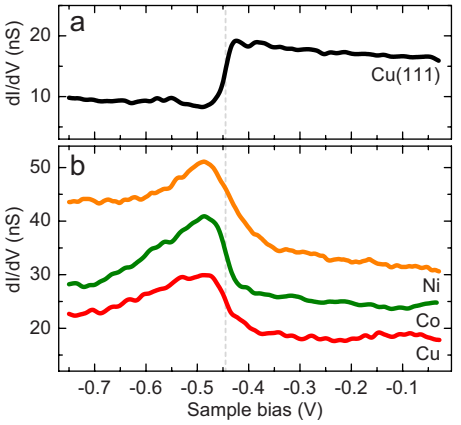

FIG. 3. (Color online) dI/dV spectra over: (a) Cu(111) and (b) Ni, Co, and Cu atoms on Cu(111); atoms are 2 nm away from any surface defect. The Ni and Co spectra are shifted vertically by 14 and 7 nS, respectively. The dashed line is centered at the surface-state onset. All spectra are averaged over various atoms. Feedback loop opened at 0.5 nA and −0.03 eV. Atomiclike resonances are also predicted for Ni in this energy range (Ref. 26).

Fig. 2(a). Just below the Fermi energy (E_F), the spectrum is dominated by a resonance falling at −0.28 V, which originates from the minority d band of the island.[15,18] In order to have a reproducible electronic structure, islands of hcp-like crystallographic stacking with lateral dimensions greater or equal to 12 nm were privileged for the study.[18] Upon atom transfer, isolated atoms ~0.1 nm high reside near the center of the cobalt nanoislands [Fig. 1(b)]. Their dI/dV [dashed line of Fig. 2(a)] is considerably attenuated relative to the one of the island. A resonance falling at roughly −0.30 V is found for Ni, Co, and Cu atoms residing on hcp-like islands [Fig. 2(b)], as well as for atoms on fcc-like islands but at a lower energy [dashed spectrum of Fig. 2(b)]. Over Fe, a similar resonance was also observed.[19] Based on these findings, the resonance over the atoms likely reflects an island-related property. For the Ni atom, a marked upturn of the dI/dV also occurs near E_F.

Insight into the origin of the observed spectral features can be gained within the framework of a Newns-Anderson model describing a single adsorbate level interacting with a surface.[21] The adsorbate local density of states (LDOS) is described by the imaginary part of the self energy $\Delta(\epsilon) \simeq \pi\langle V^2\rangle n(\epsilon)$ and its Hilbert transform. The first term $\langle V^2\rangle$ describes the hybridization between the substrate and the adsorbate level, and the second term $n(\epsilon)$ is the surface-states LDOS in the absence of the adsorbate. A featureless $n(\epsilon)$ only shifts and broadens the adatom energy level into an atomiclike resonance, while any feature of $n(\epsilon)$ produces in the adatom LDOS an additional surface-induced structure. Since the LDOS of the cobalt nanoislands is spin-polarized [see Fig. 4(b)], surface-induced states of majority or minority character are expected over atoms adsorbed on these islands.

To clearly picture the majority surface-induced states expected for an atom, STS over Cu(111) can be performed. Similarities exist in fact between the LDOS of the cobalt nanoislands and of Cu(111). The copper surface bears a dispersive Shockley state with a typical stepped onset falling at −0.45 V [Fig. 3(a)], which corresponds to the bottom edge of the parabolic band. Atoms have been demonstrated both experimentally[22,23] and theoretically[24–26] to localize these states and produce a bound state at an energy exponentially close to the bottom edge of the band [Fig. 3(b)]. A similar steplike onset also exists for the majority s-p states of the cobalt islands, but it is believed to be buried below the dominant d-like resonance of Fig. 1(a) [see also Fig. 4(b)].[15,16] The band edge is estimated at −0.22 V or lower.[17] As for atoms on Cu(111), we therefore expect a bound state in the atom LDOS but of majority character. Because the atoms in the present study are isolated, the amplitude of the bound state should be fully preserved.[22]

To confirm these assumptions, we performed *ab initio* calculations based on the density-functional theory implemented in the multiple-scattering Korringa-Kohn-Rostoker (KKR) Green's function method in the atomic sphere approximation.[27] A nanoisland in our calculations is treated as a cobalt bilayer of hcp or fcc stacking placed on a semi-infinite Cu(111) substrate. A height of 0.42 nm relative to the clean surface and the adatoms are used to calculate the LDOS [Fig. 4(a)], in order to grossly account for the STM tip position in vacuum. All atoms have their magnetic moment parallel to the magnetic moment of the cobalt nanoisland, except Cr which is antiparallel, in agreement with Ref. 19. The calculated magnetic moments are $4.16\mu_B$ (Cr), $3.18\mu_B$ (Fe), $2.00\mu_B$ (Co), $0.74\mu_B$ (Ni), and $0.03\mu_B$ (Cu).

