Atomic relaxations and magnetic states in a single-atom tunneling junction

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A detailed theoretical investigation of structure, electronic and magnetic properties of a single atom magnetic junction is presented. Our studies are based on the density functional theory and the multiple scattering approach. We concentrate on a Cu tip interacting with the Co adatom on Cu(001), and study this junction for the tip-substrate distances ranging from the tunneling to the contact regime. We demonstrate that atomic structure of the tip and position of the adatom above the surface significantly depend on the tip-substrate distance. The adatom-surface distance is found to vary nonmonotonically as the tip approaches the surface. A pronounced change in the spin-polarized local density of states on the Co adatom, and a strong suppression of its magnetic moment are found when the tip is about 4 Å away from the surface.

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The scanning tunneling microscope (STM), as one of the most important experimental techniques for surface science studies, has been extensively used for imaging of surface structure and for studying of surface phenomena.[1] A new field of atomic engineering pioneered by Eigler and Schweizer[2] is based on the manipulation of single adatoms using the STM tip. By bringing the tip of an STM close to an adsorbed surface atom, the atom can be dragged along and positioned to build artificial atomic-scale nanostructures, for example, quantum corrals,[3] atomic chains,[4] etc. Experimental and theoretical studies of such artificial structures have significantly contributed to our understanding of electronic and magnetic properties at the atomic scale.[5,6] The possibility to control an atomic motion by the STM tip has been recently demonstrated by Stroscio and Celotta in experiments on Co adatoms on Cu(111).[7] The STM has also opened the possibility of studying many-body phenomena at surfaces, for instance, the Kondo effect. Using the scanning tunneling spectroscopy (STS), and placing the tip on top of magnetic adatoms, the Kondo effect was observed on single magnetic adatoms on metal surfaces.[5,8] Very recent STM experiments have demonstrated the ability to measure the spin excitation spectra of individual magnetic adatoms.[9]

The location of the STM tip at the proximity of surfaces and adatoms can cause perturbations due to the tip-sample interaction.[10,11] Even a very small change in the tip-sample distance can significantly affect the tunneling current since it depends exponentially on the distance. Normally, the tip-sample distance is not accessible to direct measurements and could be inferred from measurements of current, voltage, and displacement of the piezoelectric scanner tube.[12] Probe-sample distances from tunneling (5–10 Å) to the contact regime (2–4 Å) are covered by the modern STM experiments and calculations.[13–18] However, it has been shown that the real separation between the tip and the surface can differ substantially from the value estimated from the experimental setup due to relaxations of the surface atoms and the tip.[11,18]

Very recent work of Limot *et al.*[13] has revealed that the tip-adatom interaction is significantly different from the interaction of the tip with a flat surface. In contrast to a flat surface, no material is transferred when the tip is approaching a single adatom. The conductance over a single Ag and Cu adatoms has been found to exhibit a smooth transition from tunneling to contact regime.

In this paper, we demonstrate that electronic and magnetic properties of a single atom magnetic junctions are significantly affected by the tip. We study the effect of the tip on Co adatoms on Cu(001) performing combined *ab initio* and atomic-scale calculations. We show that the tip significantly affects the position of adatoms above the surface. Atomic relaxations in the tip and the substrate are revealed. The electronic states and the magnetic moment of the Co adatom are found to depend strongly on the distance between the tip and the adatom.

First, we perform fully *ab initio* calculations to find an equilibrium position of the Co adatom on Cu(001) in the absence of the tip. We apply the Korringa-Kohn-Rostoker (KKR) Green's function method[6,19,20] in the full-potential approximation and calculate the Hellmann-Feynman forces acting on the adatom near the surface. We find that the relaxed vertical position of the adatom is at 1.51 Å distance from the surface (reduced by about 14% compared to the unrelaxed one) when the Co adatom is positioned over the hollow site of the surface.

To study the effect of the tip on the position of the adatom and atomic relaxations in the substrate we perform atomic-scale simulations with *ab initio* based interatomic potentials.[21] We construct the many-body interatomic potentials formulated in the second moment approximation of the tight-binding (TB) theory[21,22] by fitting their parameters to the *ab initio* data for surface and bulk properties calculated by the KKR Green's function method. Binding energies of supported and embedded clusters of different sizes and geometries, Hellmann-Feynmann forces acting on the Co adatom for different positions above the surface and such bulk properties as bulk modulus, lattice constants, cohesive energies, and elastic constants are used in fitting of parameters of potentials. Reliability of our potentials for different atomic structures (single adatoms, supported clusters, embedded clusters, nanocontacts) has been demonstrated.[23–26] Our recent studies[27] have shown that such potentials describe

atomic relaxations in very good agreement with fully *ab initio* calculations. The combination of the *ab initio* and the TB methods allows one to perform atomic relaxations for very large systems having *d* electrons. To the best of our knowledge, a fully *ab initio* calculation of atomic relaxations in magnetic junctions has not been performed so far.

The electronic and magnetic properties of the adatom in the presence of the tip are calculated by means of the density functional theory in the framework of the method mentioned above in a fully relaxed geometry. We consider the tip, the adatom, and the surface as a single system. First, we find the Green's function of the ideal surface which is used in the Dyson equation to calculate the Green's function of the tip-adatom-substrate system:

$$G_{LL'}^{nn'}(E) = \mathring{G}_{LL'}^{nn'}(E) + \sum_{n''L''} \mathring{G}_{LL''}^{nn''}(E)\Delta t_{L''}^{n''}(E) G_{L''L'}^{n''n'}(E), \quad (1)$$

where $G_{LL'}^{nn'}(E)$ is the energy-dependent structural Green's function matrix of the surface with the adatom and the tip, and $\mathring{G}_{LL''}^{nn''}(E)$ the corresponding matrix for the ideal surface; $\Delta t_L^n(E) = t_L^n(E) - \mathring{t}_L^n(E)$ describes the difference in the scattering properties at site *n* between the *t*-matrices of the surface with the tip and the adatom and the ideal surface. We note that the positions of the tip atoms, vacuum sites between the tip and the adatom, vacuum sites between the adatom and the substrate, as well as the substrate atoms are considered to be perturbed, i.e., they are treated fully self-consistently. The spin-polarized self-consistent calculations are performed in the full-potential approximation. Using the Green's function of the tip-adatom-substrate system, the local density of states (LDOS) and the spin magnetic moments on the Co adatom for different positions of the tip above the surface are calculated. We would like to emphasize that the electronic structure of the tip, the adatom and the substrate are considered on the same footing, and the charge transfer which takes place due to the tip-adatom-substrate interaction is calculated fully self-consistently. In our approach bias-induced surface relaxations are neglected. Such approximation is suitable for most STM experiments when relatively weak voltages are used. For example, the tunnel voltage of 20–100 mV is usually used in STS experiments on single magnetic adatoms on metal surfaces.[3,5,8] Such bias proved to be sufficiently small for electrostatic forces to produce negligible effects.[28–30]

In our studies we model the tip by a Cu pyramid consisting of 14 atoms (see Fig. 1). The main results of our work are practically unchanged if we increase the size of the tip as long as it ends with one single atom. We consider the tip to be positioned above the adatom. When the distance between the tip-apex and the substrate reduces, both the tip-apex and the adatom exhibit strong vertical displacements. A relatively small atomic relaxation also occurs in the substrate under the adatom (see Fig. 1). In the range between 5.5 Å and 4.5 Å, the tip-apex is pushed down, while the adatom and the substrate atoms are pushed up. During this stage the adatom-tip separation reduces by almost 1.4 Å (see Fig. 2). Considering that a distance reduction by 1 Å typically results in a tenfold increase of the tunneling current, it is obvious that the dynamics of the relaxation found here must have profound influence on the appearance of STM images. The attractive interaction between the tip and the adatom at this stage is the driving force for the observed atomic relaxations. However, at a closer tip-substrate distance (4.5–3.5 Å), the repulsive interactions between the tip and the adatom, and between the adatom and the substrate begin to play an important role.

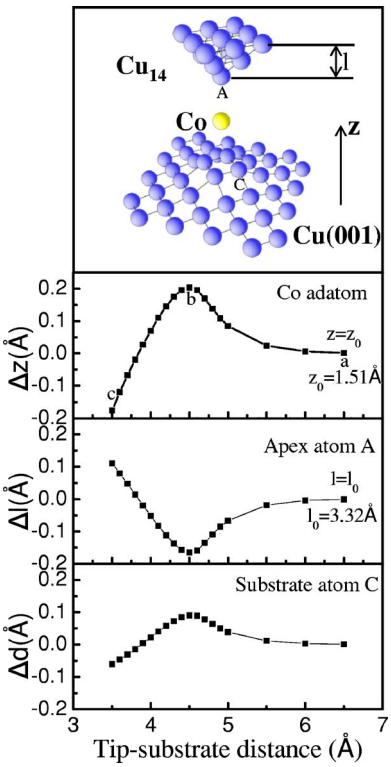

FIG. 1. (Color online) One-atom magnetic junction consisting of the Cu tip, the Co adatom, and the Cu(001) substrate. The tip is above the adatom. With the decrease of the tip-substrate distance, both the tip-apex and the adatom exhibit strong vertical displacements. A relatively small atomic relaxation also occurs in the substrate underneath. In this figure, $\Delta l = l_0 - l$ is the change of the tip length, where l and l_0 are the tip length with and without tip-adatom interaction; Δz and Δd are the displacements of the adatom and the substrate atom C along the z axis, where z_0 is the relaxed adatom-substrate distance without tip-adatom interaction.