The calculated LDOS for atoms on a hcp cobalt bilayer is presented in Figs. 4(c)–4(g) (similar results were obtained for the fcc bilayers). The total LDOS is representative of the data collected by STS and is the sum of majority [red lines Figs. 4(c)–4(g)] and minority (blue lines) states. As expected from the Newns-Anderson picture, a majority bound state is clearly visible in all cases right below the majority steplike onset of the dispersive s-p states (the calculated onset is indicated by a dashed gray line). The minority structure of

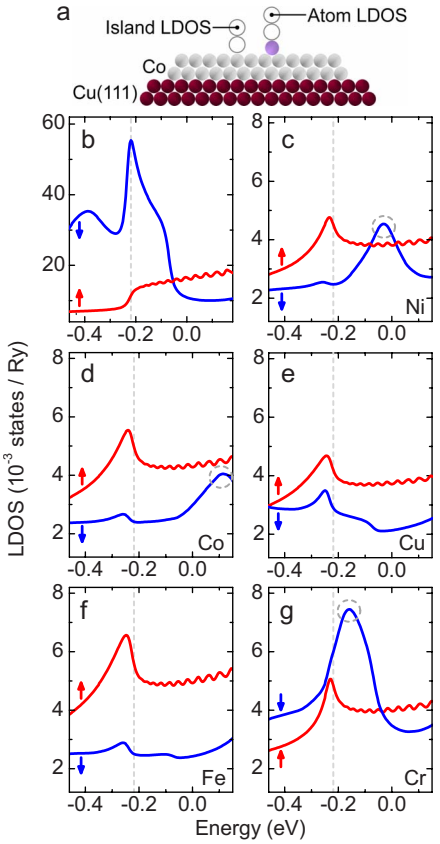

FIG. 4. (Color online) Calculated spin-polarized LDOS. (a) Sketch (adatom in hollow position), (b) spin-polarized LDOS above a cobalt hcp bilayer on Cu(111), and [(c)–(g)] above Ni, Co, Cu, Fe, and Cr atoms on the bilayer. Dashed circles indicate atomiclike resonances. The dashed lines indicate the majority surface-state onset.

the cobalt bilayer [blue line Fig. 4(b)] also produces structure in the atom LDOS, the induced states falling at energies close to the cobalt bilayer states. The intensity of the majority and minority structures depends on the nature of the atom. Based on our *ab initio* calculations, the resonance detected by STS over Ni and Co is most likely a bound state of majority character, while over Cu it is a mixture of majority and minority contributions. Using the high-energy flank of the Ni and Co resonances [dashed line on Fig. 2(b)], we evaluate the onset of the *s-p* states to be at −0.27 V and −0.30 V for hcp-like and fcc-like islands, respectively. Finally, a significant contribution to the LDOS comes from the *s-p* states hybridized with atomiclike *d* resonances of the adatoms.[26] In Fig. 4 these features are marked by dashed circles. For the Cr atom, a *d* resonance of minority character falls at −0.18 eV, causing the minority LDOS to be stronger than the majority LDOS below E_F. No atomic resonance falls close to the bound state of Fe and Cu. The Ni and Co atoms are in an intermediate situation, since a minority *d* resonance causes an upturn of the LDOS near E_F. The experimental upturn detected for Ni [Fig. 2(b)] is then likely linked to an atomiclike resonance.

The relation between the two spin channels can be quantitatively described by the value of the polarization defined as $P=(n_\uparrow-n_\downarrow)/(n_\uparrow+n_\downarrow)$, where $n_\uparrow$ and $n_\downarrow$ stand for the majority and minority LDOSs. The spin polarization calculated above the island is −66% at −0.23 eV, while it is of opposite sign for the Fe (+41%), Co (+37%), Ni (+31%), and Cu (+19%) adatoms. At E_F, the polarization of Fe is slightly reduced to +37%, while the polarization of Cu increases to +27%. The nonmagnetic copper atom has therefore a stronger polarization at E_F compared to Co and Ni, since the polarization of these two atoms drops back to +18% and −5%, respectively, due to minority atomiclike resonances near E_F. The polarization of Cr, which is governed in the examined energy range by the minority *d* resonance, reaches a minimum of −30% at −0.18 eV where the atomic resonance is centered and becomes positive at E_F (+7%). The presence of a single adsorbate on a magnetic nanolead can therefore locally change the polarization of a magnetic surface,[28] along the lines of recent simulations carried out for Cr-coated W tips.[4] Aside from contributions of atomiclike resonances, the net effect of the ferromagnetic atoms investigated is to favor the majority channel in an energy range where the island is governed by minority surface states. Remarkably, the polarization of the flat magnetic surface can be opposite to the polarization of an atomic protrusion. Compared to the pristine surface, the spin polarization averaged over the entire surface is reduced in the limit of weak atomic protrusions, i.e., weak interface roughness, and may even change in sign when the coverage increases.

A priori differences are to be expected between the polarization based on the LDOS and the conductance polarization of a MTJ. Quite interestingly, however, our findings of weakened *d* states due to the presence of atoms agree with recent tunneling spin-transport calculations in a Fe|vacuum|Fe MTJ accounting for interface roughness (atomic resonances were not evidenced).[6] We may also tentatively discuss the SP-STS reported for Fe and Cr atoms residing on the cobalt nanoislands.[19] An encouraging agreement is found for the Cr atom,[29] since the experimental polarization is indeed weak near −0.30 eV and negatively enhanced at −0.15 eV where the atomiclike resonance is predicted. On the other hand, while the spectra acquired above Fe adatoms in Ref. 19 agree with our calculations, the experimental polarization is opposite to the predictions. This last point may indicate that the antiferromagnetic Cr tips employed in Ref. 19 favor a negative polarization of the tunnel junction. A theoretical description in terms of spin transport,[30] which is beyond the scope of the present study, may be necessary to conclude.

In summary, we studied how atomic protrusions modify the spin structure of a pristine magnetic nanolead. Our combined experimental and theoretical study unambiguously proved that even small amounts of atomic roughness on magnetic nanoleads can significantly change the local spin polarization and even reverse its sign. This opens up interesting perspectives for controlling and engineering spin-polarized phenomena in magnetic junctions at the nanoscale.

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