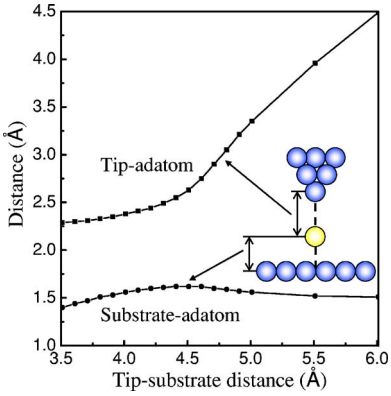

FIG. 2. (Color online) The tip-adatom and the adatom-substrate distances calculated in a fully relaxed geometry.

Figure 1 shows that at this stage the adatom and the substrate atoms are pushed down as much as 0.4 Å and 0.15 Å, respectively. The distance between the tip and the adatom is reduced by 0.3 Å (see Fig. 2). Figure 2 shows how the adatom-tip and the adatom-substrate distances change during approaching the tip to the substrate. When the tip-substrate distance decreases from 5.5 Å to 4.5 Å, the tip-adatom distance decreases almost linearly while the adatom-substrate distance increases. At a shorter tip-substrate distance (4.5–3.5 Å), both the tip-adatom and the adatom-substrate distance slightly decrease. We have found that for a tip-substrate separation less than 3 Å the junction is destroyed: the Co adatom is strongly pushed inside the substrate. We would like to note that magnetic effects can significantly affect atomic relaxations in nanostructures.[31] However, our calculations for magnetic and nonmagnetic single-atom junctions show that magnetic effects included in the adatom-substrate and the tip-adatom interactions practically cancel each other, which results in similar atomic relaxations in magnetic and nonmagnetic junctions.

The following important question arises: What is the effect of the tip on the electronic and magnetic properties of single magnetic adatoms? We believe that the answer to this question is of great importance for our understanding of the one-atom magnetic contacts. We made the self-consistent *ab initio* calculations in a fully relaxed geometry for three different vertical distances between the tip and the Co adatom in the range between 6.5 Å and 3.5 Å (denoted *a*, *b*, and *c* in Fig. 1 and Fig. 3).

The LDOS of the Co adatom is shown in Fig. 3. The results for both spin directions are plotted with the energies given relative to the Fermi energy. For the tip-substrate distance larger than 5 Å, the interaction of the tip with the adatom is rather weak, and the LDOS on the Co adatom is very much similar to the LDOS of a single Co adatom on Cu(001): the majority states are filled, and the minority states cross the Fermi level. However, for distances corresponding to the points *b* and *c* in Fig. 1, the interaction between *d* states of the adatom and the *s* states of the tip-apex and the Cu atoms of the substrate is found to strongly affect the electronic and magnetic states of the Co adatom. Our analysis of the charge distribution reveals that the *sd* hybridization

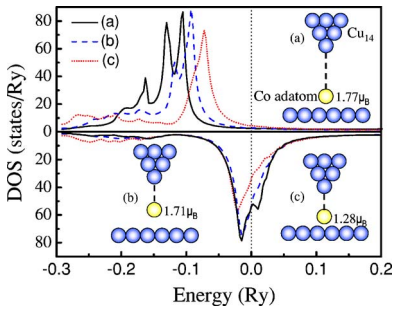

FIG. 3. (Color online) Effect of the tip on electronic and magnetic properties of Co adatom on Cu(001) in a fully relaxed geometry. The tip is above the adatom. The LDOS corresponding to three different tip-substrate separations denoted in Fig. 1.

depletes the majority *d* states of the Co adatom, and increases the population of the minority states. As a result, the majority states move to the Fermi level and become slightly depopulated, while the minority states are shifted to lower energies. For the distances between 4.5 Å and 3.5 Å the effect of the *sd* hybridization drastically influences the LDOS and the magnetic moment. We find that in this case the magnetic moment strongly reduces from $1.71\mu_B$ to $1.28\mu_B$ which is very close to the magnetic moment of a single atom of Co incorporated in the Cu(001) surface.[25] We believe that changes in the spin resolved LDOS demonstrated by our calculations may lead to measurable effects in the tunneling conductance.

In summary, our results establish that the tip induced changes in structure, electronic and magnetic properties of a single-atom magnetic junctions significantly depend on the tip-surface distance. Our studies give clear evidence that electronic and magnetic properties of a single-atom junctions are strongly affected by atomic relaxations in the contact regime. Effects found in our work may have consequences for the measured STM current in magnetic atomic junctions, and for understanding of single-atom spectroscopy experiments on magnetic adatoms.

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